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Classification, Synthesis, and Application of Luminescent Silica Nanoparticles: a Review

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Abstract

Luminescent materials are of worldwide interest because of their unique optical properties. Silica, which is transparent to light, is an ideal matrix for luminescent materials. Luminescent silica nanoparticles (LSNs) have broad applications because of their enhanced chemical and thermal stability. Silica spheres of various sizes could be synthesized by different methods to satisfy specific requirements. Diverse luminescent dyes have potential for different applications. Subject to many factors such as quenchers, their performance was not quite satisfying. This review thus discusses the development of LSNs including their classification, synthesis, and application. It is the highlight that how silica improves the properties of luminescent dye and what role silica plays in the system. Further, their applications in biology, display, and sensors are also described.

Keywords: Luminescent silica nanoparticles, Classification, Synthesis, Application

Introduction

Luminescent materials are widely applied because of their special optical properties [1]. However, their application is limited by many restrictions, such as low hydrophobicity and biocompatibility, or owing to disadvantage, such as high toxicity, poor biocompatibility, and low absorbance [2–5]. Thus, it is necessary to modify luminescent materials to satisfy the requirements of practical applications.

LSNs with improved properties have attracted more and more attention in biology [6, 7], lighting [8], and sensors [9]. Their characteristic optical properties make them unique in optical materials [10]. Silica is transparent to light which makes silica an ideal candidate as matrix for fluorescent materials. Thermodynamic and chemical stability are also important factors as a matrix and silica coincides with these basic factors [11]. Moreover, the surface of silica can be easily modified, allowing further functionalization with various functional groups to adapt diverse requirements [12]. Silica having many of the above advantages is naturally an ideal substrate

for improving the properties of luminescent materials [13]. Multifunctional nanosystems can be created by assembling, encapsulating, or integrating one or more different nanomaterials within and on the surface of silica nanoparticles using different processes [11]. As modifying luminescent materials, LSNs with the excellent properties are attracting more and more attention in frontier researches [14]. Montalti et al. summed up many excellent researches in medical imaging with organic dyes doped silica [6]. Silica provides a stable and multifunctional platform for phosphors, but long-term toxicity needs to be studied. Michael Schäfrling demonstrated the art of luminescent sensors [9]. Selectivity and sensitivity are the core of the sensor materials. Zou Hua et al. elaborated on the means of organic silica modification. Nanocomposites have superior properties to separate components [15]. There are many wonder reviews focusing on a specific area such as biology [6, 7, 16], but lacking a systematic introduction to LSNs and their excellent performance in other fields.

This review starts with the classification of LSNs following with their synthetic methods. The categories of LSNs are systematically established based on the classification of luminescent materials. In terms of chemical properties and luminescence mechanisms, organic molecule dyes, luminescent metal, and quantum dots (QDs)

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doped phosphors are three typical phosphors, all of which have their own unique luminescence mechanisms and advantages as representatives of LSNs [17–19]. The highlight is how the silica enhances the properties of phosphors. With the deficiency of luminescent materials applications, the possible strategies are discussed to improve their performances for LSNs. It involves not only biological applications but also displays and sensors.

Classifications of LSNs

Luminescence emitting various brightness has great value in material fields [20]. A lot of researches on the modification of luminescent materials have been carried out around how to improve the signal-to-noise ratio, stability, and environmental adaptability for the potential applications. The introduction of antenna ligands in lanthanide complexes to enhance luminescence performance is a typical example of modification. Silica is a good matrix for mixing materials with different functions and different chemical properties. Phosphors have been doped into silica matrix to modify their natural defects and improve their properties, which is advantageous for broad applications with facile modified and non-toxic silica surfaces and protection for luminescent dyes. With multifunction and tunable adaptability, LSNs have attracted more and more attention. Among all the luminescent phosphors, organic luminescent molecules, luminescent metal-doped phosphors and QDs are the three most representative categories which deserve highlighting. So the above three dyes are shown as typical LSNs in combination with silica. Representative examples are listed in Table 1.

Organic Luminescent Molecules Doped LSNs

Organic luminescent molecules are important luminescent materials with π -conjugated ring structures and small size [16]. However, non-specific labeling and bleaching hinder their application. Organic dyes doped silica nanoparticles are widely studied with excellent stability, selectivity and biocompatibility [52, 53]. Van Blaaderen et al. [21] made a preliminary attempt to synthesize luminescent silica spheres. Fluorescein isothiocyanate (FITC) was coated on the surface of silica with the help of APS ((3-aminopropyl)triethoxysilane) which provided a feasible way to combine dyes with silica by covalent bonds. Inspired by this process, Andrew et al. [22] synthesized dual-emission fluorescent silica nanoparticles with two layers. Two dyes, tetramethylrhodamine isothiocyanate (TRITC) and FITC, were conjugated to the silica by means of APS in an anhydrous nitrogen environment. The schematic diagram and SEM image (Fig. 1a) showed the nanostructures of the nanoparticles. Silica with TRITC was synthesized firstly as the core of the dual-emission nanoparticles and FITC was conjugated on the surface of the core with further tetraethoxysilane (TEOS). The

synthesized dual emission fluorescent silica nanoparticles investigated the intracellular pH value successfully in rat basophilic leukemia mast cells (RBL-2H3) in Fig. 1b–d.

