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Effects of nanostructure on clean energy: big solutions gained from small features

Jinyan Xiong
University of Wollongong, jx513@uowmail.edu.au

Chao Han
University of Wollongong, ch861@uowmail.edu.au

Zhen Li
University of Wollongong

S X. Dou
University of Wollongong, shi@uow.edu.au

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Keywords
small, gained, solutions, big, energy, clean, nanostructure, features, effects

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Keywords Clean energy · Functional nanostructures · Photocatalysis · Solar energy · Electrochemical energy conversion and storage · Thermoelectric conversion

1 Introduction

With the explosive growth of population and the threat of global warming, as well as severe pollution problems, human beings have been pushed to develop cost-effective, high-efficiency solutions to meet the ever increasing demand for clean energy. Advanced functional nanomaterials and relevant nanotechnologies are playing a crucial role in resolving some energy issues. As one of the internationally recognized and highly influential academic journals of China, *Chinese Science Bulletin* has devoted close attention to state-of-the-art clean energy-related materials. A special issue on "Advanced Materials for Clean Energy" was published in June 2014 to highlight recent advances in clean energy harvesting, conversion, storage, and utilization through artificial photosynthesis, dye-sensitized solar cells (DSSCs), perovskite solid-state solar cells, electrochemical supercapacitors, rechargeable Li-ion/Na-ion batteries, and thermoelectric materials [1–8]. Here, we summarize the recent promising applications of nanostructures in the field of clean energy (Fig. 1).

2 Photocatalysis: utilization of solar energy

Solar energy, as an important inexhaustible source of clean energy, has been investigated for several decades. Although utilizing solar energy includes many aspects, such as solar cells, photocatalytic degradation of pollution, and water splitting, they are all based on the photocatalysis process, which is the acceleration of a photoreaction in the presence of a catalyst and the absorption of solar energy by an adsorbed substrate. The photogenerated catalysis activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which is able to undergo redox reactions with other species. According to the utilization of the photoelectrons, applications of solar energy based on the photocatalysis process could be divided into the following groups.

J. Xiong · C. Han · Z. Li · S. Dou
Institute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, University of Wollongong, North Wollongong, NSW 2500, Australia

Z. Li (✉)
School of Radiation Medicine and Radiation Protection, Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Soochow University, Suzhou 215123, China
e-mail: zhenli@suda.edu.cn

Fig. 1 (Color online) Applications of nanostructures in the field of clean energy

2.1 Solar energy conversion

Solar cells are devices that directly convert sunlight into electricity on the basis of the photovoltaic effect, for example meaning that the generated electron–hole pairs are directly used as charge carriers, representing a most promising method for utilization of solar energy. Apart from the expensive traditional p–n junction-based silicon solar cells, new prototypes of solar cells have been developed such as sandwich-like dye- or quantum-dot-sensitized solar cells, which consist of a counter electrode, electrolyte, and a photoanode [9, 10]. Usually, two basic important processes rule the performance of solar cells: (1) the excitation process, for example generation of photoelectrons by the photoelectrode under irradiation of light and (2) the transport process for the photoelectrons, including the transfer of photoelectrons from inside the photoelectrode to the surface and the transport between the electrolyte and electrodes. Nanostructures not only offer huge surface areas for excitation, but also tune the absorption of light and excitation of photoelectrons via quantum effects [11]. Moreover, the transport of photoelectrons across the interface between the photoelectrode and the electrolyte could be easily tuned by different nanostructures. Hence, the performance of solar cells could be effectively improved by nanostructures with different morphologies and compositions, such as nanowires, mesoporous materials, and monodisperse beads, as well as surface modification through nanotechnology [3, 12, 13]. Hitherto, relatively high power conversion efficiency has been realized for traditional photovoltaic devices; for example, a maximum efficiency of 19.6 % and 20.3 % has been achieved in CdTe quantum-dot solar cells [14] and $Cu(In,Ga)Se_2$ (CIGS) cells [15], respectively. Despite the high power conversion efficiency, however, their wide applications are strongly limited, either by their expensive fabrication and the rarity of their natural resources or by the high toxicity of some elements. Moreover, the risk of liquid electrolyte leakage is a big issue for long-term operation without degradation.

