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► To cite this version:

Andrei Kabashin, Ajay Singh, Mark Swihart, Irina Zvestovskaya, Paras Prasad. Laser-Processed Nanosilicon: A Multifunctional Nanomaterial for Energy and Healthcare. ACS Nano, American Chemical Society, 2019, 13 (9), pp.9841-9867. 10.1021/acsnano.9b04610 . hal-03098779

HAL Id: hal-03098779

<https://hal.archives-ouvertes.fr/hal-03098779>

Submitted on 6 Jan 2021

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ACS Nano, **Just Accepted Manuscript** • DOI: 10.1021/acsnano.9b04610 • Publication Date (Web): 06 Sep 2019

Downloaded from pubs.acs.org on September 10, 2019

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Laser Processed Nanosilicon: A Multifunctional Nanomaterial for Energy and Health Care

Andrei V. Kabashin,^{†,‡} Ajay Singh,[§] Mark T. Swihart,^{§,||} Irina N. Zvestovskaya,[‡] and Paras N.

Prasad^{§,‡}

[†]Aix-Marseille Univ, CNRS, LP3, Marseille, France

[‡]MEPhI, Institute of Engineering Physics for Biomedicine (PhysBio), 31 Kashirskoe sh., 115409
Moscow, Russia

[§]Institute for Lasers, Photonics, and Biophotonics, The University at Buffalo, The State
University of New York, Buffalo, New York, 14260-3000, USA

^{||}Department of Chemical and Biological Engineering and RENEW Institute, The University at
Buffalo, The State University of New York, Buffalo, New York, 14260-4200, USA

Abstract: This review describes promising laser-based approaches to produce silicon nanostructures, including laser ablation of solid Si targets in residual gases and liquids and laser pyrolysis of silane. These methods are different from, and complementary to, widely used porous silicon technology and alternative synthesis routes. One can use these methods to make stable colloidal dispersions of silicon nanoparticles in both organic and aqueous media, which are suitable for a multitude of applications across the important fields of energy and health care. Size tailoring allows production of Si quantum dots with efficient photoluminescence that can be tuned across a broad spectral range from the visible to near-IR by varying particle size and surface

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3 functionalization. These nanoparticles can also be integrated with other nanomaterials to make
4 multifunctional composites incorporating magnetic and/or plasmonic components. In the energy
5 domain, this review highlights applications to photovoltaics and photodetectors, nanostructured
6 silicon anodes for lithium ion batteries, and hydrogen generation from water. Application to
7 nanobiophotonics and nanomedicine profit from the excellent biocompatibility and
8 biodegradability of nanosilicon. These applications encompass several types of bioimaging and
9 various therapies, including photodynamic therapy (PDT), RF thermal therapy, and radiotherapy.
10 The review concludes with a discussion of challenges and opportunities in the applications of laser-
11 processed nanosilicon.
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28 **Keywords:** nanosilicon, silicon nanoparticles, silicon quantum dots, nanosilicon for energy,
29 pulsed laser ablation, pulsed laser ablation in liquids (PLAL), laser pyrolysis, nanobiophotonics,
30 and nanomedicine
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Vocabulary:

Pulsed laser ablation: a physical vapor deposition technique in which a high-power pulsed laser beam is focus on a target material that is to be deposited as a thin film on a substrate in vacuum, or converted into nanoparticles in a low-pressure background gas.

Pulsed laser ablation in liquid (PLAL): a method in which a high-power pulsed laser beam is used to vaporize material from a solid target in a liquid environment to directly produce colloiddally-dispersed nanoparticles.

Laser pyrolysis: a method of preparing nanoparticles *via* laser-induced heating of a gas-phase precursor mixture. Laser heating allows very rapid initiation and quenching of particle formation, producing nanocrystals of more uniform size compared to other gas-phase methods of nanoparticle synthesis.

Silicon quantum dot: a crystalline silicon nanoparticle with diameter significantly less than twice the Bohr exciton radius in silicon (~4.5 nm) such that size-dependent properties emerge due to quantum confinement effects.

Nanophotonics: the study and application of the interaction of nano-scale objects, with light and the behavior of light at nanometer scales.

Bionanophotonics: the application of nanophotonics to biological and medical research and applications.

Nanomedicine: the application of nanotechnology, including nanoscale materials and phenomena specifically occurring at the nanoscale, to medical diagnostics and therapy.

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3 Silicon (Si), which makes up 28% of the mass of the Earth's crust, has a variety of useful properties
4 and can be refined by relatively inexpensive methods. Si is best known for its outstanding
5 semiconductor properties, as its conductivity can be controlled through addition of small
6 concentrations of doping elements (typically, boron and phosphorus). On this basis, Si has become
7 the core material of modern electronics, from which a plethora of devices, such as transistors, solar
8 cells, and photodetectors for computers, television, smart phones and other applications, are
9 created.¹ On the other hand, being present as orthosilicate (SiO_4^{4-}) in many tissues, silicon (Si) is
10 an essential element in living organisms.²⁻⁴ This abundance in nature and presence in living
11 systems are the basis for the excellent compatibility of Si and silicon-containing compounds with
12 biological systems. Furthermore, elemental Si is biodegradable and safely excreted from the
13 body,^{5, 6} which is a rather unusual feature for inorganic elements, making it promising for
14 biomedical applications.

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31 Even more astonishing properties of silicon become possible upon decreasing the Si crystal size
32 down to the nanoscale. Due to significant modification of electronic energy bands⁷ and other
33 phenomena, nanostructured Si (nanosilicon) can become strongly luminescent in the visible and
34 near infrared,^{8, 9} although bulk crystalline Si has only a small (1.11 eV at room temperature) and
35 indirect band gap. These luminescent properties of nanosilicon open up many opportunities for
36 optoelectronic applications¹⁰ and for the development of fluorophores and contrast agents for
37 bioimaging.¹¹⁻¹³ On the other hand, nanosilicon structures can exhibit dramatically increased
38 absorption of light in the ultraviolet, visible and infrared,¹⁴⁻¹⁶ which promises attractive
39 applications in photodetectors, image sensors, thermal imaging cameras, and solar panels. In
40 addition, Si nanostructures can provide much-improved characteristics as anode materials in
41 lithium-ion batteries compared to conventional microparticle counterparts¹⁷⁻²⁰ and, due to a large
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3 highly-active surface area, can be used for hydrogen generation from water to power fuel cells.²¹⁻
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5 ²³ Nanosilicon can finally enable a variety of therapeutic modalities, including drug vectoring,^{24,}
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7 ²⁵ photodynamic therapy,²⁶⁻²⁸ and infrared,²⁹ radio frequency,³⁰ and ultrasound-induced³¹
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9 hyperthermia for cancer treatment.
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13 The diverse array of possible nanosilicon applications necessitates the choice of the most suitable
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15 methods for its synthesis for each application. Most of these applications require the fabrication of
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17 luminescent silicon nanostructures with emission at a particular wavelength in blue, green or red-
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19 infrared range.^{8, 9} In addition, optoelectronic, photovoltaic, image sensor, and solar panel
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21 applications may require “dry” fabrication routes that could be compatible with Si processing
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23 technology for further integration of functional devices into standard microelectronic
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25 chips/platforms.¹ On the other hand, biomedical applications typically require luminescence
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27 emission in the window of relative tissue transparency, *i.e.*, the near-infrared range (650-850 nm).
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29 These applications also require water-dispersibility and purity of nanosilicon.³²⁻³⁴ Methods for the
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31 fabrication of silicon can be divided into chemical, physical, physicochemical, and
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33 electrochemical. Wet chemical synthesis routes, including solution-phase reduction,³⁵⁻³⁷
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35 microemulsion techniques,^{38, 39} supercritical fluid synthesis,⁴⁰ solid-state disproportionation,^{41, 42}
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37 microwave synthesis,^{43, 44} sonochemical synthesis,⁴⁵ and mechano-chemical synthesis,⁴⁶ have been
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39 reported for producing luminescent Si nanocrystals. However, many of these methods use toxic
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41 substances (*e.g.*, organosilicon precursors, reducing agents, or etching agents) whose residual
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43 presence in the product can complicate biomedical applications. Some of these methods may not
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45 be reproducible in other labs, may not actually produce fully reduced and crystalline silicon, or
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47 may produce silicon by routes other than those proposed in the original publications. Our purpose
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49 here is not to critically evaluate each of these reports, but simply to provide an entry into the diverse
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3 literature on non-laser-based nanosilicon fabrication methods. Dry fabrication methods such as
4 thermal annealing of SiO_x polymers,^{47, 48} slow combustion,^{49, 50} thermal decomposition,⁵¹
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6 microwave plasma,^{9, 52} low-pressure non-thermal plasma,⁵³⁻⁵⁵ gas-evaporation,⁵⁶ and chemical
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8 vapor deposition (CVD)^{57, 58} are also efficient for fabricating luminescent Si crystals and more
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10 compatible with silicon processing technology, but they typically require additional chemical
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12 processing steps to separate and water-disperse crystals and stabilize luminescence emission in
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14 solutions.⁵⁹ Porous silicon technology based on electrochemical etching of silicon is the most
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16 popular approach to fabricate luminescent Si crystals, and has been used in more than 80-85% of
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18 studies.^{8, 33, 34} Formed originally on a silicon wafer, porous silicon crystals can later be milled,
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20 dispersed in aqueous solutions and employed in biological applications, *e.g.*, as markers in
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22 bioimaging.^{33, 34} However, so formed nanostructures may have a wide dispersion of both size and
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24 shape of crystals, and may be contaminated by hydrofluoric acid derivatives,⁶⁰ which is not
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26 desirable for many applications. In addition, wet porous silicon synthesis is not well compatible
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28 with silicon microelectronics technology, which complicates many applications that require the
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30 integration of porous silicon structures into microelectronics platforms. Spectral position and
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32 efficiency of luminescence are considered key parameters for the majority of projected
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34 applications. These parameters are determined by the luminescence mechanisms and depend on
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36 both the methods of nanocrystal preparation and surface conditioning.⁶¹⁻⁶⁵ Silicon nanoparticles
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38 (NPs) produced by wet chemical methods typically have a low crystallinity and most commonly
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40 emit blue photoluminescence,⁶⁶ which is typically attributed to defect states,^{67, 68} although
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42 luminescence emission can be modified and shifted toward the green or red range by appropriate
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44 surface engineering. Dasog *et al.*⁶⁹ demonstrated the important role of trace nitrogen, as well as
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46 oxygen, in producing blue luminescence from silicon nanocrystals of high apparent crystallinity.
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3 In contrast, porous silicon technology^{8, 33, 34} and high temperature routes^{40, 41, 53-55} can produce
4 material with higher crystallinity and high purity, which is capable of generating size-tunable
5 photoluminescence associated with emission from quantum-confined excitonic states in ultrasmall
6 crystalline silicon cores.⁷⁰⁻⁷²
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13 A series of studies over the years have shown that many problems in applications of nanosilicon
14 can be solved using laser processing-based fabrication routes. Laser radiation can be delivered
15 through gaseous or liquid media (inert or reactive) and be focused to cause ablation of material
16 from a Si target⁷³ or initiate decomposition and particle-forming chemical reactions in Si-
17 containing gases (*e.g.*, silane, SiH₄).^{74, 75} Through these processing routes, one can synthesize high
18 quality nanosilicon crystals in the form of nanostructured films, nanopowders, and colloidal
19 dispersions. Some laser-based synthesis methods, particularly pulsed laser ablation in liquid, can
20 produce stable aqueous dispersions in a single step,^{73, 76} while others, such as gas-phase laser
21 pyrolysis, are similar to other dry synthesis methods with respect to the required post-processing
22 steps.^{77, 78} Moreover, laser processing enables one to fabricate contamination-free nanosilicon
23 structures when performed in clean conditions (deionized water, non-toxic gases). This review
24 article aims to provide an overview of laser processing methods for the fabrication of nanosilicon
25 and describes possible uses of these nanosilicon materials in energy and health care applications.
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44 **Laser Fabrication of Nanosilicon**

45 ***Laser-ablative Synthesis***

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49 Laser ablation has proved its high efficiency in producing a variety of nanostructured
50 materials, including silicon-based ones.⁷³ The action of intense laser radiation on a solid Si
51 target can ablate the target material leading to the production of periodic micro- and
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3 nanoarchitectures on the surface.^{15, 16, 79} Furthermore, material is typically ablated in the
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5 form of atoms and nanoclusters,⁸⁰⁻⁸² which then experience condensation in the vapor phase
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7 upon interaction with their environment, to form larger clusters. When produced in a
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9 gaseous/vacuum ambient, these nanoclusters can then be crystallized on a substrate to form
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11 a nanostructured film or a powder-like deposit. When produced in a liquid ambient, the
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13 nanoclusters can form a colloidal nanoparticle dispersion. Notably, nanostructures formed
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15 by laser ablation in both media can exhibit very promising properties for a variety of
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17 applications.
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22 **Pulsed laser ablation in gaseous environment.** The straightforward configuration is
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24 based on a conventional Pulsed Laser Deposition (PLD) geometry, which does not imply
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26 any synthetic selection of ablated nanoclusters. A typical PLD geometry is shown in Figure
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28 1. Here, radiation from a nanosecond laser with an intensity of $10^8 - 10^9$ W/cm² is focused
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30 on a rotating Si target at an inclined angle of incidence ($\sim 45^\circ$). The intense radiation causes
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32 ablation of the material and formation of a plasma plume that expands perpendicular to the
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34 target surface. Such experiments are normally performed using UV radiation from excimer
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36 lasers (248 nm from KrF or 193 nm from ArF), which is transmitted through the plasma
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38 plume. This enables one to minimize losses of radiation energy before reaching the target
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40 and allows rapid cooling of ablated clusters. A substrate is typically installed at some
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42 distance (generally 2-3 cm) from the target. The ablation can be performed either in vacuum
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44 or in a residual gas. When the ablation is performed at a relatively low gas pressure ($< 10^{-2}$
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46 Torr), the growth of nanoclusters is hardly controllable and they typically arrive to the
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48 substrate as-ablated and crystallize directly on its surface, forming mostly amorphous film
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50 with minimal porosity.⁸³⁻⁸⁶ In contrast, laser ablation in an inert residual gas (He, Ar) at a
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moderate pressure of 0.1-10 Torr allows a degree of control of the characteristics of the product nanostructures.⁸³⁻⁹⁴ In this case, gas atoms (or molecules) and their ionized species serve to control the growth and crystallization of nanoclusters during their collisions.⁸⁰⁻⁸²

As shown in Figure 1b, laser-ablated Si nanoclusters are typically 2-4 nm in diameter, while high resolution TEM images reveal that the nanoclusters can be highly crystalline (Figure 1c). The deposition of these gas suspended nanoclusters on a substrate facing the target leads to the formation of a thin nanostructured Si-based film. When relatively thick (several

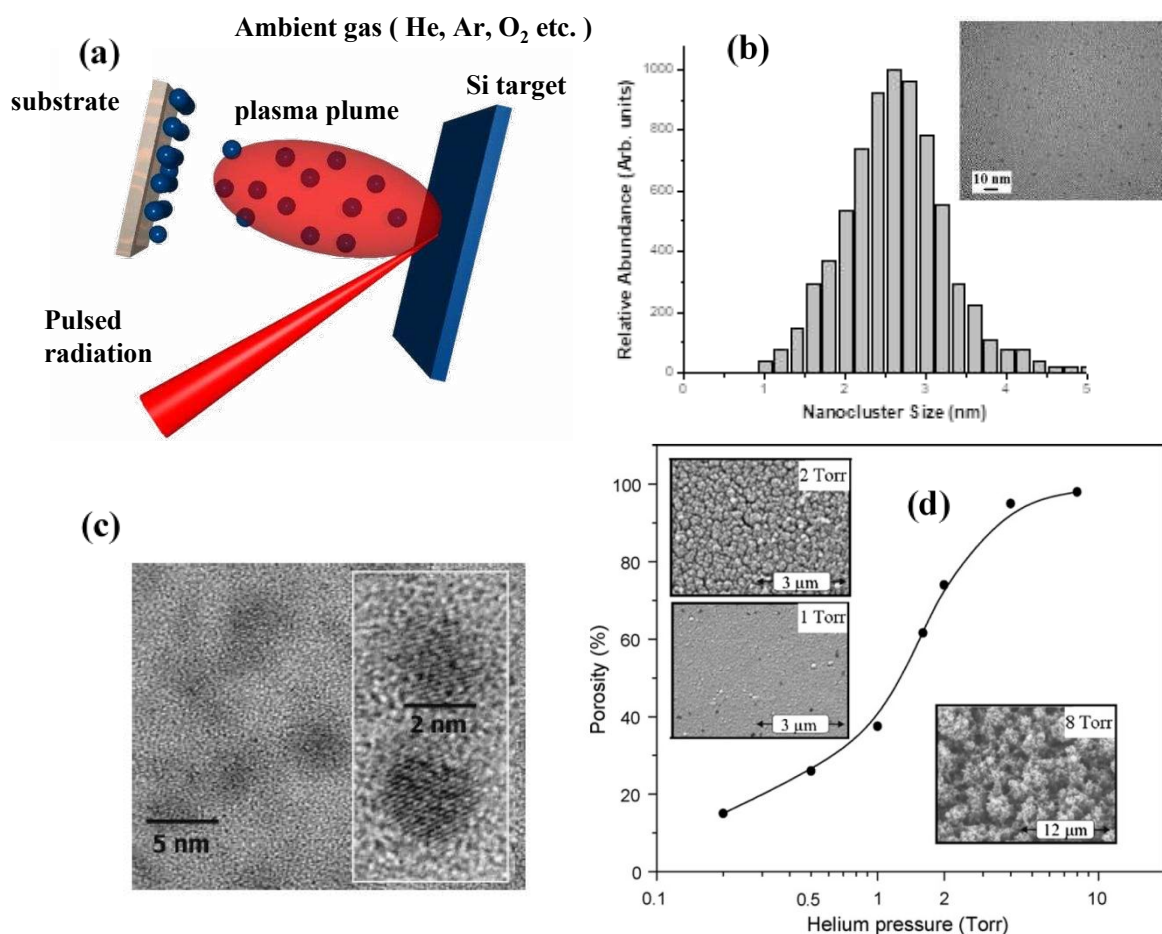
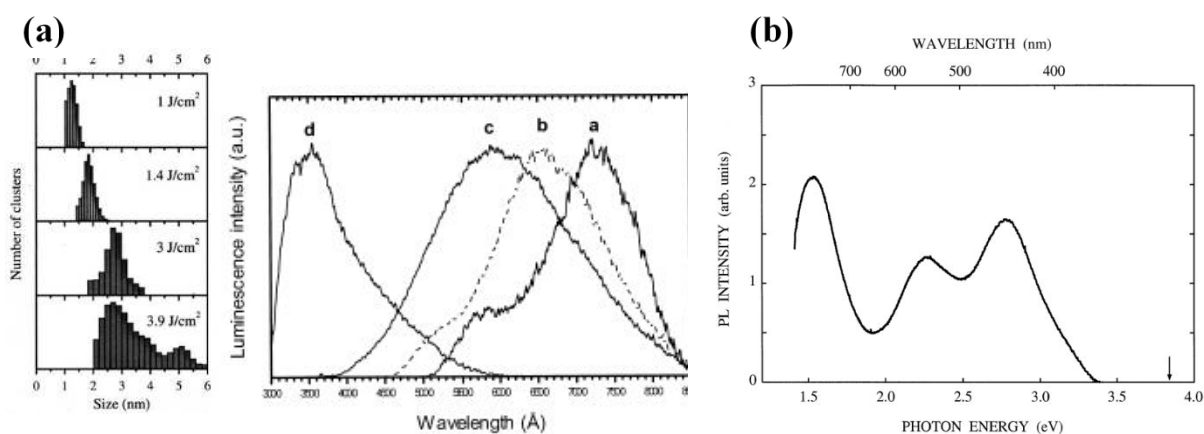