In order to improve the photostability of organic fluorophores, silica encapsulation is a commonly used method of modification. Long Jiao et al. [23] chose four aminocyanine dyes as the near-infrared (NIR) fluorescent probes and coupled them correspondingly with 3-aminopropyltriethoxysilane (APTES), a common silane coupling agent. TEOS hydrolyzed with the treated NIR dyes in the microemulsion system. The cyanine-loaded fluorescent silica nanoparticles (FSNPs) were obtained after centrifugation and washing. The whole process was shown in Fig. 2a. As it can be seen in Fig. 2b, the four FSNPs encapsulated into the silica showed better fluorescence intensity pH stability than that of free dyes. The four FSNPs improved their brightness at the same time (Fig. 2c). They tested their photostability in living cells by a confocal laser scanning microscope (CLSM). FSNP-3 and FSNP-4 (more anchoring sites) got improved photostability than that of free dyes while FSNP-1 and FSNP-2 did not get any improvement. More anchoring sites reinforced the structure of the dye molecule. A dye with rigid structure had a less nonradiative decay and hard intramolecular rotation which make the dye brighter. Silica layer can protect the encapsulated materials which has reinforced molecule structure and improve their brightness without photobleaching. FSNP-3 and 4 also had low biological toxicity according to the methyl tetrazolium (MTT) method in Fig. 2d. Biocompatibility is another advantage of silica.

Agglomeration is one of the main reasons of quenching for most luminescent dyes. Phosphors can keep in an appropriate concentration with silica steadily. Aggregation-induced emission luminogens (AIEgens), unlike the traditional luminophores, do not suffer from this issue. Conversely, aggregation leads to strong emission [54]. To improve the performance of AIEgens in biological fields, many polymer matrices are used to encapsulate AIEgens. Moreover, there are some other issues that can cause AIEgens quenching, such as water and oxygen, which has a negative effect on application. Silica can prevent them from the quenchers [55]. Based on these analysis above, TPETPAFN (a typical fluorogen consisting of two tetraphenylethylene pendants and an intramolecular charge transfer core), an AIEgen, was biofunctionalized by F127 (poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol)) to form the core micelle [24]. TEOS was hydrolyzed to obtain silica shell coated on the core micelle via modified sol-gel method. As Fig. 3 showed, the synthetic TPETPAFN-F127-SiO₂ nanoparticles exhibited better photoluminescence properties benefited from the protection of the silica shell.

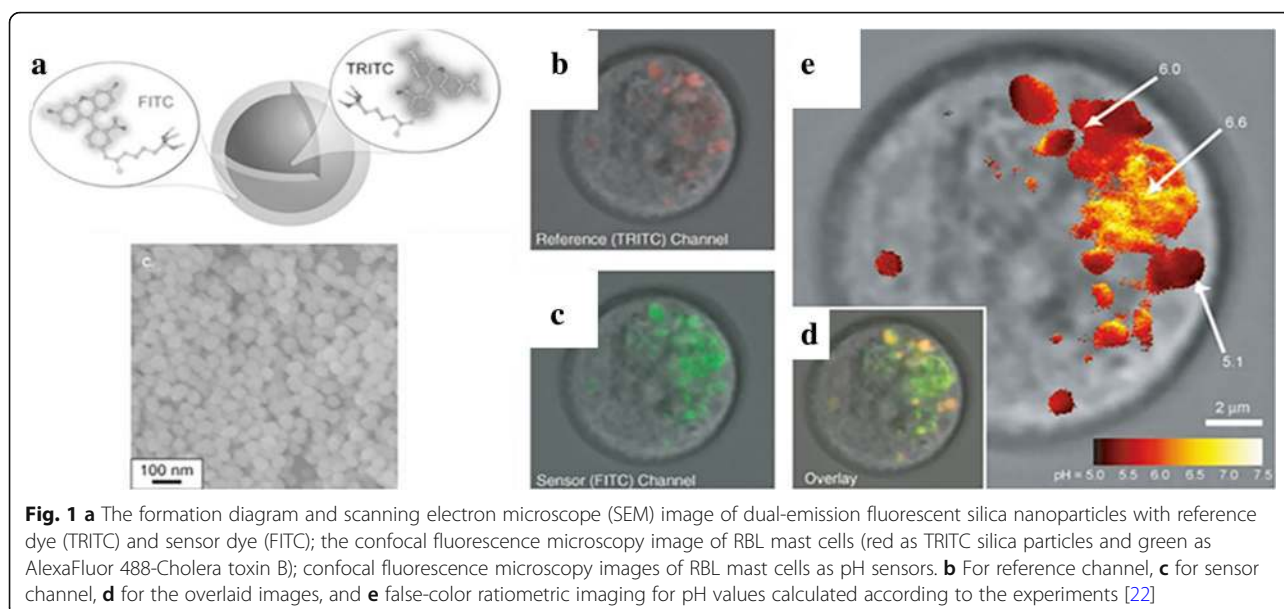
Table 1 The composition and synthetic methods of reported LSNs