Another breakthrough in solar cells lies in the usage of organolead halide perovskite ($CH_3NH_3PbI_3$) as the sensitizer for high-efficiency solid-state semiconductor-sensitized solar cells [16]. More recently, a high efficiency of 15 % was achieved in $CH_3NH_3PbI_3$-sensitized hybrid solar cells by modifying the deposition of the perovskite light absorber and by increasing the conductivity of the hole transport materials [12]. The conversion occurred within the nanoporous host upon PbI_2 and CH_3NH_3I came into contact, permitting much better control over the perovskite morphology than the previously employed routes [12]. Another rapid rise in solar-to-electric power conversion efficiency to more than 18 % was achieved by incorporation of methylammonium lead bromide ($MAPbBr_3$) into formamidinium lead iodide ($FAPbI_3$) as the light-harvesting unit by optimizing phase stability, perovskite morphology, hysteresis in *I–V* characteristics, and overall performance as a function of chemical composition [13]. Zhang and Cai [8] have summarized the progress on organolead halide perovskite-based solar cells. It is highly likely that the conversion efficiency could be further boosted by nanotechnology, which makes it highly promising for large-scale commercialization [17].

2.2 Generation of hydrogen and oxygen by water splitting

Hydrogen gas is another highly promising source of clean energy because only water is produced by its burning. In addition, hydrogen possesses extremely low density and high combustion enthalpy, which leads to high energy density. In addition, it can be stored for later use. One of the impediments to its wide application, however, is the high cost of fabrication. Since Fujishima and Honda [18] reported groundbreaking work on the photolytic cleavage of water to H_2 and O_2 in 1972, the concept of using solar light and a suitable semiconductor catalyst to generate H_2 without emitting carbon dioxide via a photoelectrochemical water splitting process or by photovoltaic-driven electrolysis has received tremendous scientific attention [19]. The water splitting reactions only occur when the charge carriers (electrons and holes) generated in the semiconductor from absorption of light can reach the surface during their lifetime and manage to come into contact with protons or water [19]. Thus, the quality of the semiconductor photocatalyst plays a pivotal role in the water splitting.

Because the absorption of photons from light is strongly correlated with the size and band structure of the semiconductor catalyst, the transport of photoexcited carriers is determined by the crystal type, size, structure, defects, and surface properties of the photocatalyst. To have efficient charge carrier separation, the diffusion length of charge carriers must be longer than the particle size. The chance that the charge carrier reaches the surface of particles increases with the decreasing photocatalyst size; for example, the nanostructure has an important influence on the water splitting [4]. Intensive research has been conducted in the past several decades to develop efficient photoelectrodes, catalysts, and device architectures for solar hydrogen generation [18, 20–23]. The most investigated catalysts are TiO_2, WO_3, and α-Fe_2O_3 nanostructures [4]. Such nanoeffects have led to 50 %–90 % efficiency gain, according to the literature [24]. For example, bulk single crystal α-Fe_2O_3 has very low photocatalytic activity because its paramagnetism shortens the lifetimes and diffusion lengths (2–20 nm) of photoexcited carriers; in contrast, α-Fe_2O_3 nanoparticles with an average size of 10–20 nm exhibit high activity due to their small dimension, which allows the photogenerated carriers diffusing to the electrolyte interface and reacting with water. Furthermore, optimizing the nanostructure of the film could result in absorption of all photons with energies above the band gap [24]. Another example is reported by Chen et al. [1], in which remarkable enhancement of water splitting performance was achieved by coating a pristine TiO_2 nanorod film with Au@SiO_2 core-shell structures, resulting in an increase in the incident photon-to-current conversion efficiency from 31 % to 37 % at 380 nm at 0.7 V versus saturated calomel electrode. The enhancement of photoelectrochemical performance could be attributed to the nonconductive SiO_2 shell and the spatially nonhomogeneous electric field caused by the metallic surface plasmon resonance of Au@SiO_2 nanoparticles, which significantly promoted the migration of holes from TiO_2 nanorods to electrolyte and hence effectively improved charge carrier separation. Yamada et al. [25] reported that Ni nanoparticles acted as efficient catalysts for photocatalytic hydrogen evolution with 2-phenyl-4-(1-naphthyl) quinolinium ion ($QuPh^+$-NA) as the photocatalyst and dihydronicotinamide adenine dinucleotide (NADH) as the sacrificial electron donor. The hydrogen evolution rate of the Ni nanoparticles (6.6 nm) with hexagonal close-packed (hcp) structure was more than four times higher than the rate of the Ni nanoparticles with face-centred cubic (fcc) structure of similar size, which was 40 % of that with commercially available Pt nanoparticles (2 nm). The high catalytic reactivity of Ni nanoparticles with smaller size and hcp surface could be ascribed to their high specific surface area compared with the fcc structure. In addition to nickel and iron catalysts used for the electrodes in their electrolyser, a highly efficient and low-cost modular system has been described in which solution-processed solar cells and a catalyst derived from abundant materials were used to achieve a solar energy to hydrogen conversion efficiency of 12.3 %. Two $CH_3NH_3PbI_3$-based photovoltaic cells connected in series generated sufficient potential to enable water splitting with a NiFe-layered double hydroxide electrode [26]. However, this system suffered from the lack of stability of the perovskite photovoltaic cells. More recently, another modular system that utilizes concentrated solar power and an electrode based on the earth-abundant material Ni showed a solar energy to fuel energy conversion efficiency of 22.4 % under various electrolyte conditions [27]. The overall performance of such a system can be optimized by choosing the right electrode material and particle size, as well as the right electrolyser conditions (e.g. electrolyte, operating temperature) [27].