Figure 1. (a) Schematic of PLD experiment for deposition of Si-based nanostructured films; (b) Transmission Electron Microscopy (TEM) image of laser-ablated Si nanoclusters and corresponding nanocluster size distribution (Adapted from Ref. 93 with permission from AIP Publishing); (c) High resolution TEM images of as-deposited Si particles (Adapted from Ref. 94 with permission from Elsevier). (d) Dependence of film porosity on helium pressure during the deposition. Insets show morphologies of the films formed under different gas pressures (Adapted from Ref. 93 with permission from AIP Publishing).

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3 hundreds of nm or more), the films can be multi-colored due to thin film interference
4 effects. The presence of ambient neutral gas was shown to be the key parameter, which
5 determines the properties of the formed Si crystals, as this parameter can affect both the
6 size^{81, 82} and the morphology of deposited films. As shown in Figure 1d, increasing the He
7 pressure during ablation of a Si target leads to a gradual increase of film porosity. While
8 the ablation at low pressures (<0.5 Torr) leads to the formation of dense films with
9 porosities lower than 25%, increasing the background pressure leads to a gradual increase
10 of porosity to more than 90%. Ablation at high pressures (5-10 Torr) leads to the deposition
11 of web-like powders with extremely weak adhesion to the substrate.⁹³ Such a strong
12 dependence of morphology on ambient gas pressure was explained by enhanced cooling of
13 nanoclusters due to an increased number of collisions with He atoms and their
14 crystallization before reaching the substrate.⁹³

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31 The focus of early studies was mainly concentrated on the formation of Si-based
32 nanostructures, which could provide substantial photoluminescence (PL)⁸³⁻⁹⁰ and
33 electroluminescence (EL),⁹⁵ especially in the blue spectral region. In contrast to “wet”
34 chemistry-produced porous silicon, the films fabricated by “dry” laser-ablative synthesis
35 were expected to have excellent compatibility with the Si microelectronic processing
36 technology, which would facilitate the implementation of Si-based optoelectronic emitters
37 and other devices. Indeed, laser-synthesized nanostructured films have been observed to
38 exhibit PL with quantum yields reaching several percent, but reported PL properties were
39 rather contradictory. Several groups tried to establish a correlation between the spectral
40 positions of PL peaks and the size of formed nanostructures, and obtained some interesting
41 data. As an example, by changing the laser pulse fluence during ablation, Patrone⁸⁸

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3 managed to obtain size-dependent PL spectra (Figure 2a). In contrast, Makimura^{85, 86} and
4 Yoshida^{84, 87, 90} recorded three fixed PL peaks at 1.5-1.75 eV, 2.2-2.3 eV and 2.7-2.8 eV
5 from films prepared under similar conditions (Figure 2b). On the other hand, Yoshida^{95, 96}
6 demonstrated efficient electroluminescence from laser-ablated films, and the observed 1.66 eV
7 emission matched one of the PL peaks. Later, Kabashin⁹³ showed that conditions for
8 producing size-dependent or fixed PL bands can be reached using different ambient
9 pressures of He during the deposition, leading to different porosities of the formed films
10 (Figure 1d). Low porosity films deposited under relatively low pressures could indeed
11 exhibit tunable PL spectra that red-shifted with increasing nanoparticle size, but the
12 intensities of these emissions were much weaker. This spectrally tuned emission can be due
13 to quantum confinement effects, but other mechanisms cannot be ruled out, taking into
14 account rather different manifestation of properties of quantum confinement effects
15 recorded in the case of porous silicon.³²⁻³⁴ Highly porous films formed at $P > 1.5$ Torr
16 provided 1-2 orders stronger signals, presenting two fixed bands (1.5-1.75 eV and 2.2-2.3
17 eV), similar to the ones observed by other groups⁸⁴⁻⁸⁷ (the third band around 2.7 eV could



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52 **Figure 2.** (a) Nanoparticle size distributions and PL spectra of nanosilicon films produced using different
53 laser fluences: 3.9 J/cm²- a; 3 J/cm² - b; 1.4 J/cm² - c; 1 J/cm² - d. Adapted from Ref. 88 with permission
54 from AIP Publishing; (b) PL spectrum of Si nanocrystal-based film synthesized by laser ablation in
55 residual He and then annealed in Ar (1000 C, 30 min). The data were taken from Ref. 86 with permission
56 from Elsevier.

not be observed due to overlap with the 488 nm excitation wavelength). The generation of two fixed bands with much enhanced intensity could be related to both better crystal quality as a result of nanocluster crystallization in the vapor phase (before reaching the substrate) and better conditions for oxidation of inner layers of porous films to passivate the crystals in order to remove non-radiative centers.⁹⁷

Based on the similarity of PL bands for alternative nanosilicon structures, the origin of 2.2-2.3 and 2.7-2.8 eV emissions can be assigned to defects in SiO_x structures,^{32, 34, 67, 68} while the origin of 1.5-1.75 eV (640-800 nm) emission can be attributed to quantum-confined excitonic states in Si nanocrystals.^{32-34, 70-72} The defect- and quantum confinement mechanisms of 2.7-2.8 and 1.5-1.75 eV emissions were confirmed by their characteristic PL time decays, having ns and μs scales, respectively (Figure 3b). In the case of porous silicon, the generation of the 1.5-1.75 eV excitonic band becomes possible due to a hydrogenation step that involves exposing the Si surface to solutions of HF or a mixture of HF and HNO₃, followed by natural oxidation in air or ethanol, to provide hydroxyl-based passivation of the surface and the removal of non-radiative recombination centers.^{32, 34, 97}

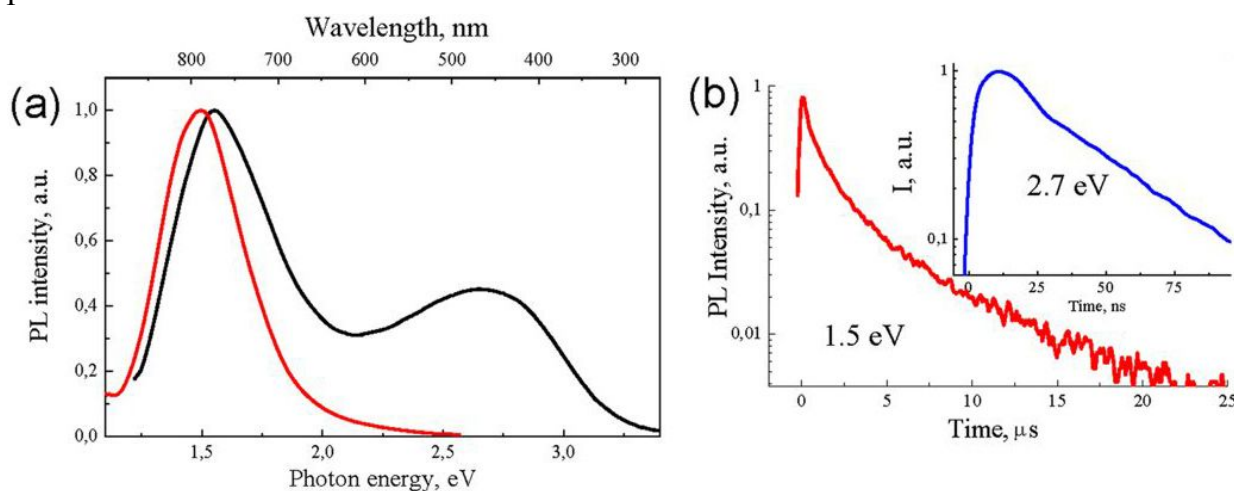


Figure 3. (a) PL spectra of nanosilicon films synthesized by PLD (red curve) and aqueous dispersions of Si nanoparticles obtained by milling of these films by ultrasound (black curve); (b) Transient PL signal for 1.5 eV exciton band and 2.7 eV defect-related band (inset). Adapted from Ref. 13 with permission under a Creative Commons CC-BY license.

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3 In contrast, in the case of laser-synthesized nanostructures, the exciton-based PL emission
4 was recorded despite the absence of such a hydrogenation step. Gongalsky¹³ later explained
5 the recorded emission by specific conditions of nanocluster growth in the plasma plume
6 (involving rapid heating and cooling stages). Laser-ablated nanoclusters move through a
7 long-living plasma plume, which contains He ions and hot electrons having a significant
8 excess of energy (tens of eV).^{81, 82} Since electron-ion recombination events can increase
9 temperature of small nanoclusters up to 1000 K,⁹⁸ laser-ablated nanoclusters are expected
10 to be strongly heated before reaching the substrate. A subsequent cooling of nanoclusters
11 *via* their collisions with He atoms outside the hot plume conditions the production of nearly
12 perfect low-defect Si quantum dots. Such nanocrystals start to exhibit exciton PL just after
13 their exposure to ambient air, with gradually increasing intensity during the first 2-4 weeks
14 of their aging under these conditions. Such purely oxygen-related passivation of the Si
15 crystal surface appears to be very efficient when high quality crystals are formed *via* PLD.
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17 Gongalsky¹³ also showed that Si nanocrystals can be efficiently removed from the substrate
18 and milled using ultrasound, to form separated nanoparticles that can be easily dispersed in
19 water or physiological solutions. Notably, the PL emission of the exciton band remained
20 significant, even after dispersion of these nanoparticles in aqueous solutions (Figure 3a),
21 which suggests their potential use as markers for bioimaging. A huge advantage of these
22 markers is that their emission lies in the window of relative tissue transparency (700-1000
23 nm). The very long time decay (μ s) of their emission (Figure 3b) renders possible an easy
24 removal of background biological autofluorescence (with ns time decay) using time gating
25 techniques like those demonstrated by Gu *et al.*¹².

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3 Additional size control of laser-synthesized Si nanoparticles can be achieved by the application of
4 size-selective synthetic routes. Several studies have used external control of plume dynamics and
5 cluster size selection. As an example, El-Shall introduced the laser vaporization-controlled
6 condensation method, in which an external gradient of temperature was applied to control the
7 plasma plume evolution. Despite better control of structural characteristics of deposited films, their
8 photoluminescent properties were similar to those of films prepared by conventional PLD. Seto⁹⁹,
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100 achieved a narrow size distribution of laser-synthesized silicon nanoclusters by applying a
differential mobility analyzer (DMA). Here, laser-synthesized nanoclusters were transported by a
helium gas stream and then size-classified in the gas phase using the DMA. Nanostructured films
prepared by such a size-selection method exhibited sharp size-dependent PL spectra with the peak
shifting from 1.34 eV to 1.79 eV with decreasing nanocrystal size from 4.9 nm down to 2.1 nm
(Figure 4). The latter results are of importance for optoelectronics applications.

A series of studies were devoted to laser-ablative fabrication of Si-based nanowires with great
potential in applications including nanoelectronics, optoelectronics, and solar cells. Here, most
approaches have been based on the use of metal (Fe, Ni, Au, *etc.*) catalysts, which enable the
formation of anisotropic Si-based structures under high temperature conditions.¹⁰¹⁻¹⁰⁴ In a common
configuration, a metal-doped Si (or Si + SiO₂) target is placed in a quartz tube within a furnace
maintained at high temperature (100-1200 °C). A water-cooled finger is inserted to the furnace to
collect product nanostructures, while Ar gas flows through the chamber, and vacuum is created by
pumping. Radiation from an ultraviolet excimer laser (248 nm) is used to ablate the target, while
the material is collected on the finger surface. Such a configuration enables one to fabricate a
variety of nanowire architectures having diameters of 15-20 nm and consisting of a silicon
crystalline core covered by a silicon dioxide shell.

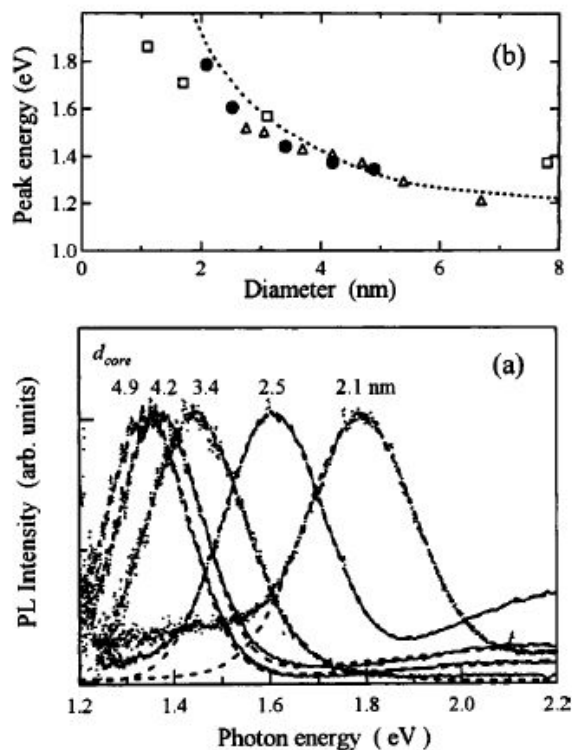


Figure 4. (a) PL spectra of nanosilicon films for different mean crystal sizes. (b) Dependence of PL peak energy on Si crystal size. Adapted from Ref. 100 with permission from AIP Publishing.