Materials		Synthetic methods	Ref
Organic luminescent molecules doped LSNs	FITC-APS@silica	Stöber method	[21]
	TRITC:SiO ₂ @FITC:SiO ₂	Modified Stöber method	[22]
	Aminocyanine dye-silica hybrid nanoparticles	Reverse microemulsion	[23]
	AIE-F127-SiO ₂	Sol-gel method	[24]
	HPTS-adsorbed Ag@SiO ₂	Stöber method	[25]
	Rhodamine-conjugated silica	Direct micelles assistant method	[26]
	An18-SiO ₂	Stöber method	[27]
	Y ₂ O ₃ :Eu ³⁺ @SiO ₂ with FITC	Stöber method	[28]
	FSCHP	Stöber method	[29]
Luminescent metal-doped LSNs	Eu@Si-OH	Reverse microemulsion	[30]
	Eu@Si-NH ₂		
	NaGdF ₄ :Yb,Er@SiO ₂ @Eu (TTA)3Phen	Reverse microemulsion	[31]
	Eu-mesoporous silica nanospheres	Modified sol-gel method	[32]
	SiO ₂ -[Eu (TTA) ₃ (Bpy-Si)]	Modified Stöber method	[33]
	Perovskite QD/silica composites	Other method	[34]
	Mesoporous silica particles integrated with all-inorganic CsPbBr ₃ absorption		[35]
	CD/silica composites heating silica film		[36]
	Silica@EuCP	Solvothermal method	[37]
	Ru (bpy) ₃ doped silica	Reverse microemulsion	[38]
	Ru (bpy) ₃ @SiO ₂ :Gd	Reverse microemulsion	[39]
Ru (bpy) ₃ @SiO ₂	Stöber method	[40]	
Er,Yb:GdVO ₄ @SiO ₂	Stöber method	[41]	
QDs-doped LSNs	Carbon dot-silica-phosphor composite	Stöber method	[42]
	CdSe/CdS/ZnS@SiO ₂	Stöber method	[43]
	BAM-SiO ₂ -CdSe MQDs	Reverse microemulsion	[44]
	Quantum dot/SiO ₂ /Au	Reverse microemulsion	[45]
QDs-doped LSNs	CdS/CdSe/CdS@SiO ₂	Reverse microemulsion	[46]
	FL-SiO ₂ (carbon dots)	Direct micelles assistant method and calcination	[47]
	SiO ₂ /Fe ₂ O ₃ -CdSe	Reverse microemulsion	[48]
	Silica encapsulated polymer dots	Stöber method	[49]
Silica quantum dots	Organosilica nanocrystals	Stöber method	[50]
	Silica NPs	Hydrothermal method	[51]

Luminescent Metal-Doped LSNs

Rare-earth metal [56] and transition metal [57] are common luminescent metal materials based on the charge transfer transition. Luminescence after complexing with the ligand is the most obvious feature of this material. There are two main mechanisms of metal luminescence, LMCT (ligand to metal charge transition) and MLCT (metal to ligand charge transition). Lanthanide metals and transition metals are their typical examples, respectively. Due to abundant electronic energy levels, there are diverse luminescent metals that have great potential for application in the field of luminescence with different

emission [58]. Noble metals with LSPR have been widely used in enhanced luminescence materials and are involved in this section. Nevertheless, low sensitization efficiency and quenching limit the applications of luminescent metals [59]. In order to improve their photostability and biocompatibility, Francis et al. added a substituted silyl group into the ligands for the further modifications [30]. Eu@Si-OH nanoparticles were obtained after coating silyl group modified Eu complexes with silica via reverse microemulsion method. The product finally got amine functionalized with APTES as Eu@Si-NH₂ nanoparticles. The silica layer kept the complexes from the quenchers



(OH and NH₂ groups). As a result, both of them showed better photostability in Fig. 4. Eu@Si-NH₂ nanoparticles exhibited good performances in bioimaging.