Furthermore, much effort has been devoted to developing robust and efficient catalysts for H_2O oxidation, to provide the necessary reducing equivalents for the production of solar fuels. Particular attention has been devoted to the design of active artificial water oxidation catalysts. During past decades of research, a great variety of strategies have been explored for the construction of water oxidation catalysts, ranging from molecular complexes based on ruthenium to various kinds of metal oxide materials that are based on three-dimensional (3D) transition metals, such as cobalt and manganese cubanes and spinel phase materials [28]. Gaining a fundamental understanding of structure–activity relationships will certainly offer the key to developing more efficient water oxidation catalysts.

Hydrogenation of nanostructured semiconductors is an effective way to improve their performance in water splitting, and hydrogenated TiO_2 and WO_3 show significant enhancement in water splitting ability under solar light, because of the increased amount of oxygen vacancies that act as shallow electron donors [4].

2.3 Degradation of pollutants by photocatalysts

Semiconductor photocatalysts have demonstrated high efficiency in degrading a wide range of organic pollutants into biodegradable or less toxic organic compounds, as well as inorganic CO_2, H_2O, NO_3^-, PO_4^{3-}, and halide ions. As a low-cost route to efficient removal of organic pollutants from waste water, however, the low solar energy conversion efficiency of these inorganic catalysts strongly limits their large-scale application [29]. Now, nanostructuring has become an effective and widely used way to enhance their performance. For example, TiO_2 and ZnO, as the most prominent and suitable materials for solar energy harvesting, are being widely studied for

photodegradation of inorganic and organic pollutants [30]. Their wide band gap limits their light absorption in the ultraviolet (UV) region, however, leading to less use of sunlight. Tian et al. [31] constructed a hybrid nanostructured photocatalyst with enhanced broad spectrum photocatalytic properties by assembling Bi_2WO_6 nanosheets on TiO_2 nanobelts, which could harness UV, visible, and near-infrared light to decompose organic contaminants in aqueous solution. The enhanced photocatalytic efficiency of the Bi_2WO_6/TiO_2 nanobelt heterostructures can be attributed to their heterointegration, oxygen vacancies, and high specific surface area. Ai et al. [32] prepared N-doped TiO_2 nanocrystals with exposed {001} facets by the sol–gel method and the solvothermal method, respectively, and the as-prepared samples exhibited high visible light photocatalytic performances, as evidenced by decolouration of methylene blue (MB) under visible light irradiation ($\lambda > 420$ nm), which could be ascribed to their excellent crystallization, strong adsorption ability, and the enhancement of absorbance in the visible light region. The photodegradation rate of Pt-ZnO-reduced graphene oxide (RGO) rods synthesized by a novel Pt-induced electrochemical route with different RGO contents towards aqueous RhB was markedly improved under UV–visible light irradiation, compared with that of Pt nanoparticle-loaded ZnO. The enhanced photocatalytic activity of Pt-ZnO-RGO towards RhB could be attributed to the synergistic effects of ZnO rods and RGO nanosheets, of which RGO nanosheets facilitate the adsorption of RhB molecules, prevent agglomeration of ZnO rods, and ensure separation of photoexcited electrons and holes on ZnO rods [33]. In addition, visible light-driven bismuth-based photocatalysts with various morphology and structures show excellent photocatalytic activities, which could be mainly attributed to the unique hierarchitecture layered structure, large BET surface area, and strong adsorption capacities [34–39]. Bi_2WO_6 nanoplates can be also used to oxidize NH_4^+/NH_3 into NO_3^- and a trace of NO_2^- in an alkaline solution under fluorescent light irradiation, and the transfer of photogenerated holes could play a crucial role in the photocatalytic oxidation process of the ammonia [40]. Our group [41] also prepared a novel class of one-dimensional (1D) plasmonic $Ag@Cu_2O$ core-shell heteronanowires by a facile solution process at room temperature, which exhibited much higher photocatalytic activity towards degradation of organic contaminants than $Ag@Cu_2O$ core-shell nanoparticles or pure Cu_2O nanospheres under solar light irradiation. The drastic enhancement in photocatalytic activity could be attributed to the surface plasmon resonance, the electron sink effect of the Ag nanowire cores, and the unique 1D core-shell nanostructure.