More recently, interest in the fabrication of relatively large spherical Si nanoparticles (100-400 nm) and arrays of these particles on a substrate has grown rapidly. Interest in these structures arises from a series of recently-discovered effects associated with the excitation of optical magnetic and optical electric dipole resonances within dielectric spheres.¹⁰⁵⁻¹⁰⁹ Such resonances are somewhat similar to split ring resonators, but they have much smaller losses and are able to shift the spectral position of the magnetic resonance into the visible range. Because the excitation of such resonances requires relatively high refractive index of a nanoparticle material, silicon with its refractive index exceeding 3.5 is one of the best candidates. Laser ablation in gaseous ambient was shown to enable the fabrication of large Si-based nanoparticles of the required quality. Here, methods of femtosecond laser ablation in air appeared to be most effective for obtaining the desired characteristics. In one geometry, the material was ablated from a Si wafer by laser radiation (800

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3 nm, 100 fs) and then redeposited on the same substrate, leading to the formation of Si nanoparticles
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5 with sizes ranging from several tens of nm to 200 nm.¹⁰⁷ In another geometry of light-induced
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7 forward transfer (LIFT), fs radiation (120 fs, 800 nm) was transmitted through a transparent glass
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9 substrate and then used for the ablation of material from a bulk Si wafer placed at a small distance
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11 from the substrate.¹⁰⁶ Due to the specific hydrodynamics of LIFT, the ablated material was
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13 transferred to the substrate, forming spherical nanoparticles with sizes from several tens to several
14
15 hundreds of nm. We note that the second approach appears preferable, as dielectric resonances can
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17 be more easily observed and investigated when the nanoparticles are deposited on a transparent
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19 substrate. However, in both geometries, controlling the size and shape distributions of the Si
20
21 nanostructures was difficult. As one solution to this problem, a ring-shaped distribution of intensity
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23 on a Si wafer surface was used under LIFT, and this approach made possible the production of
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25 large (> 400 nm) nanoparticles.¹¹⁰ Later, Chichkov and his colleagues proposed an important
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27 modification of the LIFT technique to solve the problem of nanoparticle size control.¹⁰⁹ Here,
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29 instead of a bulk Si target, they used a silicon-on-insulator wafer, consisting of an upper crystalline
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31 silicon layer (100 nm) deposited on a 200 nm silicon dioxide layer grown on a bulk Si wafer. When
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33 such a structure was illuminated by a tightly focused fs beam, the upper Si layer was rapidly heated
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35 and melted, while the SiO₂ layer remained unaffected. Under appropriate radiation intensity,
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37 increased surface tension led to the formation of a droplet, which moved toward the substrate
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39 placed at some distance (5 μm) from the target where it solidified. Using this approach, the authors
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41 were able to produce amorphous Si nanoparticles with controllable sizes ranging from tens of nm
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43 to hundreds of nm. As a next step, the nanoparticles were fully crystallized by applying a second
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45 laser pulse of appropriate duration and intensity.¹⁰⁹ Thus, the LIFT geometry enables one to easily
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3 obtain Si nanoparticle arrays exhibiting dielectric resonances, while the position of these
4 resonances can be tuned by changing conditions of LIFT experiment.
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8 **Laser spark processing (LSP).** LSP is an alternative method for material nanostructuring
9 in the gaseous phase, which implies the production of a hot plasma in order to modify
10 material properties.¹¹¹⁻¹¹⁴ LSP typically requires infrared laser radiation like that of a pulsed
11 CO₂ laser (10.6 μm wavelength, 1 μs pulse), which is strongly absorbed by the laser-
12 induced plasma itself *via* inverse Bremsstrahlung mechanism.¹¹⁵ When focused in air or
13 other atmospheric pressure gas, such radiation can initiate a gas breakdown avalanche,
14 which emerges as a bright flash (laser spark) moving toward the focusing lens (Figure 5a).
15 The placement of a target near the lens can lower the breakdown threshold by 2-3 orders of
16 magnitude by providing initial avalanche-triggering electrons.¹¹⁶ Because almost all
17 radiation energy is absorbed in the front of the plasma shock wave moving toward the lens,
18 a laser spark plasma can accumulate a huge amount of energy. Therefore, nanoclusters
19 ablated from the target by LSP find themselves in a hot plasma with temperatures higher
20 than 10⁴ K¹¹⁵ and intense electromagnetic fields,¹¹⁷⁻¹¹⁹ which can lead to modification of
21 their properties. The clusters then return to the focal spot due to hydrodynamic processes
22 in the laser plasma¹¹⁵ to form a crystalline nanostructured film.
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44 After multi-pulse treatment by LSP in air or other atmospheric pressure gases (Ar, N₂, *etc.*),
45 the Si surface presents an eroded area covered by redeposited nanostructured material with
46 the absence of any notable crater.¹¹³ Note that the morphology of a Si surface, subjected to
47 multi-pulse treatment by conventional ultraviolet or visible laser radiation, is characterized
48 by the formation of characteristic deep craters with microspike structures on the bottom
49 encircled by a “hill” of redeposited material.¹¹³ SEM studies reveal nanoparticles with sizes
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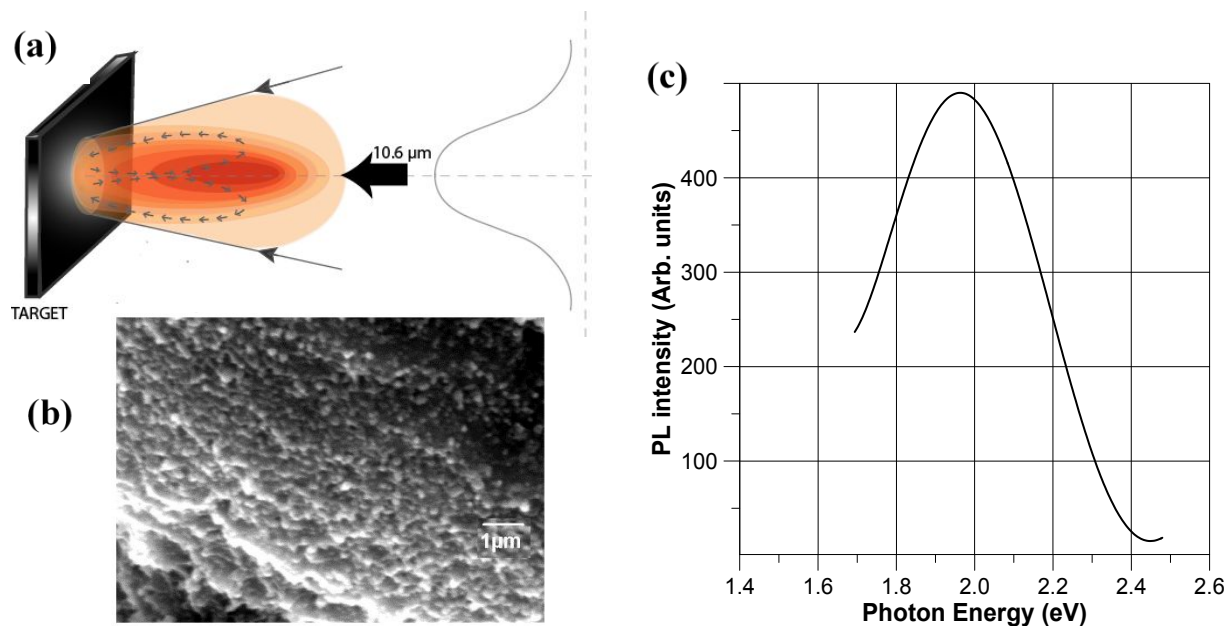


Figure 5. (a) Schematics of laser-induced air breakdown initiation: A target generates the first electrons, which trigger the avalanche discharge of cold gas molecules. The discharge moves toward the focusing lens absorbing most of the incident radiation power in the plasma forefront. The plasma-based mechanism of radiation power absorption leads to the increase of plasma temperatures up to 10^4 - 10^5 K; (b) Typical SEM image and (c) PL spectrum from Si nanostructures formed by laser spark processing. PL was excited by 488 nm pumping. Adapted from Ref. 112, 113 with permission from AIP Publishing and Elsevier, respectively.

ranging from 20 to 70 nm, which are densely packed to form a nanostructured film (Figure 5b). Increasing the laser energy igniting the spark can also lead to formation of microscale flower-like structures associated with coagulation of nanoparticles. Nevertheless, a detailed analysis of the properties of Si layers by XRD and XPS reveals the presence of 2-5 nm crystals embedded into a SiO_x matrix to form larger nanoscale structures.¹¹² As shown in Figure 5c, the layers prepared by LSP exhibit strong PL with a characteristic band around 1.9-2.0 eV (640-650 nm) having similar characteristics to layers prepared by PLD. The nanocrystals can be dispersed using ultrasound to form colloidal dispersions and then used in bioimaging or optoelectronics applications.

Pulsed laser ablation in liquids (PLAL). PLAL has appeared as an alternative laser-assisted method to fabricate a variety of colloidal nanoparticles in liquid ambients.^{76, 120-123}

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3 PLAL is now experiencing spectacular growth due to its simplicity of synthesis (no vacuum
4 equipment is required) and properties of synthesized nanostructures (*e.g.* high purity,
5 spherical shape, and unusual chemistry).¹²⁴ In a common ablation geometry, a solid target
6 immersed in a liquid is ablated by laser radiation, forming nanoclusters, which then
7 coalesce during their cooling in the liquid environment to yield a colloidal nanoparticle
8 dispersion.⁷³ However, in cases of ablation of Si and other materials by conventional ns
9 lasers (*e.g.* Nd-YAG), size characteristics of the produced nanoparticles are difficult to
10 control. Indeed, a nanosecond laser radiation typically has high energy (mJ/pulse and
11 larger), which leads to the initiation of hot plasma near the target, whose energy is then
12 transferred to the liquid to form a cavitation bubble.⁷³ Subsequent phenomena associated
13 with target heating by the plasma and the collapse of the cavitation bubble (releasing
14 mechanical energy) inevitably lead to uncontrolled parasitic ablation of the material and
15 the appearance of a second broadly size-dispersed population of nanoparticles, in addition
16 to the first narrow population caused by purely radiative ablation.¹²³ Therefore, Si
17 nanoparticles prepared under a nanosecond ablation regime, are typically relatively large
18 and broadly size-dispersed.^{122, 125-127} As we have shown,^{123, 128} the size dispersion problem
19 can be solved by operating in the ultrashort (femtosecond) laser ablation regime, which is
20 characterized by a 10 times lower energy to initiate ablation of material. In this case,
21 ablation under low intensities (near the ablation threshold) minimizes plasma heating and
22 bubble collapse effects, and thus suppresses the formation of the second broadly dispersed
23 population of nanoparticles. An example of Si nanoparticles prepared by fs laser ablation
24 from a Si target near the ablation threshold, is shown in Figure 6.
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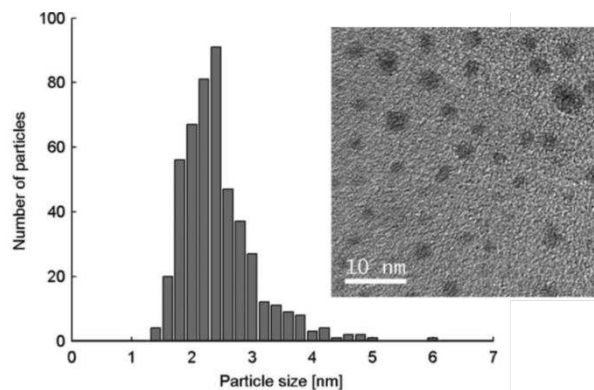


Figure 6. A TEM image of Si nanoparticles produced by femtosecond laser ablation from a silicon target in deionized water (near-threshold ablation conditions) and corresponding TEM image of formed nanoparticles. Adapted from Ref. 128 with permission under a Creative Commons CC-BY license.

Laser fragmentation from pre-prepared colloids is another important modification of the PLAL method to improve size and structural characteristics of formed Si nanoparticles. Here, fs laser fragmentation looks especially promising due to advantages offered by the non-linear character of interaction of ultrafast laser radiation with a liquid environment. We have shown that such an interaction leads to the generation of a white light “supercontinuum” of fs duration,^{129, 130} which can illuminate the whole liquid volume. As a result, the supercontinuum-based radiation can ablate micro/nano colloids in a large volume, creating identical conditions for re-growth of nanoclusters in order to obtain uniform size characteristics of the formed nanoparticles. In the case of Si, fs laser fragmentation can further be simplified by using a mechanical milling step to prepare initial colloids.¹³¹ Here, a Si wafer is milled to form arbitrarily-shaped particles with characteristic sizes of 0.5-5 μm (Figure 7a). In a second step, the radiation from a fs laser is focused in the very center of a glass vessel filled an aqueous dispersion of Si microparticles, while the solution is constantly mixed by a magnetic stirrer (Figure 7b,c). As shown in Figure 7, such fs laser fragmentation leads to the production of dispersions of low polydispersity Si nanoparticles. The size of these nanoparticles can be varied between a few nm and several

tens of nm by changing the initial concentration of the microcolloid (Figure 7d). As seen in high-resolution TEM and electron-diffraction images (Figure 7e), laser-synthesized nanoparticles possess a crystalline Si core (Figure 7e), while XPS studies reveal the presence of a few nm thick oxide shell on their surface.^{131, 132} The number of oxygen-related defects in the Si core can be controlled by varying the oxygen content of the solvent during the ablation process. This can be done by fragmenting Si microcolloids in oxygen-rich conditions (deionized water) or oxygen-free conditions (with O₂ concentration reduced *via* Ar gas bubbling).¹³² Although the formed nanoparticles are bare (ligand-free), dispersions of these nanoparticles exhibit very high stability due to a strong negative charge of nanoparticles (exceeding -35 mV according to zeta-potential studies).¹³¹ In contrast to

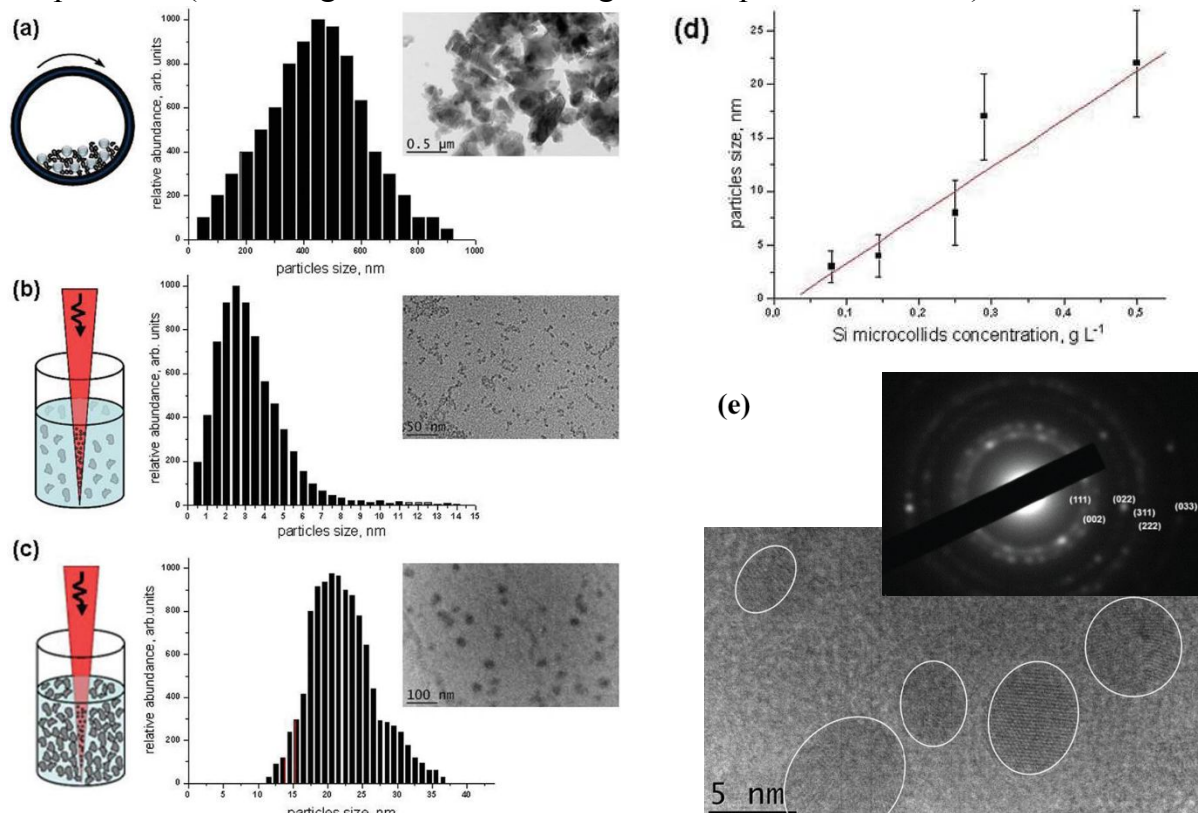


Figure 7. (a–c) Size distributions and typical TEM images of Si particles after: mechanical grinding of *c*-Si wafer (a); femtosecond laser fragmentation of Si microcolloids in aqueous solutions under their low (b) and high (c) concentrations. (d) Dependence of mean size of fragmented nanoparticles on initial microcolloid concentration; (e) High-resolution TEM image and electron diffraction pattern of formed nanoparticles. Adapted from Ref. 131, 132 with permission of the Royal Society of Chemistry.