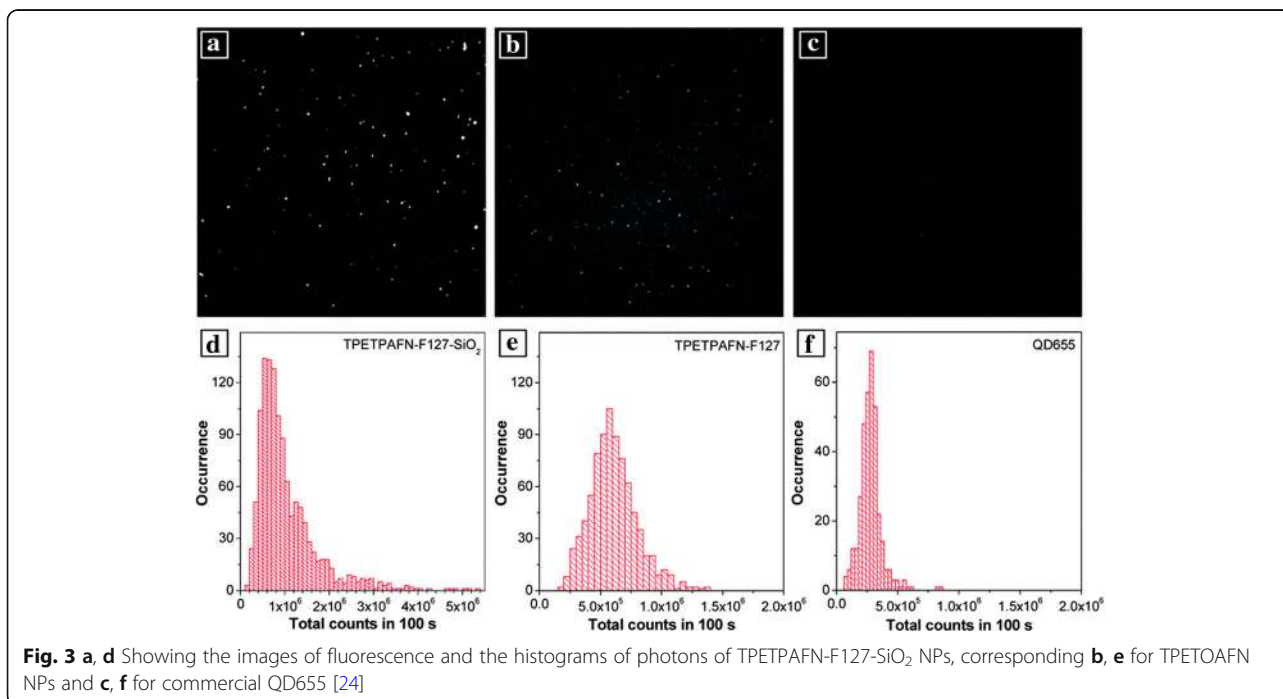
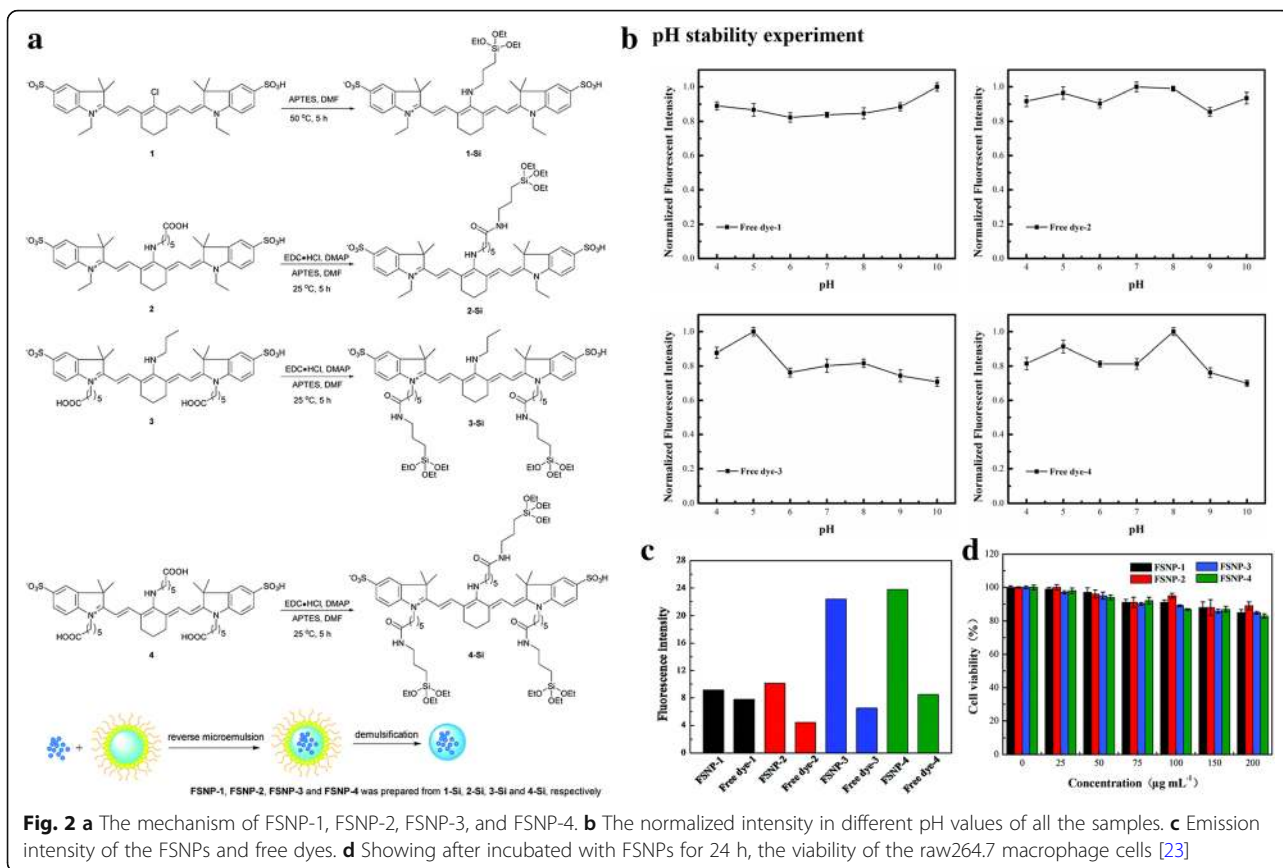
Ezquerro et al. incorporated Ir complexes, MLCT luminescent complex, into the silica framework for enhanced stability and photophysical properties via sol-gel process [60]. With the protection of silica, these phosphors showed excellent stability under not only ambient conditions but also harsh environments which have further application in white light-emitting diode (WLED).