3 Electrochemical energy conversion and storage

Lithium-ion batteries, usually based on insertion–extraction of lithium ions, are primarily used for energy storage [7]. Compared with other batteries, they show relatively high energy density and emit low pollution to the environment. Recent progress on these batteries has made electrically powered vehicles realistic alternatives, which could significantly reduce the pollution due to waste exhaust from petrol vehicles. Nevertheless, the two biggest challenges for realizing electrically powered vehicles lie in how to realize: (1) fast charge and discharge with good retention of capacity and (2) good cycling stability for a long service life to reduce the cost. The performance of an energy storage device is primarily dependent on the properties of the electrode materials. The charge/discharge speed of the lithium-ion batteries is mainly controlled via the electrochemical reaction speed and the ion diffusion speed, and the cycling stability is related to the volume changes before and after charge/discharge. It has been both theoretically and experimentally proved that nanostructures could solve these problems [4, 6, 7, 42–44]. This is because the high surface area of nanostructures offers plentiful reaction sites for the electrochemical reactions, and the diffusion paths of charge carriers (or ions) could also be significantly shortened by nanoscale electrode materials. Moreover, pulverization of the electrode materials can be significantly improved by nanostructuring.

For example, lithium-ion batteries employing $Cu_{2-x}Te$ nanosheets as anode showed superior cycling stability up to 5,000 cycles with a charge/discharge rate of 2 C and a capacity of 100 mAh/g, which was attributed to their variable compositions and structures, better electronic contact, and small volume expansion/shrink during charge and discharge [45]. Hybrid carbon–$Li_4Ti_5O_{12}$ nanocomposites with diameters of a few micrometres, composed of numerous nanosheets, exhibited a reversible charge–discharge capacity of $\sim$169 mAh/g ($\sim$97 % of its theoretical capacity, 175 mAh/g) at the 10 C rate, superior to pure n-$Li_4Ti_5O_{12}$ ($\sim$106 mAh/g), porous $Li_4Ti_5O_{12}/TiO_2$ (103.7 mAh/g) nanostructures, and commercial $Li_4Ti_5O_{12}$ powders ($\sim$85 mAh/g). This excellent performance is attributed to the good conductivity, large surface area, and stable structure of such micro-nanostructures, which could be explored as promising anode materials for lithium-ion batteries [6]. Doping graphene with nitrogen, boron, phosphorus, or their composites is an effective way to increase the specific energy storage capacity and rate performance, both of which are critically important in designing effective energy storage systems for large-scale applications, including renewable energy [7].