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3 porous Si or other counterparts prepared by wet chemistry, laser-synthesized nanoparticles
4 prepared in deionized water do not contain any impurities on their surface, which can
5 facilitate their direct use in biological systems.
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10 Nanosecond laser fragmentation from pre-prepared colloids presents another interesting
11 implementation of PLAL, which can provide quite different properties of formed
12 nanostructures. Li¹³³ used an unfocused ns beam for the fragmentation of pre-prepared Si
13 colloids and obtained a trend opposite to that observed in the fs fragmentation case, namely
14 an increase of the final size of formed Si structures. The final product presented ideally
15 spherical narrowly-size-dispersed microcolloids with crystalline structure. It was suggested
16 that such structures are formed under a steady regime of laser heating, when radiation
17 intensity is relatively low.¹³³
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30 We note that the PLAL technique provides opportunities for the formation of Si-based
31 composite structures, as it renders possible easy mixing of different nanomaterials and their
32 subsequent co-ablation (co-fragmentation). One promising strategy is the synthesis of
33 nanoparticles of material A in aqueous (deionized water) or organic (acetone, ethanol)
34 media, and then ablation of material B in the presence of nanoparticles of material A.
35 Ablating a gold target in the presence of pre-prepared Si colloids in deionized water, we
36 recently showed the possibility of forming Au-Si core-shell structures with controlled
37 percentage of Si in their composition.^{134, 135} A specific advantage of such nanostructures
38 consists in the combination of plasmonic and semiconductor properties, while the Si shell
39 surface can provide excellent biocompatibility of the core-shell.
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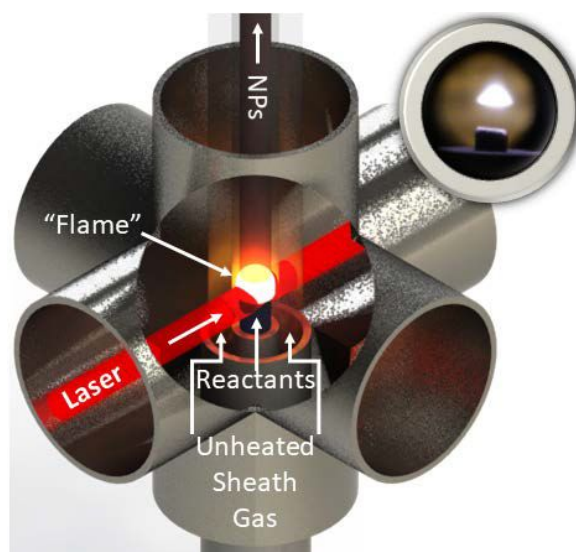
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3 Many studies on PLAL-based synthesis of Si nanoparticles were related to the search for
4 conditions that yield materials with strong PL emission.^{125-127, 136, 137} However, these efforts
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6 to achieve bright PL were less successful than in the case of laser ablation in gaseous
7
8 environments. Here, most work reported blue (2.7-2.7 eV)¹²⁵⁻¹²⁷ and green (2.2-2.3 eV)¹³⁷
9
10 PL bands when the ablation was performed in water or organic solutions (ethanol, *etc.*).
11
12 Such PL bands are normally associated with defect-related mechanisms in SiO_x.^{67, 68} Red
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14 PL associated with quantum confinement effects⁷⁰⁻⁷² was not detectable, suggesting a
15
16 defect-rich structure of Si nanocrystals formed by PLAL. Svrcek¹³⁸ studied the effect of
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18 laser fragmentation on properties of water-dispersed nanocolloids of milled porous silicon,
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20 which originally exhibited strong exciton-based PL. They found that irradiation of porous
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22 silicon colloids leads to a significant quenching of the original PL and the appearance of
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24 another band in the green range, while fs laser fragmentation led to much stronger green
25
26 PL signals compared to the ns case. Saitow¹³⁹⁻¹⁴¹ presented an interesting modification of
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28 PLAL by performing laser ablation in supercritical CO₂. Si nanoparticles formed under
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30 these conditions could exhibit conventional PL bands in the blue, green and red ranges,
31
32 although the quantum yield of these emissions was not presented. The authors explained
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34 the reported PL properties based on the conditions of cooling of nanoclusters in
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36 supercritical fluids.
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45 Several studies focused on the functionalization of laser-synthesized nanoparticles by
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47 organic molecules during laser-ablative processing. Such functionalizations are especially
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49 important for some potential biomedical applications. As an example, Intartaglia¹⁴²
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51 reported 1-step conjugation of the Si nanoparticle surface by oligonucleotides by adding
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53 them to the solution during the synthesis. As another possibility, Tamarov³⁰ reported
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3 conjugation of Si nanoparticles by dextrans, and a subsequent use of such conjugated
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5 complexes in cancer treatment.
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8 9 ***Laser Pyrolysis of Silanes***

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11 Soon after the invention of the CO₂ laser, Cannon *et al.* demonstrated that CO₂ laser
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13 irradiation could be used to heat gaseous mixtures containing silane (SiH₄), initiating silane
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15 decomposition and nucleation of silicon nanoparticles.^{74, 75} This is facilitated by the strong
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17 absorbance of silane at the CO₂ laser wavelength of 10.6 μm. In this laser pyrolysis process,
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19 a CO₂ laser directly heats gas phase species to a temperature (typically >1000 °C) high
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21 enough to decompose silane or other precursor gases. If the precursor gases are transparent
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23 at the laser wavelength, a photosensitizer such as SF₆ is added. The precursor stream is
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25 usually surrounded by a “sheath gas” stream, as shown in Figure 8. The sheath gas is
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27 transparent to the laser and is therefore not heated. Upon leaving the laser beam, the product
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29 particles are very rapidly cooled by mixing with unheated gas, quenching further particle
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31 growth and sintering. The small high-temperature region in which particle formation
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55 **Figure 8.** Schematic illustration of laser pyrolysis reactor. The inset shows a photo of the laser “flame”
56 that is visible in the region where the laser beam intersects the precursor gas stream.
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3 occurs, is often called the laser “flame”. Although it is not a flame in the conventional
4 sense, the rapid deposition of energy from the laser directly into the gas, produces visible
5 thermal emission from the heated particles and gases that has the appearance of a flame.
6
7 Laser pyrolysis provides short reaction times for precursor decomposition and particle
8 formation (a few ms), which allows production of loosely agglomerated particles of small
9 size at substantial production rates,¹⁴³ from hundreds of mg per hour in laboratory-scale
10 systems to nearly kg per hour rates using high-power industrial lasers.
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20 The laser pyrolysis method employs no solvent, gases are available in extremely
21 high purities (*e.g.* semiconductor grade silane, of 99.9999% purity), and the reactor walls
22 are not heated, eliminating potential sources of contamination. The particle formation
23 atmosphere can be precisely controlled to exclude oxygen and other species that can react
24 with silicon. In the pioneering studies of Cannon *et al.*, the silicon nanoparticles were 10 to
25 100 nm in size.^{74, 75} However, our group showed that by tuning pressure, laser power, and
26 the reactive environment, the mean size for silicon nanoparticles can be reduced below 5
27 nm.¹⁴³ This is close to the size at which silicon nanoparticles begin to exhibit efficient size-
28 dependent photoluminescence due to quantum confinement. To produce Si nanoparticles
29 with bright, size-dependent photoluminescence, we further etched the nanoparticles with
30 nitric/hydrofluoric acid mixtures to produce a desired final size and photoluminescence
31 emission color.^{77, 78, 143} The photoluminescence of these nanoparticles can be stabilized *via*
32 covalent attachment of organic ligands through hydrosilylation reactions, which also makes
33 them dispersible in non-polar solvents.^{77, 78} Attachment of ligands that make the silicon
34 nanoparticles directly dispersible in water is possible,^{144, 145} but has proven much more
35 difficult. This combined bottom-up and top-down approach to silicon nanoparticles
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synthesis is a powerful method for achieving well-controlled size and photoluminescence performance from particles produced in macroscopic quantities.

Table 1 summarizes details of various laser-based techniques to fabricate nanosilicon structures.

Table 1. Summary and comparison of different laser processing methods.

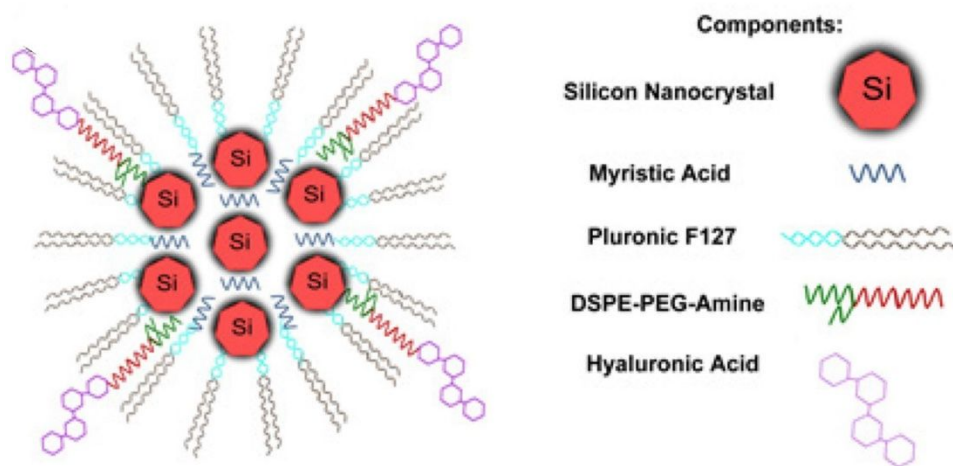
Technique	Pulsed Laser Ablation in gaseous ambient			Pulsed Laser Ablation in gaseous ambient		Laser pyrolysis of silanes
	PLD	LIFT	Laser spark	Long pulse ablation	Short pulse ablation	
Configuration	PLD	LIFT	Laser spark	Long pulse ablation	Short pulse ablation	
Typical laser source	Excimer	Ti/Sapphire	CO ₂	Nd/YAG	Ti/Sapphire, Yb:KGW	CO ₂
Wavelength	248, 193 nm	800 nm	10.6 μm	532 nm, 1.06 μm	800 nm, 1025 nm	10.6 μm
Pulse length	20-30 ns	100-140 fs	~ 1 μs	10-20 ns	100 fs – 2 ps	~ 1 μs
Typical ambient	Buffer gas (He, Ar, H)	Air	Air	Aqueous or organic (ethanol, acetone)	Aqueous or organic (ethanol, acetone)	SiH ₄ gas, H ₂ , or He
Final product	Nanostructured films or nanopowders, crystal size 2-4 nm, can be dispersed in liquids	20 nm – 400 nm NPs of amorphous Si, can be crystallized by laser irradiation	Nanostructured films or powders, crystal size 2-4 nm, can be dispersed in liquids	Colloidal solutions of nanoparticles, 10 nm – 500 nm, widely size-dispersed	Colloidal solutions of nanoparticles, 10 nm – 150 nm, low size-dispersed	Nanopowders, minimum crystal size 2-4 nm, tunable up to >30 nm.
Merits	High quality crystals, providing exciton PL band	Able to produce large Si NPs on a substrate	High quality crystals, providing exciton PL band	Defect-rich structure, which can enable a variety of therapies	Controllable size, defect-rich structure, which can enable a variety of therapies, fast biodegradability	High purity and crystallinity, relatively high throughput
Limitations	Wide size-dispersion after milling		Wide size-dispersion after milling	No exciton PL, wide size dispersion	No exciton PL	Post-processing required for exciton PL and dispersion in solvents

Surface Functionalization and Encapsulation in Nanocapsules

Most as-synthesized photoluminescent silicon quantum dots (Si QDs) do not form stable dispersions in water, which prevents their direct use in most biological applications. Polymer or micelle encapsulation not only makes them water dispersible, but also preserves their optical properties and protects them from oxidation and degradation.^{11, 146} While we focus here on

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3 methods applied to laser-synthesized silicon nanoparticles, consistent with the theme of this
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5 review, most of these approaches are also applicable to Si QDs produced by other means. PEG-
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7 terminated polymers form stable micelles that exhibit long circulation times *in vivo*. PEGylated
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9 phospholipids form particularly stable micelles, even at high dilution, *i.e.* they have very low
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11 critical micelle concentration (CMC). Hydrophobic materials can be transported within their
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13 hydrophobic core, while targeting agents such as antibodies, aptamers, proteins, or peptides can
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15 be attached to the micelle surface to promote localization and cellular at a disease site.
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19 In one example, we used Pluronic® F127 and DSPE-PEG-NH₂ to co-encapsulate laser-
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21 synthesized silicon quantum dots and myristic acid.¹⁴⁷ Hyaluronic acid was attached to the micelle
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23 surface (Figure 9) to target CD44 (Figure 9). Such Si QDs have been used for cancer theranostics.
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25 The slow release of myristic acid from the core of the structure provides sustained delivery. In
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27 related work, we encapsulated Si QDs in Pluronic® block copolymers to make them water-
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29 dispersible for use in cancer imaging. Interaction between the poly (oxypropylene) (PPO) block of
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31 F127COOH and ethyl undecylenate attached to the Si QDs stabilized the micelles.¹⁴⁸ The poly
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33



53
54 **Figure 9.** Schematic of a theranostic nanoconstruct using pluronic, DSPE-PEG-Amine, and hyaluronic
55 acid for encapsulation and targeting of Si QDs and myristic acid. Adapted from Ref. 147 with permission
56 under a Creative Commons CC-BY license.
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(oxyethylene) (PEO) and carboxylate groups of the F127COOH formed a hydrophilic shell at the exterior surface of the micelle, making them water-dispersible.

Our group has extensively employed phospholipid micelles as Si QD carriers, with each micelle transporting many Si QDs.^{11, 149} The interaction of the hydrophobic phospholipid domain of amphiphilic phospholipid-PEG molecules with the hydrophobic Si QDs produces micelles loaded with multiple Si QDs (MSi QD). This approach allows simultaneous co-encapsulation of other hydrophobic entities within the micelles (Figure 10). In one study, we functionalized Si QDs with hydrophobic moieties including styrene, octadecene, and ethyl undecylenate to make them dispersible in chloroform.¹⁵⁰ Transfer of these hydrophobic Si QDs into phospholipid micelles enabled their stable dispersion in water. We employed amine-functionalized phospholipid-PEGs to create luminescent probes for *in vitro* cell labeling studies.

The polymeric micelles have much lower CMC values ($\sim 10^{-6}$ M) compared conventional detergents like CTAB or SDS. Thus, they are much less dynamic than detergent micelles.

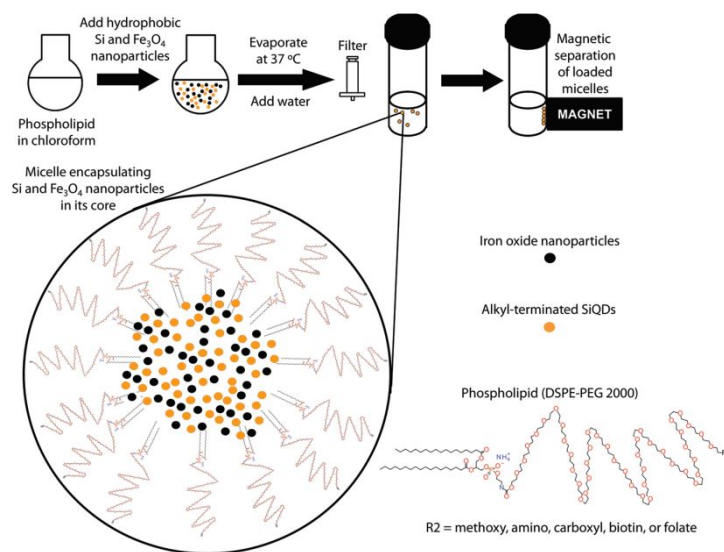


Figure 10. Schematic illustration of co-encapsulated silicon quantum dots and magnetic iron oxide nanoparticles and their preparation. The nanoparticles are functionalized with hydrophobic ligands that interact with the alkyl chains of the phospholipid. These interactions stabilize the phospholipid-PEG micelles with multiple encapsulated nanoparticles. Adapted from Ref. 149 with permission from the American Chemical Society.

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3 Nonetheless, like detergent micelles, these polymeric micelles incorporate “oil-like” hydrophobic
4 molecules or particles within their hydrophobic core. Meanwhile, the PEG layer on the exterior of
5 the micelle is both hydrophilic and uncharged. These features extend circulation time and broaden
6 biodistribution *in vivo*. Functionalization of a fraction of the PEG lipids with specific groups
7 facilitates the attachment of targeting moieties to promote delivery to particular tissues or cell
8 types.
9

19 **Applications of Laser-Processed Nanosilicon**

21 *Applications in Energy*

23
24 Silicon nanoparticles, including those prepared by laser-based methods, can be used
25 in a wide range of energy-related applications that take advantage of their optical,
26 electronic, and chemical properties. Among other possibilities, they can serve as absorbers
27 in photodetectors or solar cells,¹⁵¹⁻¹⁵⁵ serve as emitters in LEDs,¹⁵⁶⁻¹⁵⁹ be used as
28 photoluminescent components in solar concentrators,¹⁶⁰ react with lithium ions in high-
29 performance anodes for lithium ion batteries,^{161, 162} and be used in hydrogen generation *via*
30 reaction with water.²³ This section briefly describes specific selected examples of these
31 applications in which laser-synthesized silicon nanoparticles have been employed. For
32 some of these applications, particularly where large quantities of nanoparticles are needed
33 and costs must be low, other nanostructuring methods may be more appropriate than laser
34 processing. Nonetheless, nanoparticles from laser processing can be quite valuable in
35 demonstrating these applications and developing devices.
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3 **Photovoltaics and Photodetectors.** Silicon, in the form of single-crystalline or
4 polycrystalline wafers, is the dominant material used for photovoltaics and photodetectors
5 for visible light, from the CMOS cameras in cell phones to large-scale solar power
6 installations. Silicon, as an indirect bandgap material, is inherently a weak absorber of
7 visible light, so these bulk silicon devices rely on thick silicon layers for light absorption.
8 One manner in which silicon nanoparticles have been used in conventional silicon
9 photovoltaics is in preparation of silicon inks for fabrication of selective emitter structures
10 by screen printing on top of conventional silicon solar cells. The Dupont Innovalight
11 CougarTM process provides one example of this approach.¹⁶³ However, such applications
12 do not rely on any special properties of the silicon nanoparticles, other than the ability to
13 formulate them into a screen-printable ink. Theoretical studies have described the potential
14 of silicon nanoparticles in third-generation photovoltaics that achieve carrier
15 multiplication.¹⁶⁴ However, many challenges related to weak absorbance of silicon and
16 poor charge transport within silicon nanoparticle films remain to be overcome before such
17 devices can be realized.

18
19 Silicon absorbs strongly at UV wavelengths, below about 365 nm (3.4 eV), where a direct
20 band-to-band transition can occur. Thus, a thin film of luminescent silicon nanoparticles
21 can enhance the efficiency of conventional silicon solar cells by serving as down converters
22 – absorbing UV wavelengths that are poorly harvested by the underlying solar cell, and re-
23 emitting at wavelengths well-matched to the underlying solar cell. Such approaches have
24 been demonstrated with Si QDs produced by electrochemical etching,¹⁶⁵ nanosecond
25 pulsed laser ablation,¹⁶⁶ and low-pressure plasma¹⁶⁷ methods, among others. Si QDs from
26 these different methods, and others, have produced similar levels of enhancement of overall

power conversion efficiency, up to a few percent, but direct performance comparisons are not possible, because each study used different underlying solar cells with different efficiencies and wavelength responses.