Y. Li et al. [31] synthesized oleic acid stabilized upconversion nanoparticles (UCNPs). Then they coated a silica layer on the UCNPs via a microemulsion method and water-soluble UCNPs were obtained. Introducing Eu (TTA)₃phen complexes into the system, they synthesized NaGdF₄:Yb,Er@SiO₂@Eu (TTA)₃Phen (UCNPs@SiO₂@EuTP) nanospheres. The surface quenching was suppressed after silica coating and as a result the emission intensity enhanced as shown in Fig. 5. The water-soluble nanoparticles with two different emissions were obtained with the help of silica.

Chen et al. [42] successfully used carbon dots (CDs) and rare-earth ions for WLED. They synthesized CDs by one-pot organic pyrolysis method, which had a maximum of blue emission at 470 nm, and two excitation peak at 251 and 364 nm, respectively. To get white light-emitting composite, CDs were used as the blue emission core and Sr₂Si₅N₈:Eu²⁺ phosphor was used as the orange emission component. CDs were put into the Stöber system. As TEOS hydrolyzed, CDs would be coated by a silica layer with red phosphor. The carbon dot-silica-phosphor composite (CDSP) was synthesized after centrifuging, drying, and grinding. CDSP had a broad absorption ranging from the UV (ultraviolet) to yellow region (200–600 nm),

especially strong in the UV region. After testing excitation at different wavelengths, they found that the CDSP got the closet Commission Internationale de l'Éclairage (CIE) coordinate (0.32, 0.32) to that of pure white light (0.33, 0.33) at the excitation at 400 nm in Fig. 6. And it was a good attempt to get the emission of CDSP by tuning the mass ratio of CD and the phosphor. Under excitation at 400 nm, they got the nearest mass ratio (3.9% (0.32, 0.32) and 5.1% (0.34, 0.32)) to white emission. CDSP showed better white emission (0.30, 0.31) in light-emitting diode (LED) packaging than that of CD&P (mixing up with CDs and phosphor directly) (0.28, 0.29). Two components dispersed homogeneously with silica and decreased the probability of aggregation and phase separation. Finally, they got a WLED with CDSP powder on a UV diode chip (375 nm), and a white light (0.30, 0.33) was obtained. The color rendering index (CRI) was about 94, higher than that of the YAG:Ce based commercial WLED (CRI < 75).

Silica is commonly used as protective layer for luminescent materials to keep proper distance from noble metals in order to enhance fluorescence. This is due to the standing oscillation of free electrons caused by light. In order to enhance the luminescence, it needs to be kept in an appropriate distance between dyes and noble metal particles. As for noble enhanced materials, metal nanoparticles themselves can cause the chromophores quenching (within 5 nm) but their fluorescence can enhance up 100-fold (at around 10 nm). In the early research, Tuo Li et al. [61] synthesized Ag nanoparticles with the silica shell in the microemulsion matrix (Ag/SiO₂ nanoparticles). The reagents needed to produce silica (TEOS and cyclohexane) were injected into the microemulsion after silver reduced. They carefully studied the effects of different conditions (water/surfactant for R and