Sodium-ion (Na^+) batteries have recently attracted increased attention for electrical energy storage owing to

the natural abundance and low cost of sodium, which could enable sodium-ion batteries to act as a low-cost substitute for lithium-ion batteries. Nanocomposites with ultra-small magnetite (Fe_3O_4) nanoparticles (about 3 nm) uniformly anchored on the surfaces of RGO nanosheets were synthesized by a novel single-step high-temperature coprecipitation approach for use as anodes in sodium-ion batteries. The electrodes showed superior cycling performance with a reversible Na-storage capacity of 204 mAh/g and outstanding cycling stability (i.e., 98 % capacity retained after 200 cycles) due to the synergetic effect of the uniform distribution of the ultra-small Fe_3O_4 nanoparticles (3 nm) and the buffering role of the highly conductive RGO nanosheets [46]. Mesoporous carbon with 9.5-nm pores synthesized by packing and carbonization of resorcinol and formaldehyde nanospheres (50 nm), exhibited a high initial capacity (410 mAh/g) and good capacity retention (125 mAh/g after 100 cycles) as anode for sodium-ion batteries. The improved efficiency (>97 %) and cycling stability could be attributed to their high surface area, the large mesopores and micropores in the carbon spheres, and the superior connectivity and conductivity of the mesoporous network [42]. Such results suggest the possibility of constructing low-cost sodium-ion batteries by using mesoporous carbon with large nanopores and RGO-based nanocomposites.

Besides sodium and lithium-ion batteries, nanostructuring has also proved to be an effective way to enhance the performance of other energy storage systems, such as supercapacitors [4, 47, 48], Li–S batteries [49], Li–air batteries [50], microbial fuel cells [51], and solid oxide fuel cells [52].

4 Thermoelectric conversion

Thermoelectric technology based on the Seebeck effect, which was discovered in 1836 by Thomas Johann Seebeck, can convert heat into electricity directly via a flow of charge carriers from the hot side to the cold side in semiconductors [53]. It has distinct advantages, such as reliability, silent operation without mechanical movement, simplicity, and zero emissions [2]. Although this technique has many merits and a long history, only niche applications of this technology have appeared due to its extremely low conversion efficiency (typically <6 %), which is related to the low value of the dimensionless figure of merit (*ZT*). The difficulty in increasing *ZT* lies in the fact that it is very difficult to simultaneously optimize the three "interlocked" factors: high electrical conductivity, high Seebeck coefficient, and low thermal conductivity. Hence, *ZT* values have been limited to below 1 until Hicks and Dresselhaus [54, 55] theoretically proved that low-dimensional materials could have higher *ZT* than their bulk analogues, due both to their lower thermal conductivity and to quantum confinement effects. The highest known *ZT* value (*ZT* =3.0 at 550 K) was achieved in Bi-doped n-type PbSeTe/PbTe quantum-dot superlattices (QDSLs) grown by molecular beam epitaxy (MBE) [56]. Han et al. [2] summarized the recent progress on different kinds of thermoelectric materials in their comprehensive review and pointed out that nanostructuring was the most important strategy for enhancing *ZT* values, not only because nanostructuring could effectively decrease thermal conductivity, but also because it could cause an energy filtering effect that increases the Seebeck coefficient. Later, they proposed a low-cost surfactant-free route to the synthesis of different nanostructured thermoelectric materials, and obvious enhancement of *ZT* was achieved [57–60]. In particular, the pronounced enhancement in *ZT* of some metal chalcogenide nanostructures was achieved due to the presence of nanograins or nanopores, which can effectively decrease the thermal conductivity [57].

5 Others

In addition to the above-mentioned clean energy applications, there are some other systems for clean energy applications. Advanced materials and nanotechnology related to clean coal and fossil fuels, biofuels and biomass conversion, biosystem, and bioinspired system for energy conversion, piezoelectric conversion, and CO_2 capture, storage, and utilization, as well as hydrogen storage, have been researched intensively for clean energy applications in recent decades [48, 61–69]. For example, synthesis of methane (CH_4) from syngas ($CO + H_2$) has been applied for the removal of unwanted CO for ammonia production, fuel cells, and others, as well as the production of natural gas derives [70]. Yan et al. [70] prepared Ni/SiO_2 catalysts for CO methanation by dielectric-barrier discharge (DBD) plasma decomposition, and the resultant catalyst exhibited significantly improved activity with enhanced stability due to its smaller particle size with higher dispersion, less defects, and enhanced metal–support (Ni–SiO_2) interactions. Gong et al. [71] developed the simultaneous saccharification and enhanced lipid production (SSELP) process for efficient conversion of lignocellulosic materials into microbial lipids with higher lipid coefficient than those obtained by using the conventional process. Specifically, *Cryptococcus curvatus* cells were cultivated in corn stover containing hydrolytic enzymes. When cellulose was loaded at 32.3 g/L, cellulose conversion, cell mass, lipid content, and lipid coefficient reached 98.5 %, 12.4 g/L, 59.9 %, and 204 mg/g, respectively. The SSELP process greatly reduced time

and costs and appeared promising for the production of fatty acid-derived products from lignocellulosic biomass.