One can also exploit the UV absorbance of silicon to create a UV-sensitive photodetector by using silicon nanoparticles as the only absorber in the device. We demonstrated this using laser pyrolysis of silane followed by HF etching to produce H-terminated silicon nanoparticles. We then grafted diallyl disulfide to the surface of the nanoparticles.¹⁵¹ This laser synthesis and surface functionalization allows production of a high-quality colloidal silicon nanocrystal ink with short covalently bound surface ligands that allow reasonable charge transport within a solid film of the nanocrystals. In addition to the spin-cast film of functionalized silicon nanocrystals, the finished device included a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) electron blocking layer and top- and bottom-contacts. Photogenerated charge separation in the device was driven by the

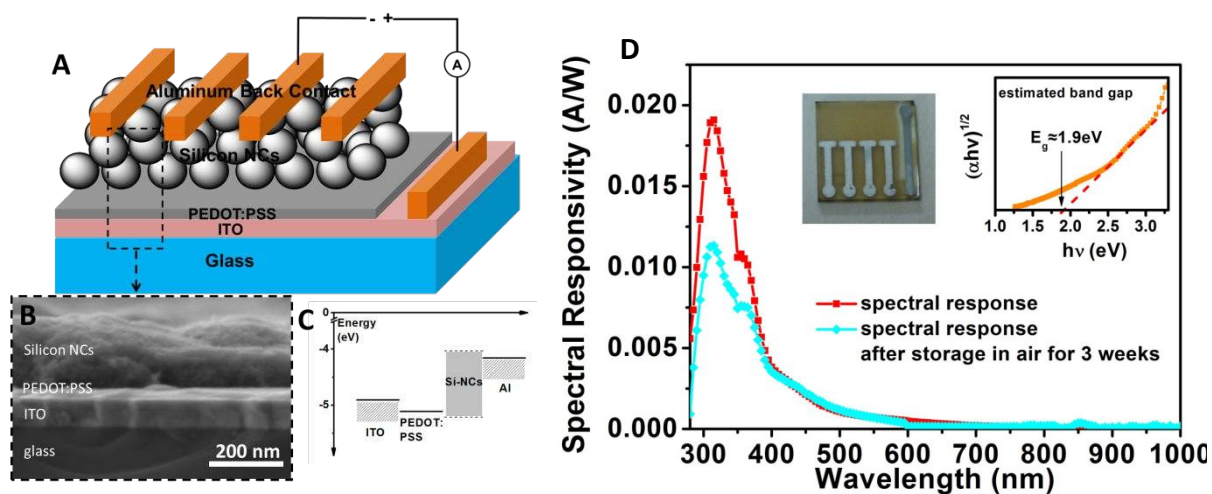


Figure 11. Structure and characterization of a silicon nanocrystal-based UV photodetector, A) Overall device structure, B) Actual device imaged with SEM, C) device energy band diagram, and D) Spectral responsivity before (red curve) and after (blue curve) 3 weeks of storage in air. Indirect bandgap estimation by the Tauc method and a photograph of representative SiNC devices are shown as insets. Adapted from Ref. 151 with permission from John Wiley and Sons.

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3 Schottky-junction formed at the interface between the Al back electrode and the silicon
4 nanocrystal layer. Figure 11 illustrates the device structure and its performance. The peak
5 photoresponse of 0.02 A W^{-1} at UV wavelengths, from the unpackaged diode, is
6 approaching that of III-V and SiC-based UV photodetectors that are commercially
7 available. This provides a route to large-area solution-processed UV photodetectors and
8 demonstrates the potential of inks formulated from laser-processed silicon nanocrystals for
9 broader applications in solution-processed optoelectronics. Alkis *et al.*¹⁵⁴ took a different
10 approach in which they coupled silicon nanoparticles produced by laser ablation to
11 plasmonic silver nanoparticles to achieve enhanced visible response in a silicon
12 nanoparticle-based photodetector. Yu *et al.*¹⁶⁸ combined nonthermal-plasma synthesized
13 silicon quantum dots with graphene to fabricate a photodetector with very impressive
14 performance. This same approach could be taken with laser-synthesized Si QDs.
15 Unfortunately, direct comparisons between photodetector performance achieved with Si
16 QDs from laser pyrolysis, laser ablation, and low-pressure plasma synthesis is hindered by
17 the fact that each study used a different device architecture.

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39 Laser-synthesized silicon nanoparticles have also been incorporated into organic
40 photovoltaic devices, where they have provided improved overall efficiency and higher
41 open circuit voltage. In one study, we demonstrated a hybrid organic-inorganic
42 photovoltaic device that combined poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl-C61-
43 butyric acid methyl ester (PCBM) with silicon nanocrystals from laser pyrolysis. The Si
44 NCs were etched with HF and then mixed with P3HT/PCBM without any additional surface
45 modification.¹⁵³ Adding the Si-NCs to the bulk heterojunction device produced an extended
46 optical excitation response and increased the short-circuit current by 26%.

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3 In a separate study, we incorporated silicon nanoparticles into hybrid organic-inorganic
4 photovoltaics without including P3HT as an absorber.¹⁵² In this case, PCBM and PEDOT:PSS
5 served as electron and hole transport layers, respectively. The silicon nanoparticles were
6 sandwiched between the PCBM and PEDOT:PSS. This study focused on relating the solar cell
7 performance to the size of the silicon nanoparticles. We showed that both the size of the Si-NCs
8 and their crystallinity (amorphous fraction) affected the open circuit voltage (V_{OC}) of the device.
9 Both of these properties can be tuned by varying the operating conditions in the laser pyrolysis
10 process. Band-gap widening in smaller or less crystalline (higher amorphous fraction) silicon
11 nanoparticles increases the V_{OC} when PCBM is used as the acceptor in the device. The
12 observed V_{OC} reached 0.634 V in a cell made with 5.7 nm Si-NCs. However the overall efficiency
13 remained low, because of the relatively weak absorbance of the thin film of silicon nanocrystals
14 and the poor charge transport through the Si-NC film. Another study, using commercially-
15 available silicon nanoparticles (of uncertain production method) found a detrimental effect of their
16 incorporation into a P3HT/PCBM organic photovoltaic device.¹⁶⁹

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19 Meinardi *et al.*¹⁶⁰ demonstrated the use of Si QDs in luminescent solar concentrator systems, in
20 which the Si QDs embedded in a window film absorb UV light and emit visible light that is guided
21 to the window edges, where it is used by conventional photovoltaic devices. This work employed
22 Si QDs from nonthermal plasma synthesis, but such devices could equally-well employ laser-
23 synthesized Si QDs. This is a particularly promising application of Si QDs because it relies on
24 absorbance of UV wavelengths, where silicon is a strong absorber, and requires minimal re-
25 absorption of emitted light by the absorber. Based on the similar performance of Si QDs of
26 different origin as down converters in films deposited atop silicon solar cells, one would also
27 expect similar performance here.

Silicon Nanoparticle-based Lithium Ion Battery Anodes. Silicon has exceptional potential as an anode material for lithium ion batteries. Its theoretical gravimetric capacity for lithium ion storage is more than ten times that of graphite, which is used in the anodes of most current lithium ion batteries. However, silicon anodes are subject to poor cycling performance due to mechanical failure, pulverization, and formation of an unstable solid-electrolyte interphase (SEI) layer. Silicon nanostructures can accommodate significantly greater stress and strain than bulk silicon, and also have higher electrolyte-accessible surface area and shorter electronic and ionic transport distances, improving rate capabilities. Unfortunately, this can also increase the area for SEI formation. Thus, a huge amount of research effort has been devoted to developing silicon nanostructures for use in lithium-ion batteries and to stabilization of the SEI on silicon anodes. Much of this work

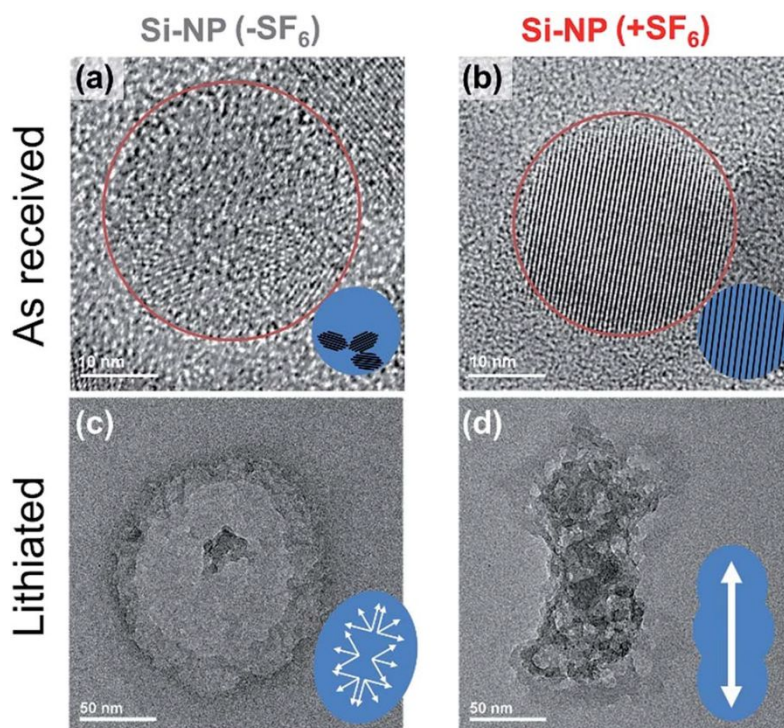


Figure 12. HR-TEM images of an amorphous Si nanoparticle (-SF₆; panels a and c) and a single crystalline Si nanoparticle (+SF₆; b and d) before (a and b) and after (c and d) lithiation. From Ref. 161. Used with permission from the Royal Society of Chemistry.

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3 was recently reviewed by Ryu *et al.*¹⁷⁰ Relatively few studies have considered the use of
4 laser-synthesized silicon for lithium ion batteries, because the large-scale use of silicon in
5 this application will require production at extremely low cost (<\$100/kg). Nonetheless, the
6 ability to control size, purity, and crystallinity using laser-based processing could prove
7 advantageous in understanding the performance of silicon nanostructure-based anodes.
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10 In one study that specifically focused on laser-based synthesis of silicon nanoparticles for use in
11 lithium ion battery anodes, Kim *et al.*¹⁶¹ optimized their reactor conditions to achieve 97%
12 conversion of silane to silicon by laser pyrolysis, producing ~20 nm, single-crystalline silicon
13 nanoparticles that performed well as a lithium ion battery anode material. In addition to achieving
14 high utilization of silane (which is essential for keeping cost down), this study demonstrated the
15 ability to control the crystallinity of the product Si nanoparticles by varying the amount of sulfur
16 hexafluoride (SF₆) used as a photosensitizer to absorb the laser energy. Although silane directly
17 absorbs the CO₂ laser energy, SF₆ is a much stronger absorber, and can therefore be used to
18 produce a much higher temperature in the laser pyrolysis process. As shown in the top two panels
19 of Figure 12, this allowed production of amorphous or poorly-crystalline Si nanoparticles (panel
20 a) without SF₆ or highly crystalline Si nanoparticles (panel b) using an appropriate amount of SF₆.
21 Although the Si nanoparticles become amorphous upon lithiation (panels c and d), the initially
22 crystalline particles expand anisotropically (panel d), which allowed them to better accommodate
23 the stress and strain associated with volume change during cycling. As a result, the highly
24 crystalline Si nanoparticles showed much better capacity retention than the amorphous or poorly-
25 crystalline particles, especially at high charge-discharge rates. This provides an example of how
26 the control of size and crystallinity provided by laser-based processing of silicon nanoparticles
27 can play an important role in the application of silicon nanoparticles in lithium ion batteries.
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3 Several studies have employed pulsed laser deposition to produce nanostructured silicon films for
4 use as lithium ion battery anodes.¹⁷¹ Radhakrishnan *et al.* used PLD to deposit nanostructured
5 silicon on multilayer graphene that had been grown by chemical vapor deposition on a nickel foam
6 substrate.¹⁷² The resulting anodes exhibited impressive capacity and better stability than pure
7 silicon anodes, but they were only tested for a few cycles. Biserni *et al.* first deposited
8 nanostructured silicon by PLD, then overcoated it with carbon by CVD.¹⁷³ Garino *et al.* employed
9 alternating PLD of silicon and carbon to make nanostructured multilayered Si/C films for use as
10 anodes in microbatteries.¹⁷⁴ They showed that controlling the porosity of the multilayer structure
11 was a key to achieving both good performance and relatively good stability of the anode.
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24 **Hydrogen Generation by Reaction of Silicon Nanoparticles with Water.** Another energy-
25 related application of silicon nanoparticles is on-demand generation of hydrogen by
26 reacting them with water.²¹⁻²³ In such a system, the silicon nanoparticles essentially serve
27 as a source of stored energy, while the water serves as a carrier of hydrogen. Aluminum
28 and other water-reactive metals can be used in a similar manner and aluminum, in
29 particular, has been much more heavily studied for this application than silicon.¹⁷⁵ Silicon
30 has the advantage of providing four electrons per silicon atom allowing each silicon atom
31 to react with two water molecules to produce two H₂ molecules and one formula unit of
32 SiO₂. As a result it has a higher theoretical gravimetric capacity for hydrogen generation
33 than aluminum, and in combination with a hydrogen fuel cell can provide an exceptionally
34 high energy density source of electricity, substantially exceeding that of the best batteries.
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36 More recently, boron has been used in a similar manner.¹⁷⁶ It has much higher theoretical
37 gravimetric capacity for hydrogen generation than either silicon or aluminum, but suffers
38 from relatively high cost and low reactivity with water.
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3 In our study of hydrogen generation by reaction of silicon nanoparticles with water, we
4 demonstrated that nanosize silicon (~10 nm diameter) prepared by laser pyrolysis of silane reacts
5 with water, *via* base-catalyzed silicon etching, to generate hydrogen 10,000 times faster than bulk
6 silicon.²³ The H₂ production rate achieved using 10 nm Si was 150 times that observed for 100 nm
7 particles. This rate increase is much too large to be explained by the increased surface to volume
8 ratio of the smaller particles. The dramatic rate increase reflects change in the dynamics of the
9 etching process at the nanoscale. Larger silicon particles are etched anisotropically, while etching
10 of the 10 nm silicon is effectively isotropic. Figure 13 summarizes these results, comparing silicon
11 of different sizes and providing comparisons to prior studies. Figure 13(c) demonstrates that
12 hydrogen produced by reaction of silicon nanoparticles with water can be used directly in a fuel
13 cell. Here, the first key advantage of the laser pyrolysis synthesis of silicon is the ability to produce
14 sufficiently small (~10 nm) particles to allow their complete and rapid base-catalyzed reaction
15 with water. Because this base-catalyzed reaction is anisotropic, larger particles rapidly become
16 faceted, leaving only unreactive surface. They therefore do not fully react. Moreover, because the
17 nanoparticles are synthesized in a hydrogen-rich environment, they are produced with hydrogen
18 bound to their surfaces. This hydrogen is released during the reaction with water, such that the
19 actual amount of hydrogen produced even exceeds the theoretically expected yield (two H₂
20 molecules per Si atom). Even if the particles were not hydrogen-terminated, they could still react
21 in the same manner. However, surface oxidation can significantly reduce the gravimetric hydrogen
22 generation capacity, both by reducing the amount of silicon available for reaction and by adding
23 mass (of oxygen). Here, the hydrogen termination of silicon particles produced by laser pyrolysis
24 in hydrogen, provides an advantage over other synthesis methods that do not produce a hydrogen-
25 terminated surface.
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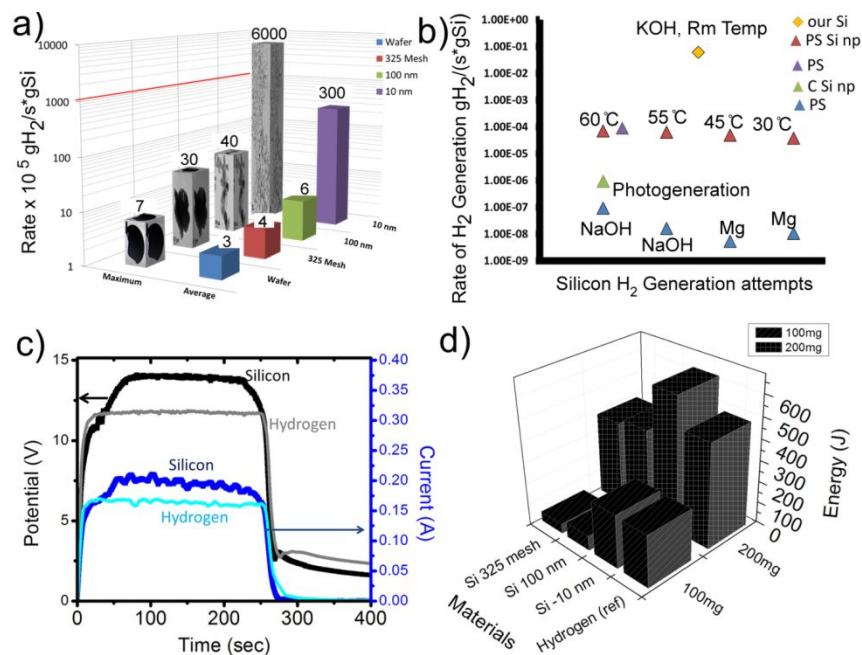


Figure 13. Rates of hydrogen generation and silicon and fuel cell performance using hydrogen produced by reaction of water and silicon. (a) Rates measured using different forms of silicon, with maximum and average rates in the left and right columns, respectively. (b) Rates reported in the prior literature and in Ref. 23 (see original paper for details) c.) Comparison of current and voltage outputs from a fuel cell using H_2 generated on demand from water and silicon nanoparticles compared to pure hydrogen in the amount expected by reaction of the amount of silicon used. d) Energy output from the fuel cell using different hydrogen sources. From Ref. 23, used with permission from the American Chemical Society.