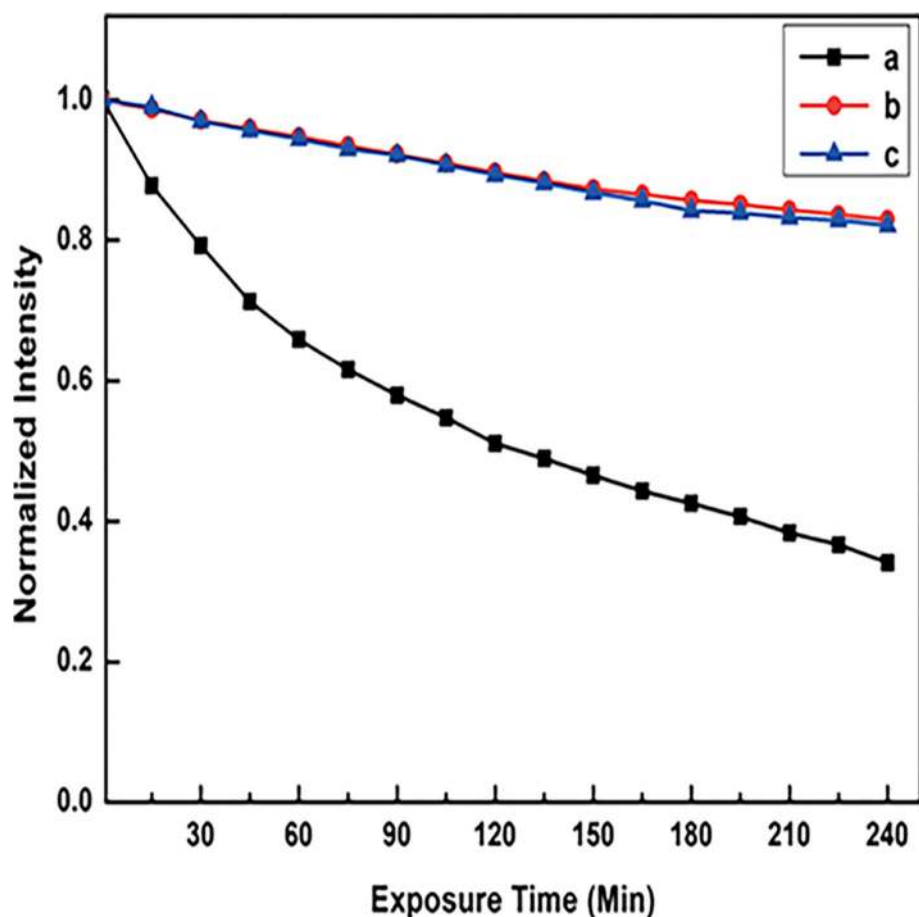


Fig. 4 The curves of fluorescence intensity changing with exposure time under 365 nm irradiation, **a** parent Eu complex in CHCl_3 solution, **b** Eu@Si-NH_2 , and **c** Eu@Si-OH nanoparticles in phosphate-buffered saline (PBS) buffer solution [30]

water/TEOS for H) on the Ag/SiO_2 nanoparticles and the results showed as Fig. 7. It is a good path to coat a uniform and thick silica layer on the core not only Ag but also other nanoparticles with microemulsion system. What Zhenhua Bai et al. [25] did is a good example. 8-Hydroxypyrene-1, 3, 6-trisulfonic acid (HPTS), a kind of fluorescent pH-sensitive dyes, is suitable to make as intracellular pH sensors owing to its unique advantages. But extreme pH conditions made it insensitive. When the solution is acidic, its fluorescence efficiency would decrease significantly. HPTS-adsorbed Ag@SiO_2 nanoparticles (Fig. 8a) were prepared based on noble metal-enhanced fluorescence effect. It could be seen from Fig. 8b that Ag@SiO_2 -8 nm@HPTS showed better fluorescence intensity especially in the extreme pH conditions.

QDs-Doped LSNs

Because of quantum confinement effect, QDs exhibit excellent luminescence properties whether they are semiconductor QDs, carbon QDs, or other types. Recently,

numerous studies have focused on the applications of QDs in optical devices. Sometimes, their properties are not good enough to adapt the complex applications. Necessary modification is imperative and silica is a suitable matrix [1].

To realize the combination of biolabel and magnetic resonance imaging, CdSe QDs were coated on the magnetic Fe_2O_3 core by a silica layer with NH_2 group. The associated pictures and characterizations were showed in Fig. 9. Combined NH_2 group with bio-anchored membrane (BAM), 4 T1 mouse breast cancer cell membranes showed specific labeling with BAM- SiO_2 -CdSe MQDs [44]. With the biocompatibility and magnetic, the multifunctional luminescence nanoparticles would gain broad applications in medicine.

To broaden QDs application, it is necessary to modify their water solubility and non-toxicity. Silica shows great potential in QDs' modification. Yunfei Ma et al. [43] introduced a homemade phase transfer reagent (adenosine 5'-monophosphate, AMP) and silane coupling agent (3-mercaptopropyltrimethoxysilane, MPS)