Liu et al. [61] fabricated a hybrid system of semiconducting nanowires and bacteria that mimics the natural photosynthetic process by using solar energy to synthesize carbohydrates from CO_2 and H_2O. The high-surface-area silicon nanowire array harvests light energy to provide reducing equivalents to the anaerobic bacterium, *Sporomusa ovata*, for the photoelectrochemical production of acetic acid under aerobic conditions (21 % O_2) with low over potential ($\eta < 200$ mV), high Faradaic efficiency (up to 90 %), and long-term stability (up to 200 h). The resulting acetate ($\sim$6 g/L) could be activated to acetyl coenzyme A (acetyl-CoA) by genetically engineered *Escherichia coli* and used as a building block for a variety of value-added chemicals, such as *n*-butanol, polyhydroxybutyrate (PHB) polymer, and three different isoprenoid natural products [61]. Zhang et al. [72] prepared a combined system ammonia borane@polypyrrole (AB@PPy), which was able to release H_2 at temperatures as low as 48°, and up to 15.3 wt% pure hydrogen could be released below 150 °C. The improvement was ascribed to the synergistic effects of nanoconfinement and N-catalysis, which suggested that the AB@PPy composite was a safe material for potential hydrogen storage.

Nanostructured ZnO is reported to be an ideal piezoelectric material with significant improvements in energy harvesting performance [69, 73]. For example, piezoelectric ZnO nanorods grown on a flexible substrate are combined with the p-type semiconducting polymer PEDOT:PSS to produce a p–n junction device that successfully demonstrated improved kinetic-to-electrical energy conversion. Both the voltage and current output of the devices were measured to be in the range of 10 mV and 10 μA/cm^2, respectively. Combining these figures for the best device gave a maximum possible power density of 0.4 mW/cm^3 [73].

6 Summary and outlook

It is easy to notice that most of the progress in clean energy is related to nanotechnology. Chinese scientists working inside and outside domestic institutes have achieved fruitful outcomes in advanced clean energy materials in recent years. The positive roles of nanostructures in clean energy research are well accepted, and there are still some fundamental issues debated in real applications. For example, high surface area leads to self-discharge, poor cycling, and calendar life of batteries and their inferior packing of nanoparticles also leads to lower volumetric energy densities. Small particle size of photocatalysts results in their poor cycling performance due to their instability. Poor stability of thermoelectric nanostructures also leads to possible crush during sintering into highly dense pellets at high temperature or high pressure, and low thermoelectric conversion efficiency.

The future efforts in nanostructures for clean energy could be considered as follows. First of all, the oriented design and synthesis of catalysts to improve their selectivity, conversion efficiency, and stability have always been a challenge in the field of catalysis research. In particular, the design and selection of catalysts play key roles in many areas of clean energy, such as photocatalysis, environmental catalysis, the oxygen reduction reaction, clean coal, and biomass conversion. Secondly, the synthesis of highly tunable and complex porous structures and 3D hierarchical nanostructures with improved accessibility, larger surface area, and better dispersion of the active species has been widely used in environmental and energy applications, such as solar cells, lithium-ion batteries, water treatment, carbon dioxide and hydrogen storage, and thermoelectric devices. At present, the biggest challenge is to select the ideal functional materials with improved conversion efficiency, catalytic efficiency, gas-stripping absorption efficiency, etc. Multifunctional nanomaterials are often required in order to create the desired synergetic effects. Finally, the large-scale commercialization of nanomaterials and devices still remains a big challenge around the world. Coincident with the giant economic development occurring in China, revolutionary advances in nanotechnology and a deeper mechanistic understanding of the properties of materials, from combining progressively improved research conditions and more significant achievements generated in domestic laboratories and industries in China, are very much expected.

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Conflict of interest The authors declare that they have no conflict of interest.

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