While our work with silicon produced by laser pyrolysis demonstrated how small particle size and hydrogen termination were advantageous for hydrogen generation by reaction of silicon with water, the practical prospects of using laser-processed silicon for this application are limited. Thus, others have focused on use of additives and processing strategies with lower-cost, larger-size silicon. Kobayashi *et al.*¹⁷⁷ and Xu *et al.*¹⁷⁸ used ball milling (or bead milling) to reduce the silicon particle size to a range where hydrogen generation was effective. Brack *et al.*¹⁷⁹ explored the formation of nanocomposite pellets of silicon with additives such as sodium hydroxide to increase the rate of hydrogen generation. Approaches like these can employ very low-cost starting materials, such as waste from the photovoltaics industry or commodity ferrosilicon. Nonetheless,

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3 the practicality of any of these approaches remains to be fully demonstrated, and significant
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5 questions remain.¹⁸⁰
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8 ***Applications in Nanobiotechnology:***

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11 **Biological Assessment of Nanosilicon Prepared by Laser Processing.** Si nanostructures
12 occupy a particular niche related to biomedical applications. Excellent biocompatibility of
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14 Si nanoparticles and its oxide form, silica (SiO₂), are well known and described in the
15
16 literature.³²⁻³⁴ However, in contrast to silica, Si nanoparticles have an additional
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18 biodegradability option, which provides a decisive advantage for biomedical applications.
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20 Indeed, in the aqueous biological environment, Si nanostructures can decompose into
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22 orthosilicic acid, Si(OH)₄, which is then excreted in the urine. The biodegradability effect
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24 was studied for ultrasonically milled and water-dispersed porous silicon-based
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26 nanostructures prepared by electrochemical etching in HF/ethanol solutions.⁵ Those studies
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28 found that Si nanostructures can indeed biodegrade and completely dissolve in biological
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30 matrices and then be excreted from the body. However, due to the wide range of sizes and
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32 shapes of porous silicon-based nanostructures, their biodegradation was slow and could
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34 take more than 4-6 weeks.⁵ We recently studied dissolution of Si nanoparticles prepared by
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36 laser fragmentation in deionized water.^{6, 132} In contrast to porous Si-based structures, such
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38 nanoparticles were spherical and with low polydispersity, which was expected to contribute
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40 to better transport *in vivo*. We found that the dissolution rate of Si nanoparticles was
41
42 dependent on the concentration of oxygen defects in the crystalline Si core, which could be
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44 controlled by the content of dissolved oxygen in the aqueous ambient during the synthesis.
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46 Dense low-defect Si nanoparticles synthesized under oxygen-free condition (when
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48 dissolved oxygen removed Ar gas bubbling) completely dissolved after 2-3 weeks (Figure
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14a), as recorded by TEM and Raman spectroscopy. In contrast, oxygen defect-rich nanoparticles prepared in oxygen-rich conditions (no bubbling) exhibited a much faster dissolution kinetics and were mostly dissolved after 4-7 days (Figure 14a). This study illustrates an important reason for the strong potential of Si nanoparticles for applications in biological systems.

In vitro tests We recently studied the interaction of Si nanoparticles with biological matrices *in vitro* and *in vivo*.^{6, 30, 132} We did not observe any notable cytotoxicity toward human cells (HMEC) up to concentrations of 100 $\mu\text{g mL}^{-1}$ (cell survival rate exceeded

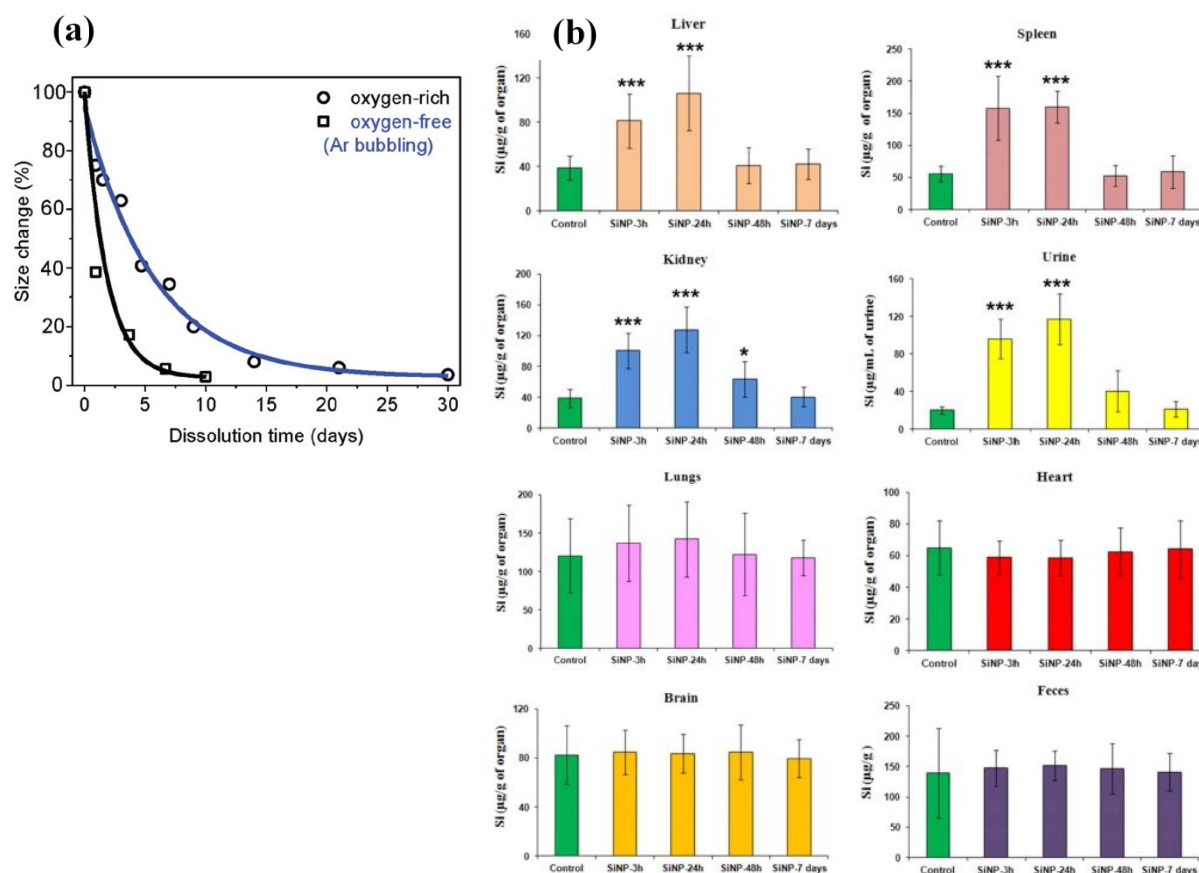


Figure 14. (a) Time evolution of the size of Si-nanoparticles prepared by femtosecond laser fragmentation in oxygen-rich (black) and oxygen-free (blue, Ar bubbling) water ambient, under nanoparticles aging in deionized water. Adapted from Ref. 132 with permission from the Royal Society of Chemistry; (b) Content of Si in mice organs and biological fluids after systemic administration with Si nanoparticle-based aqueous solutions (20 mg/kg) 3 h, 24 h, 48 h and 7 days after the injection related to mice control group. Adapted from Ref. 6 with permission under a Creative Commons CC-BY license.

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3 80%).¹³² We also found from electron microscopy that Si nanoparticles were taken up by
4 cells *via* an endocytosis mechanism.
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8 ***In vivo tests.*** To study the effect of Si nanoparticles on biological systems, we recently
9 studied the biodistribution, in a mouse model, of laser-synthesized nanoparticles.⁶ Here, the
10 worst scenario was considered, in which the nanoparticles were non-functionalized by PEG
11 and should have been immediately sequestered by the reticuloendothelial system. Four
12 groups of mice were systemically administered in the jugular vein with a single dose of 20
13 mg/kg of Si-nanoparticles in physiological solution and then examined at different
14 moments after the administration of nanoparticles. All animals remained healthy and
15 exhibited normal activity after nanoparticle administration. The body weight of mice from
16 Si nanoparticle-treated and control groups remained similar. To study biodistribution of Si
17 nanoparticles, we quantified Si concentration in different organs, including liver, spleen,
18 lungs, heart, *etc.*⁶ Here, during first hours we observed an increase of silicon content mostly
19 in the liver and spleen, evidencing a rapid sequestration of Si nanoparticles by the
20 reticuloendothelial system (Figure 14b). We then recorded the increase of Si concentration
21 in the kidneys and urine (24 h after administration), and its further progressive decrease.
22 After 7 days, we observed the return of Si content down to normal values in all matrices.
23 We observed only minor inflammation in hepatocytes during histopathological
24 examination of liver tissues, which disappeared 48 h after the injection. Such a result
25 contrasts to previous data on intravenous injection of silica (SiO₂) nanoparticles, presenting
26 an oxidized non-dissolvable form of silicon, whose accumulation in the liver led to major
27 damages.¹⁸¹ Similar clearance of Si nanoparticles within 48 hours was detected from
28 histopathological examination of spleen and kidney. We determined that the nanoparticles
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3 then biodegraded and silicon was eliminated in the urine without any side effects. Our
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5 biochemical studies confirmed that the injection of Si nanoparticles did not induce any liver
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7 or kidney toxicity, as was confirmed by ALAT, ASAT and serum creatinine levels, which
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9 were still similar to that of the control group. We additionally did not detect any significant
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11 change of oxidative stress parameters including catalase, SOD, GPx activities, Vit A, E72,
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13 as well as no significant variation in the blood content.^{6, 30}
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18 We have also done a thorough study of the *in vivo* cytotoxicity of silicon quantum dots (Si
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20 QDs) from silane laser pyrolysis that were surface functionalized with ethyl undecylenate
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22 (undecylenic acid), and encapsulated in pluronic F127,¹⁸² similar to the approach illustrated in
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24 Figure 9. Both ethyl undecylenate and pluronic F127 are non-toxic FDA-approved substances, so
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26 any toxicity in this case could be attributed to the Si QDs. For this study, we took great care to
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28 optimize the surface passivation to achieve high photoluminescence quantum yield (36%) and
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30 long-term chemical and colloidal stability. We then tested the toxicity of these materials in both
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32 mice and monkeys (rhesus macaques). We used a very aggressive dose of 200 mg/kg body mass,
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34 based on the expectation of low toxicity from these formulations. Even at this high dose, the
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36 behavior, body mass, and blood chemistry of both the mice and monkeys remained normal.
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38 However, in contrast with other *in vivo* studies of silicon, we did not observe biodegradation of
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40 this silicon formulation. Three months after intravenous injection of Si QDs, the livers and spleens
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42 of mice still showed elevated silicon content. At this same time point, histopathology indicated
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44 detectable adverse effects in the livers of mice, but not in monkeys. One key lesson from this study
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46 is that thorough passivation of silicon nanoparticles with covalently-linked organic molecules, to
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48 achieve high quantum yield and chemical stability of the Si QDs, can also prevent degradation of
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50 the Si QDs. The silicon-carbon bonds at the Si QD surface do not undergo hydrolysis, and the
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3 organic surface layer protects the Si QDs from degradation. The other key outcome of this study
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5 is that observations made in mice, which are the most common animal model used for assessing
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7 toxicity of nanomaterials, may not be applicable to primates.
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11 In general, our tests evidenced the complete safety of laser-synthesized nanoformulations,
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13 and show that silicon itself is effectively degraded and eliminated. However, formulations
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15 in which the silicon is carefully protected to preserve its properties, may not biodegrade, or
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17 may undergo much delayed degradation. Thus, surface chemistry and encapsulation
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19 strategies should be carefully considered to achieve a balance between preserving desirable
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21 properties and ensuring degradation and clearance *in vivo*. The appropriateness of laser-
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23 synthesized silicon vs. silicon from other methods, such as the porous silicon particles
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25 employed by Sailor and coworkers,^{5, 12} depends upon the specific application, as each
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27 material will exhibit different biodistribution, degradation kinetics, capacity to serve as a
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29 carrier for other agents, and spectral and temporal response to illumination.
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34 **Optical Biosensing, Bioimaging and Multimodal Imaging.** As shown in previous studies using
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36 porous silicon, PL emission from nanosilicon crystals can be efficiently quenched by exposure to
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38 various organic and inorganic molecules. Such quenching can be explained by both energy- and
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40 electron-transfer mechanisms.¹⁸³ The use of this quenching effect for sensing of various chemical
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42 substances and biological molecules has been proposed and demonstrated. Based on the same PL
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44 quenching effect, laser-synthesized nanosilicon crystals prepared by PLD were also explored as
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46 matrices for biosensing to characterize inorganic nanoparticles (WO_3 , W_2O_5)¹⁸⁴ and sense organic
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48 aromatic nitro compounds.¹⁸⁵ In a separate study, porous nanosilicon layers, deposited on a gold
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50 film by PLD in residual helium gas, were explored as matrices for bioimmobilizations in Surface
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52 Plasmon Resonance biosensing¹⁸⁶ based on a Si prism platform.¹⁸⁷ The employment of such a
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3 matrix makes possible the maximization of probed material by a much-enhanced surface area for
4 immobilizations.
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8 The size-dependent PL emission wavelength, narrow width of the emission band, and broad
9 excitation spectrum of quantum dots (QDs) have made them valuable for optical bioimaging.
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11 However, for cadmium-based QDs, which are the most widely investigated, toxicity associated
12 with cadmium is a major barrier to broad use. Si QDs are less toxic. However, stably dispersing
13 Si QDs in biological media has been a major challenge. Availability of water-dispersible Si QDs
14 represents a significant advance in both *in vitro* and *in vivo* QD-based optical imaging. Water
15 dispersible Si QDs can be prepared by directly functionalizing the Si QD surface with a carboxylic
16 acid group or an amine group. However, water dispersed Si QDs generally exhibit poor colloidal
17 stability weakened photoluminescence in aqueous solutions. Tilley *et al.* attached allylamine to Si
18 QDs to make them water-dispersible.^{38, 188} Ruckenstein and coworkers grafted poly-acrylic acid
19 onto Si QDs from with red photoluminescence, initially produced by silane laser pyrolysis, and
20 demonstrated fixed cell labeling using these hydrophilic Si QDs.¹⁸⁹ Our group functionalized Si
21 QDs with acrylic acid in the presence of HF, to prevent oxidation.¹⁴⁴ We showed *in vitro* uptake
22 of Si QDs encapsulated in micelles of amine-functionalized phospholipid-PEGs into pancreatic
23 cancer cells by confocal imaging.¹¹ Our Si QD-based probes are not enzymatically degraded or
24 rapidly captured by the reticuloendothelial system (RES), remain stable in the acidic tumor
25 microenvironment, and show stable bright photoluminescence *in vivo*. This combination of
26 properties makes them attractive for clinical applications including image guided drug delivery,
27 mapping of sentinel lymph nodes (SLN), and visualization of tumor margins (Figure 15).
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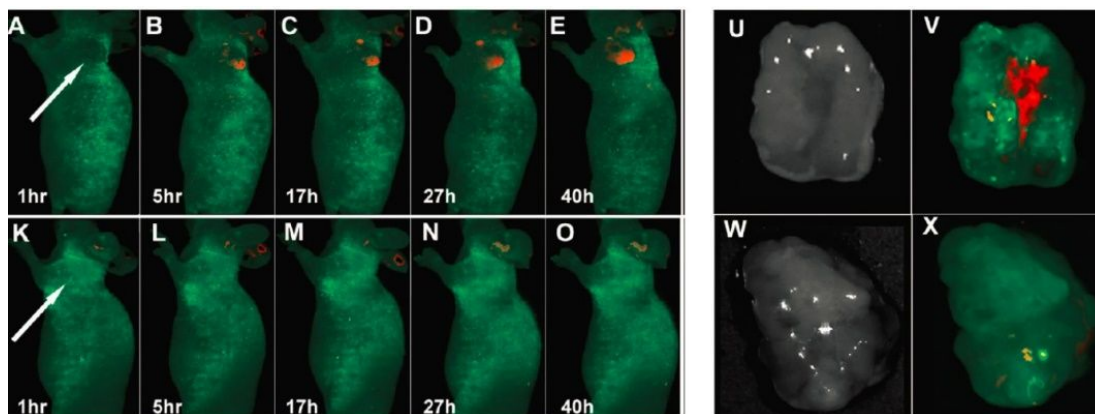


Figure 15. *In vivo* imaging of mice with xenograft Panc-1 tumors (white arrows) at the indicated times after injection with ~5mg of (A-E) targeted MSi QD-RGD or (K-O) untargeted MSi QD. Autofluorescence and Si QD emission are shown as green and red, respectively. Ex vivo photographs (U, W) and luminescence images (V, X) of tumors from mice treated with (U, V) MSi QD-cRGD or (W, X) MSi QD, excised 40 h after injection. Adapted from Ref. 150 with permission from the American Chemical Society.