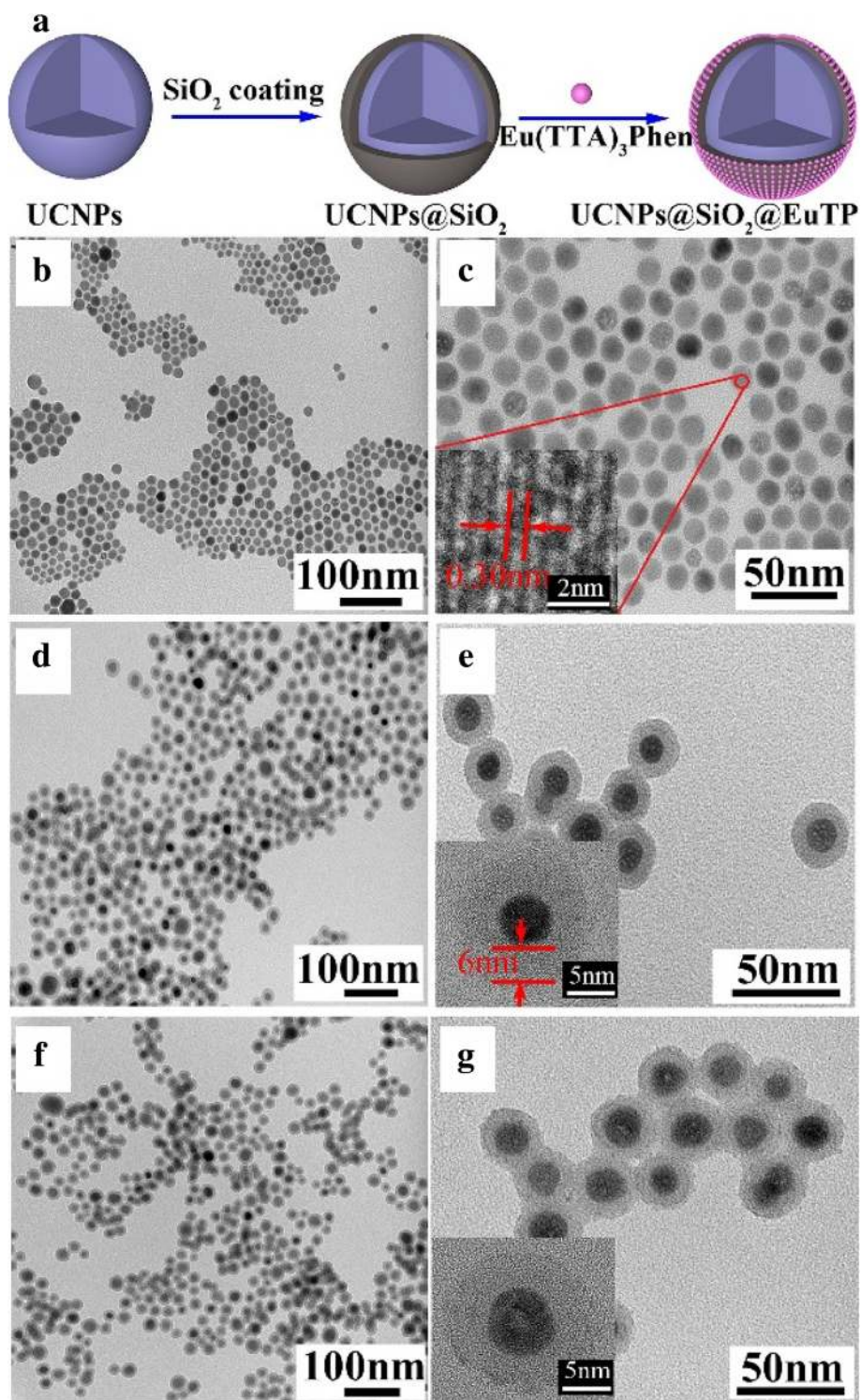


Fig. 5 a The formation of UCNP@SiO₂@EuTP and TEM (transmission electron microscope) images of the samples; **b, c** for UCNP@SiO₂, **d, e** for UCNP@SiO₂@EuTP, and **f, g** for UCNP@SiO₂@EuTP [31]

into the Stöber system. Oil-soluble (initial CdSe/CdS/ZnS QDs), alcohol-soluble (AMP-QDs), and water soluble (hydrolysis of TEOS around the QDs) were the

whole progress of solubility change. QD@SiO₂ had the same photoluminescence efficiency (50–65%) as the initial one. Wider pH range (pH 4–8 to 2–13),

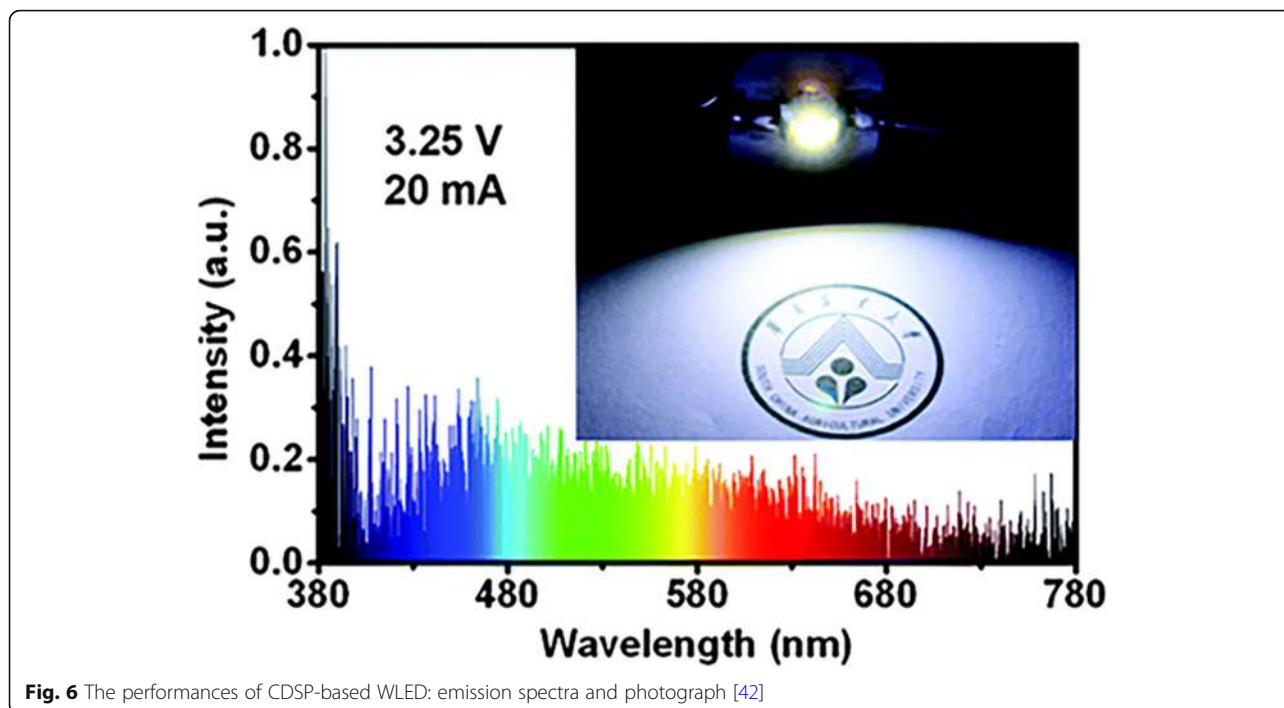


Fig. 6 The performances of CDS-based WLED: emission spectra and photograph [42]

improved stability in electrolyte, better thermal stability, and increased biocompatibility in Hela cells were the advantages of the QD@SiO₂.