We demonstrated *in vivo* imaging using Si QDs.¹⁵⁰ PEGylated micelle encapsulation and bioconjugation yielded a formulation with stable luminescence and long (>40 h) circulation and tumor accumulation time. Thus Si QDs can be suitable for use in sophisticated *in vivo* models. The Si nanoparticles also allow for incorporation of other modalities of imaging as multimodal nanoparticle platforms are desirable for application in cancer nanotechnology. One such example is a single nanoplatform that exhibits both photoluminescence and localized surface plasmon resonance (LSPR) based scattering and absorption. Here the challenge has been to overcome attenuation of optical emission caused by nonradiative decay due to plasmonic interactions. To combine gold with silicon quantum dots, we created Si QD core/Au shell constructs in which the Au and Si were separated to preserve each of their optical properties.¹⁴⁸ We employed surface FDA-approved ethyl undecylenate for surface passivation of the Si QDs. Multiple silicon quantum dots were encapsulated within each pluronic F127-COOH polymer micelle. The resulting water dispersible formulation has two key benefits compared to Si/Au core-shell nanostructures based on single Si QDs: (i) fluorescence from many Si QDs within each F127 micelle produces much

brighter emission from each nanocapsule; and (ii) rather than being attenuated (quenched) by interactions with gold, the Si QD luminescence may even be enhanced *via* plasmonic amplification of local electric fields by the gold shell. Our approach for producing these Si–Au hybrid core–shell nanostructures is illustrated in Figure 16.

We modified surface of Si QD-COOH with poly-L-histidine (PLH), which efficiently immobilizes gold ions.¹⁹⁰⁻¹⁹² The Au³⁺ was then reduced by NH₂OH to form a gold shell (yellow circle) which exhibits plasmonically-enhanced light scattering that is useful for dark field imaging. Meanwhile, the Si QDs remain photoluminescent (Figure 17). We demonstrated multimodal imaging of pancreatic cancer cells and showed that the Si QD photoluminescence coincided with light scattering from the gold shells.

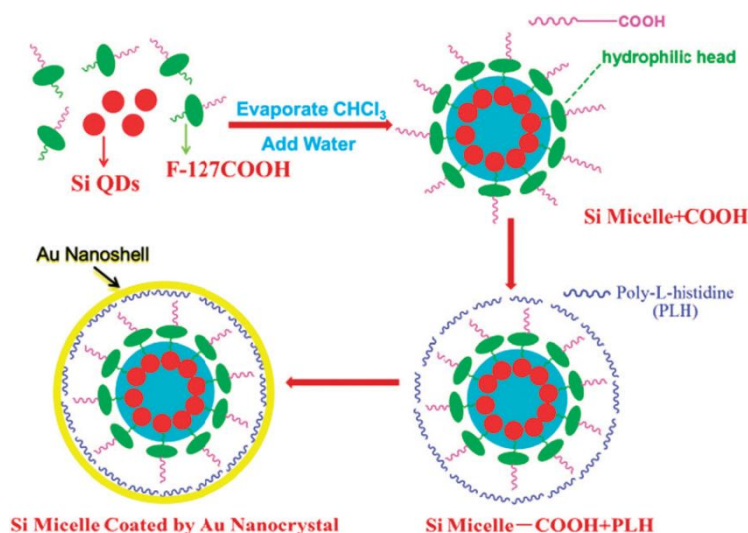


Figure 16. Si/Au hybrid nanostructures (golden-Si QD). Mixing functionalized Si QDs (red) with F127-COOH (green F127 and purple COOH) led to micelle encapsulation of the Si QDs. PLH (blue squiggles) was electrostatically attached to the micelle surface then used to immobilize Au³⁺. Gold reduction using NH₂OH produced a gold shell (yellow circle). The components are not drawn to scale. From Ref. 148, used with permission from Oxford University Press.

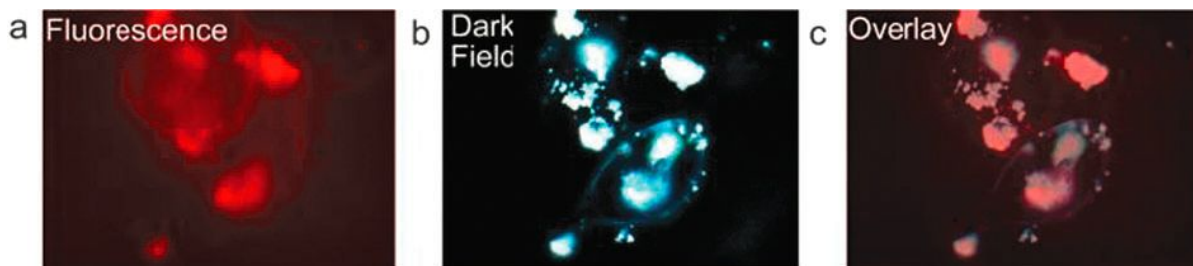


Figure 17. Fluorescence and dark-field imaging of pancreatic cancer cells treated with golden Si QDs, (a) fluorescence micrograph obtained with 400 nm excitation and 600 nm emission filter, (b) dark-field microscopy micrograph, (c) dark field micrograph overlay on the fluorescence micrograph. From Ref. 148, used with permission from Oxford University Press.

Iron-oxide nanoparticles, manganese, and gadolinium have been combined with Si QDs to produce nanoplateforms for both optical and magnetic resonance imaging.¹⁴⁹ The luminescence of Si QDs was attenuated in the presence of the iron oxide particles. Doping of silicon quantum dots with manganese for MR imaging has also been demonstrated, but manganese doping also lowers the photoluminescence quantum yield of the Si QDs.¹⁹³ Nonetheless, in both cases (iron oxide and manganese) the emission remained bright enough to be useful.

Chelated Gd^{3+} , with seven unpaired electrons that respond strongly to an applied magnetic field, is a popular MRI contrast agent.¹⁹⁴ This local magnetic field produced by Gd^{3+} reduces the relaxation time of nearby water protons,¹⁹⁵ providing contrast between tissues that have taken up Gd^{3+} and those that have not. MRI validated with NIR optical imaging can be effective for breast cancer imaging. Gd^{3+} in close proximity to quantum dots in quantum dot- Gd^{3+} complexes has been shown to increase luminescence quantum yield.¹⁹⁶ The low tumbling rate of QDs, combined with their ability to carry many Gd^{3+} ions, enhances the sensitivity of molecular MRI. Many challenges must be surmounted in order to prepare and apply multimodal nanoconstructs containing both quantum dots and Gd^{3+} moieties. Aptekar *et al.*¹⁹⁷ reported the use of silicon nanoparticles as hyperpolarized magnetic resonance imaging agents; however, they were larger in size and thus were not quantum dots. Tu *et al.* studied Mn-doped Si QDs for MRI and two photon

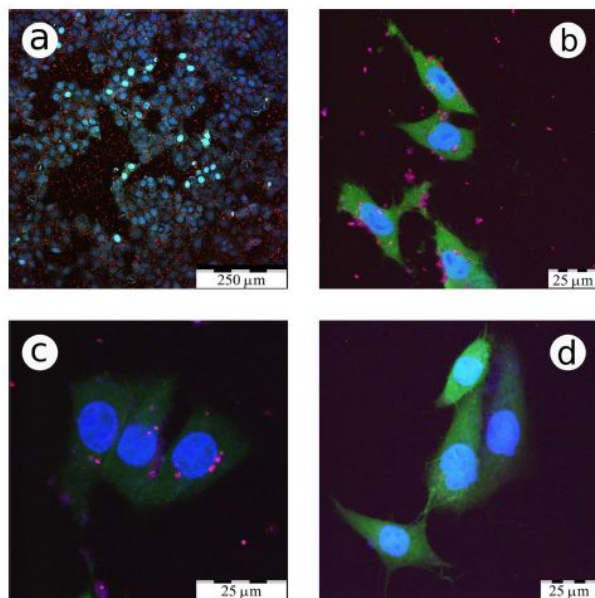
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3 optical imaging of macrophages.¹⁹⁸ However, Si QDs with emission at longer wavelength are more
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5 desirable to reduce light absorption and autofluorescence from tissues.
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8 We developed luminescent, MRI nanoconstructs comprising Si QDs encapsulated in DSPE-PEG
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10 (1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-[amino(polyethylene glycol)-2000]
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12 (ammonium salt)) micelles with DOTA-chelated Gd³⁺ covalently attached to their surface.¹⁹⁹
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14 DSPE-PEG micelles provide long circulation times by avoiding uptake by the reticuloendothelial
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16 system (RES). The hydrodynamic diameter of these nanoconstructs ranged from 25 to 60 nm. The
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18 magnetic resonance relaxivity in the presence of these nanoconstructs was 2.4 mM⁻¹ s⁻¹ (where the
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20 concentration is that of Gd³⁺ ions). This value corresponds to around 6000 mM⁻¹ s⁻¹ based on the
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22 concentration of overall nanoconstructs. We measured both optical and magnetic properties of
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24 these structures, then used them for imaging in macrophage cells and live mice. We also
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26 demonstrated magnetic field enhancement of cellular uptake *in vitro*.
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32 We have recently demonstrated use of Si nanoparticles formed by laser-plasma ablative synthesis
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34 in gaseous helium as markers for bioimaging.¹³ Si nanocrystals exhibiting strong exciton-based
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36 PL around 1.5-1.75 eV (750-850 nm) were originally formed by PLD and then milled by
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38 ultrasound and dispersed in aqueous solutions. The nanoparticles were incubated *in vitro* with a
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40 CF2Th cancer cells. Figure 18 shows confocal fluorescent microscopy images of cancer cells with
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42 incubated nanoparticles, in which the cell nuclei and cytoplasm are labelled by blue and green,
43
44 respectively. Figure 18a shows cells in different proliferation states, including mitotic cells in the
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46 metaphase, which provides evidence of normal cell proliferation in the medium containing Si
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48 nanoparticles. As follows from Figure 18b,c, laser-synthesized Si nanoparticles emit different
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50 PL bands, which is in good agreement with their PL spectra in water (Figure 18a), while the control
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52 group does not show any signal (Figure 18d). It is also important that Si nanoparticles can
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3 penetrate into the cytoplasm, but do not enter into the cell nuclei, which excludes potential gene
4 toxicity problems.
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8 We finally assessed Au-Si core-shells prepared by methods of femtosecond laser ablation in
9 deionized water^{134, 135, 200} as mobile Surface Enhanced Raman Scattering (SERS) probes for the
10 identification of biological species at ultra-low concentrations. First, we found that these core-
11 shells can strongly enhance Raman signals from R6G molecules even if the Si content of the shell
12 exceeds 70%.¹³⁵ Using such contamination-free SERS nanoprobe, we demonstrated successful
13 identification of ultra-low concentrations of 2 types of bacteria (*Listeria innocua* and *Escherichia*
14 *coli*),¹³⁵ as well as the identification of critically important spoilage yeast cultures in food
15 products¹⁴⁹. The obtained results promise more compatible SERS probes based on contamination-
16 free laser-synthesized nanomaterials with Si shell surfaces.
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51 **Figure 18.** Confocal fluorescence microscopy images of CF2Th cancer cells incubated with laser-
52 synthesized nanoparticles (red-pink-violet) under different magnification scales (a,b,c) and that of a control
53 sample without nanoparticles (d). Panel (c) presents the cells after washing out of nanoparticles from
54 extracellular space. Cell nuclei and cytoplasm are colored blue and green, respectively. Adapted from Ref.
55 13 with permission under a Creative Commons CC-BY license.
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3 **Photodynamic Therapy.** Photodynamic therapy (PDT) is a promising approach to cancer
4 treatment that is relatively noninvasive with limited systemic toxicity. In PDT, a
5 photosensitizer is activated by light, then transfers energy from its electronically excited
6 triplet state energy to nearby oxygen molecules. This energy transfer produces reactive
7 singlet oxygen ($^1\text{O}_2$) that kills the cancerous cells. Clinical applications of PDT are often
8 limited by shortcomings of the organic photosensitizing agent with poor water
9 dispersibility, susceptibility to photobleaching and poor biocompatibility. Silicon-based
10 nanoparticles can be superior to organic photosensitizers in terms of photostability and
11 water dispersability. In addition, their luminescence, biodegradability, biocompatibility,
12 and ability to generate $^1\text{O}_2$ under visible and near infra-red illumination, make silicon
13 nanoparticles good candidates as photosensitizers for PDT.
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28 We used laser ablation in liquids to prepare silicon nanoparticles that can act as photosensitizers,
29 producing $^1\text{O}_2$ and killing microbes, demonstrating potential for antiseptic or disinfectant
30 therapies.¹²⁸ The colloidal silicon nanoparticles of well-defined dimension were produced by
31 femtosecond laser ablation in a clean, contamination-free aqueous environment, which eliminates
32 the toxicity problem of alternative fabrication techniques and provides complete sterilization of
33 the resulting product. The Si nanoparticles are capable of generating singlet oxygen ($^1\text{O}_2$) upon
34 laser irradiation at various wavelengths and present no photobleaching, which makes them very
35 useful as potential photosensitizers for therapeutic, antiseptic, or disinfection tasks.
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RF Thermal Therapy. The capability of radio frequency (RF) radiation to heat tissues has been studied in many works, and in the case of cancer this heating can lead to a partial necrosis of tumors.²⁰¹ The efficiency of RF-based treatment can be much enhanced by employing electrically-conductive nanosensitizers, such as carbon nanotubes²⁰² or gold nanoparticles²⁰³. These nanostructures are normally delivered into the tumor and then heated by RF radiation to selectively destroy cancer cells. However, carbon nanotubes and gold nanoparticles are not biodegradable, which can give rise to long-term accumulation in the body and related toxicity effects.²⁰⁴

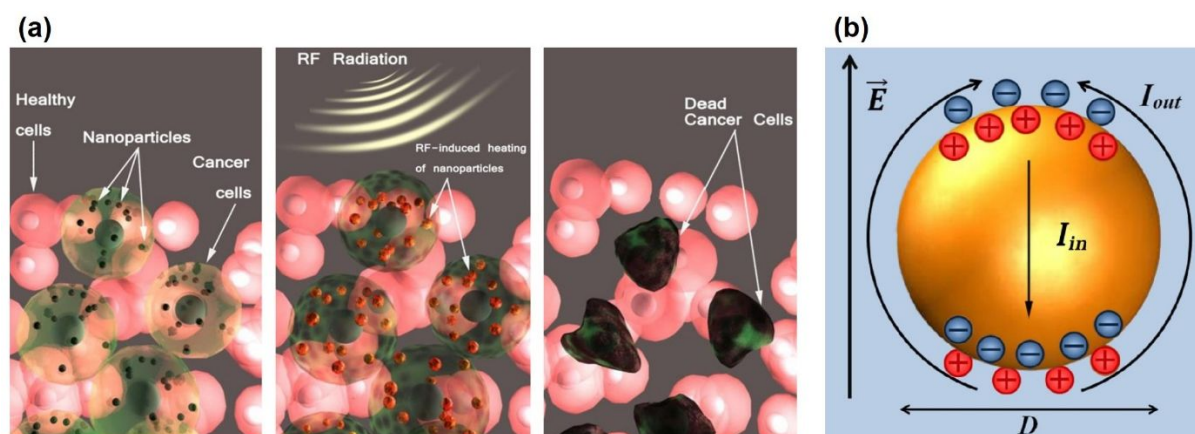


Figure 19. (a) Schematic representation of RF radiation-induced cancer treatment. nanoparticles are selectively accumulated in tumor cells and are heated, giving rise to selective death of cancer cells, (b) Distribution of electric field around a nanoparticle immersed in a liquid electrolyte under its illumination by RF irradiation. The heating is caused by the ion movement around the nanoparticles due the appearance of electrical double layer at the nanoparticles in response to its RF induced sphere polarization. Adapted from Ref. 30 with permission under a Creative Commons CC-BY license.

We recently showed that laser-synthesized Si nanoparticles can serve as efficient sensitizers of RF-induced hyperthermia despite their low conductivity, while the efficiency of such therapy was comparable to or better than that of Au nanoparticles.³⁰ The observed sensitizing effect can be explained by the generation of electrical currents at the nanoparticle/water interface, leading to Joule heating (Figure 19). We recorded efficient RF-induced heating of aqueous dispersions of Si nanoparticles to temperatures above 45-50°C using relatively low nanoparticle concentrations (1

mg/mL). Here, laser-synthesized Si nanoparticles showed much better sensitizing properties compared to porous Si-based counterparts for all used concentrations. *In vivo* experiments confirmed that Si nanoparticles could serve as sensitizers of RF radiation heating to strongly inhibit the growth of carcinoma tumors (Figure 20).

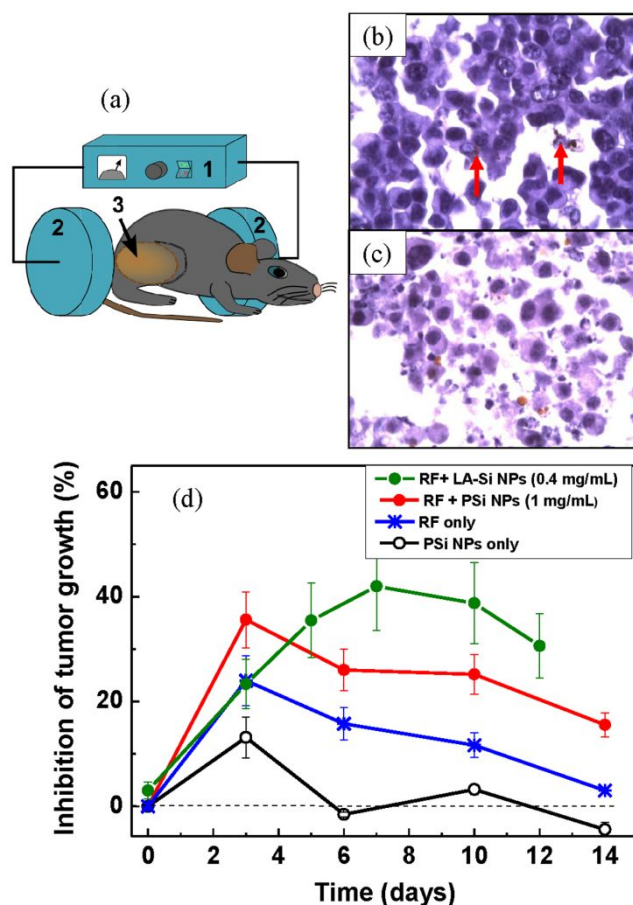


Figure 20. (a) Schematics of experimental setup for RF-induced therapy. (1) and (2) represent RF radiation source electrodes, respectively, while a tumor area in a mouse is depicted in (3). (b,c) present histological investigation of the tumor 1 hour and 3 days after RF-based treatment, respectively. Cancer cells are identified as dark blue spots, while agglomerations of nanoparticles are depicted by red arrows. (d) Tumor growth inhibition after the injection of Si nanoparticles suspension (black curve); after 2 min treatment of tumor area by RF irradiation (blue); Red and green curves show tumor growth inhibition after the injection of porous Si nanoparticles (0.5 mL, 1 mg/mL) and laser-synthesized Si nanoparticles (0.2 mL, 0.4 mg/mL), respectively, followed by 2 min RF irradiation treatment. From Ref. 30, used with permission under a Creative Commons CC-BY license.

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3 It should be also noted that laser-ablative synthesis renders possible the synthesis of hybrid SiO_x/Si
4 - graphene oxide nanocomposites, which also look as promising sensitizers for thermal
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6 therapies.²⁰⁵
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11 **Challenges and Opportunities for Laser-Processed Nanosilicon.**

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13 As demonstrated in the preceding pages, laser-processed nanosilicon is an extremely promising
14 material for numerous applications, particularly in the biomedical realm. It can combine
15 exceptional purity, which is nearly unachievable with porous silicon or other nanostructures
16 prepared by conventional wet chemical or electrochemical synthesis routes. It offers a multitude
17 of intrinsic properties, which can provide excellent opportunities for the advancement of various
18 applications in energy and healthcare.
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27 For biomedical applications, laser-processed nanosilicon can offer a combination of excellent
28 biocompatibility and biodegradability in the absence of any toxic contamination, which is rather
29 unusual among inorganic materials, as well as a series of outstanding chemical and optical
30 properties that enable promising imaging, therapy, and drug delivery functionalities. Of particular
31 importance, we envision applications of laser-synthesized nanosilicon in cancer theranostics.²⁰⁶
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39 For photodetectors, solar cells, and optoelectronics applications, “dry” laser-processed silicon
40 could offer compatibility with the silicon processing technology that forms the basis for
41 microelectronics, which promises easy scaling up of nanosilicon-based devices.
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45 Current challenges include the optimization of different laser processing technologies to match the
46 requirements of nanosilicon for particular applications. In biomedical imaging applications that
47 rely upon the photoluminescence of nanosilicon (Si QDs), surface passivation is required to
48 stabilize the photoluminescence. For many bioapplications, additional encapsulation and/or
49 surface functionalization may be required to achieve targeting of specific cells or tissues. However,
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3 the most effective means of surface passivation, encapsulation, and targeting may protect the
4 silicon nanoparticle so well that it does not degrade *in vivo*. Thus, strategies that combine desirable
5 optical and chemical properties while still allowing the nanosilicon to degrade and be excreted
6 after serving its purpose, must be further developed and optimized.
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11 In many energy-related applications, production cost can be a barrier to scaling and
12 commercialization of laser-processed nanosilicon. Production of high-purity nanosilicon requires
13 high purity precursors, whether solid silicon targets or electronic grade silane or other gases. In
14 optoelectronic applications, where the quantity of nanosilicon per device area is very small, this
15 may not be an issue. However, in applications such as lithium ion batteries and hydrogen
16 generation from water, for which much larger quantities of material are needed, both the high cost
17 of precursors and the relatively low throughput of most currently-available laser-based processes
18 present major challenges.
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30 We envision several pathways for further advancement of laser-processed nanosilicon, from the
31 improvement of laser processing technology and protocols for post-fabrication treatment and
32 functionalization, to the extension and enhancement of functionalities related to projected
33 applications. We believe that the potential of laser-assisted synthesis is not yet fully exploited and
34 one can still profit from the particular conditions of silicon nanostructuring offered by laser
35 processing. Some promising future directions are highlighted in the following brief subsections.
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45 ***Multifunctional and Nonequilibrium Materials***

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47 One promising approach is based on a combination of nanosilicon with other materials *via* doping
48 or formation of composites, which could enhance nanosilicon properties or combine them with
49 other functionalities (*e.g.* magnetic, plasmonic, optical, or photochemical properties). In this sense,
50 traditional wet methods of synthesis, including porous silicon technology and colloidal chemistry,
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3 have serious limitations, as these methods imply the production of nanoformulations from complex
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5 compounds under fixed conditions. Laser synthesis is based on quite different (mainly physical)
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7 mechanisms for nanostructuring that are not subject to many of the limitations of slower processes
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9 that occur closer to equilibrium states. The very rapid initiation and quenching of particle
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11 formation in the various laser processing approaches can allow trapping of non-equilibrium states
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13 and compositions (*e.g.* hyperdoped materials with dopant concentrations exceeding the solid
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15 solubility limit).²⁰⁷ This makes laser processing a flexible tool for the fabrication of such doped or
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17 composite structures.
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22 ***Multiscale Modeling and Materials Informatics***

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24 Design and fabrication of multicomponent nanosilicon formulations with optimized
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26 multifunctionality could be greatly accelerated by the effective use of multiscale modeling and
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28 materials informatics. Combining multiscale modeling and rapidly maturing tools of materials
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30 informatics can facilitate the rapid optimization of composition, structure, and interfaces to achieve
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32 desired properties, especially in multicomponent, multifunctional structures. Multiscale modeling
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34 adopts different treatments of interactions at different length scales and time scales. For example,
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36 local chemical interactions involving up to a few hundred atoms can be treated fully quantum
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38 mechanically (QM), while weaker, longer length scale interactions are described by molecular
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40 mechanics (MM). The surroundings (*e.g.* solvent) can be treated as a dielectric polarizable
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42 continuum. In this framework, optical responses, which are often of greatest interest for
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44 nanosilicon applications, can be extracted using density matrix-based time-dependent density
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46 functional theory (TDDFT) in the time domain.
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52 Materials informatics combines computational, statistical, and machine learning approaches to
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54 predict and optimize composition, structure, and processing of materials to achieve desired
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3 properties and to accelerate the creation and adoption of new materials. Within this framework,
4 results of both conventional experiments and high-throughput methods can be integrated with
5 computational and simulation studies in a machine learning paradigm. Experimental data,
6 physicochemical modeling, and statistical approaches are integrated to generate insights that
7 would elude conventional approaches. Materials informatics can also be used design sets of
8 physical or computational experiments that will maximize information content of each additional
9 data point or data set. These approaches can be extended to automatically conduct sequences of
10 experiments. Greater integration of multiscale modeling and materials informatics could enable
11 discovery and production of laser-processed silicon-containing nanostructures with new
12 combinations of properties.
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26 27 ***Quantum Applications*** 28

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30 Another promising direction is the creation of quantum materials, which are hierarchically
31 nanostructured hybrids in which quantum communication between different domains and quantum
32 entanglement can be manipulated. Coupled quantum dots in silicon have been extensively explored
33 for creating qubits based on a single isolated electron spin per quantum dot, as in the recent work
34 by Mi *et al.*²⁰⁸ and many references cited therein. However, such studies all employ lithographic
35 patterning and application of potentials to isolate small domains within a silicon device, such that
36 these domains behave as quantum dots. Charge carriers are confined in these dots by applied
37 potential rather than the fully material-based confinement characteristic of freestanding (or
38 colloidal) quantum dots. Achieving the level of synthetic control required to exploit quantum
39 effects in freestanding coupled quantum dots produced by laser processing is a daunting task, but
40 one worth pursuing.
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3 An example of such coupled quantum dots could be hierarchically structured and topologically
4 controlled multiphase nanoparticles generated by co-ablating multiple targets in a surrounding
5 gaseous or liquid phase. For this, manipulation of the laser wavelength, pulse width, fluence, and
6 surrounding medium together with appropriate target motion could be used to produce a mixed
7 phase (alloyed), core-multiple shells, or multidomain (*e.g.* dumbbell-like) structures with
8 controlled interdomain interactions. These hierarchical quantum materials can provide single
9 photon sources and can contribute to advances in spintronics. Their applications in quantum
10 information processing could include quantum key distribution, quantum networks, and photonic
11 quantum computing.
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24 ***Nonlinear Multiphoton Imaging***

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28 Our work has also shown that laser-processed nanosilicon can exhibit strong two- and three-photon
29 excited luminescence (nonlinear upconversion) which can be suitable for multiphoton
30 microscopy.²⁰⁹ In that study, 1-photon excitation at 339 nm, two-photon excitation at 778 nm, and
31 three-photon excitation at 1335 nm produced nearly identical photoluminescence, in terms of both
32 spectrum and lifetimes, with peak emission near 650 nm. Suitable wavelengths for two- and three-
33 photon excitation fall in the first and second windows of biological transparency, providing the
34 possibility of relatively deep tissue penetration combined with the three-dimensional imaging
35 capability of multiphoton microscopy. Chandra *et al.* demonstrated two-photon excited confocal
36 microscopy using nanosilicon prepared by a complex multi-step process that yielded particles with
37 peak PL emission at 918 nm.²¹⁰ They excited their nanosilicon with a Ti:sapphire laser at 800 nm,
38 and detected the short wavelength tail of the PL below 650 nm. Kharin *et al.* recently demonstrated
39 dual-mode bioimaging based on two-photon emission luminescence (TPEL) and second-harmonic
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3 generation (SHG) channels, using relatively large (10-30 nm) laser-synthesized nanoparticles, that
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5 did not exhibit photoluminescence from quantum-confined excitonic states.²¹¹ They also showed
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7 that non-linear response of these large nanoparticles exceeded that of smaller ones (< 5 nm), while
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9 the combination of TPEL and SHG channels enabled efficient tracing of both separated Si NPs
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11 and their aggregations in different cell compartments.²¹¹ The obtained bi-modal contrast provides
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13 a previously-lacking imaging functionality for large Si NPs as efficient sensitizers for RF-induced
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15 (see Paragraph 3.3.3.2) and other therapies. In general, the potential of nanosilicon for multi-
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17 photon excited imaging has begun to be explored, but neither the materials nor microscopy systems
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19 has been optimized, and the full potential of this imaging approach remains to be tapped. As one
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21 of promising avenues, we see the addition of a polarizable Ge component to enhance the
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23 multiphoton absorbance cross-section and shift the emission wavelength to the second window of
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25 biological optical transparency to enable high-contrast deep tissue imaging. We have demonstrated
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27 the direct production of silicon-germanium alloy nanoparticles by laser pyrolysis of silane-
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29 germane mixtures,^{212, 213} but the nonlinear optical properties of these group IV alloy nanoparticles
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31 remain to be optimized and exploited for imaging.
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39 ***Nanosilicon for Delivery of Nuclear Medicine***

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41 Nuclear nanomedicine exploits the ability of nanocarriers to endow radionuclides with tumor
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43 targeting ability and high loading capacity along with enhanced retention to avoid rapid clearance
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45 that is typical of molecular radiopharmaceuticals. Thus, nuclear nanomedicine has great potential
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47 to treat tumors and metastases. Despite these promises, progress in this field has been somewhat
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49 slow, primarily due to a lack of safe and excretable nanocarriers that also have favorable
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51 pharmacokinetics to efficiently deliver and retain radionuclides in a tumor. We recently introduced
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53 biodegradable laser-synthesized Si nanoparticles with high chemical purity, round shape,
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3 controllable size, and narrow size distribution as carriers of the therapeutic ^{188}Re radionuclide.²¹⁴
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5 Only one hour was required for conjugation of the PEG-coated Si nanostructures with radioactive
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7 ^{188}Re , which is substantially shorter than the ^{188}Re half-life of 17 hours. Upon intravenous
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9 administration in a Wistar rat model, the conjugates circulated freely in the blood stream to reach
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11 all organs and the target tumors. The observed biodistribution was dramatically different from that
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13 of ^{188}Re salt, which mostly accumulates in the thyroid gland. The nanoparticle-based delivery also
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15 ensured excellent retention of ^{188}Re in the tumor, again in contrast to the salt, which maximizes
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17 the therapeutic effect. Ultimately, the radionuclide nanocarrier exhibited complete time-delayed
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19 bioelimination. Tests of rat survival in this study showed excellent therapeutic effect, with 72% of
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21 treated rats surviving, while 0% of untreated control animals survived. This strategy of creating a
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23 nanosilicon-based biodegradable complex for radionuclide delivery could be a major step forward
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25 in nuclear nanomedicine.
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31 ***Engineering for Scale-Up***

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33 We believe that straightforward engineering approaches can be applied to scale up most laser-
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35 processing methods and reduce costs of production for applications where that is a key limitation.
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37 Nearly all studies of laser-processed nanosilicon to date have been aimed at understanding material
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39 properties or achieving proof-of-concept demonstrations of particular applications. For most of
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41 these processing approaches, serious attempts at scale-up have not yet been made. Thus, there is
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43 tremendous room for work in this direction as demand for laser-synthesized silicon increases. For
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45 examples, laser pyrolysis processes described in this paper have mainly been done using lasers of
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47 up to 100 W to produce up to 1 g/h of nanosilicon. However, CO_2 lasers are available at powers
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49 up to many kW, and laser pyrolysis processes, in general, have been scaled to kg/h volumes, which
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51 would be sufficient for many applications.
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Acknowledgements:

A. V. K. and I. N. Z. acknowledge contribution of Russian Science Foundation (Project 19-72-30012) for access to some databases and travel exchange support. A. V. K., I. N. Z and P. N. P. are also grateful to MEPHI Academic Excellence Project (Contract No. 02.a03.21.0005). This paper is dedicated to our co-author, Dr. Ajay Singh, who unexpectedly passed away on October 20, 2018.

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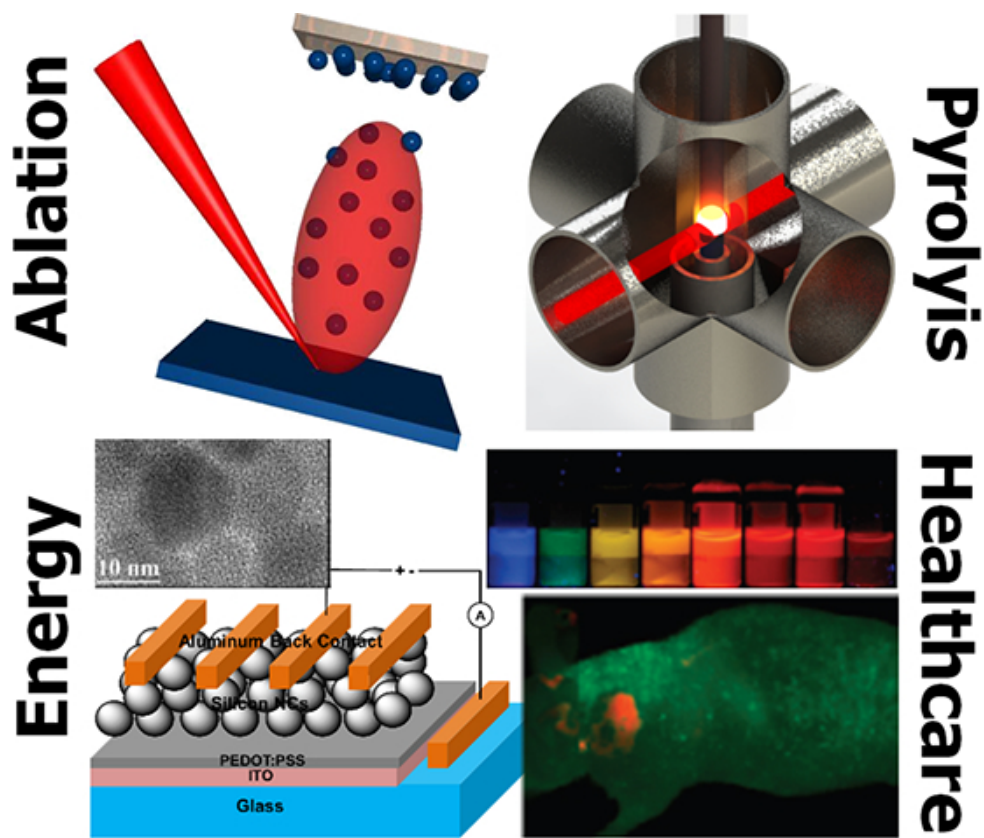
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