To ensure the stability of QDs in optical devices, it is necessary to reduce the effect of blinking. Blinking is a phenomenon with a random intermittent luminescence which affects the stability of the QDs optical devices [62]. To reduce the effect of blinking, Botao Ji et al. [45] produced CdSe/CdS QDs as the core materials and encapsulated these QDs into silica shell based on the displacement of the initial hydrophobic ligands by reverse microemulsion method. And the QDs further modified by an Au layer on

the surface of silica with poly (1-vinylimidazole-co-vinyltrimethoxysilane) (PVIS) as the silane coupling agent. The nano-sized gold shell acted as a plasmon resonator that gave the QDs enhanced optical states density. The QDs' properties can be preserved regardless of drastic changes in the local environments because of the hybrid layer. As a result, the QDs' photostability increased. The QD fluorescence lifetimes reduced from 123 to 20 ns after gold coated. The golden QDs showed efficient multiexciton emission and its neutral photoluminescence intensity was higher than that of QDs. The results of the stability test were shown in

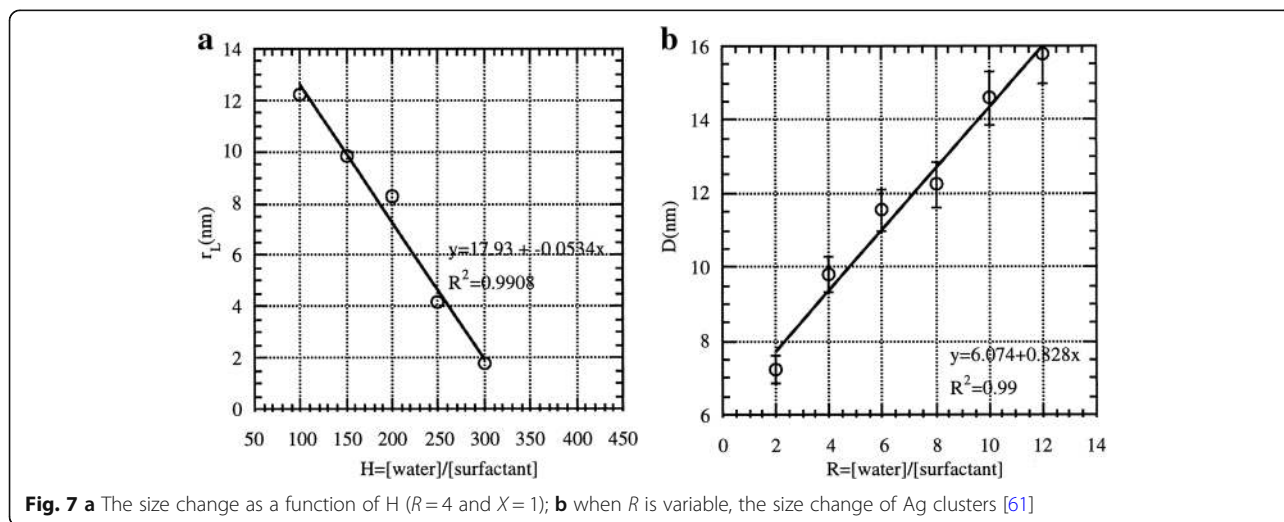


Fig. 7 **a** The size change as a function of H ($R = 4$ and $X = 1$); **b** when R is variable, the size change of Ag clusters [61]

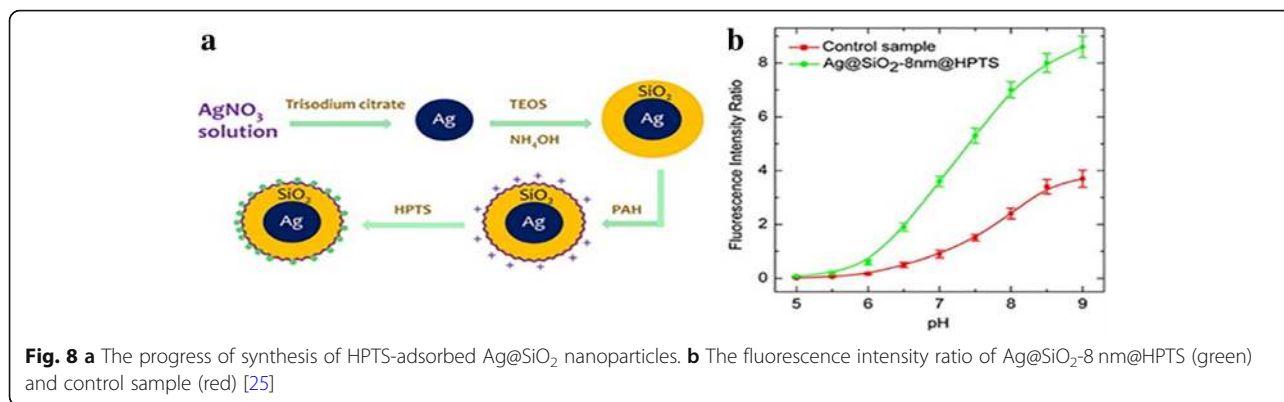
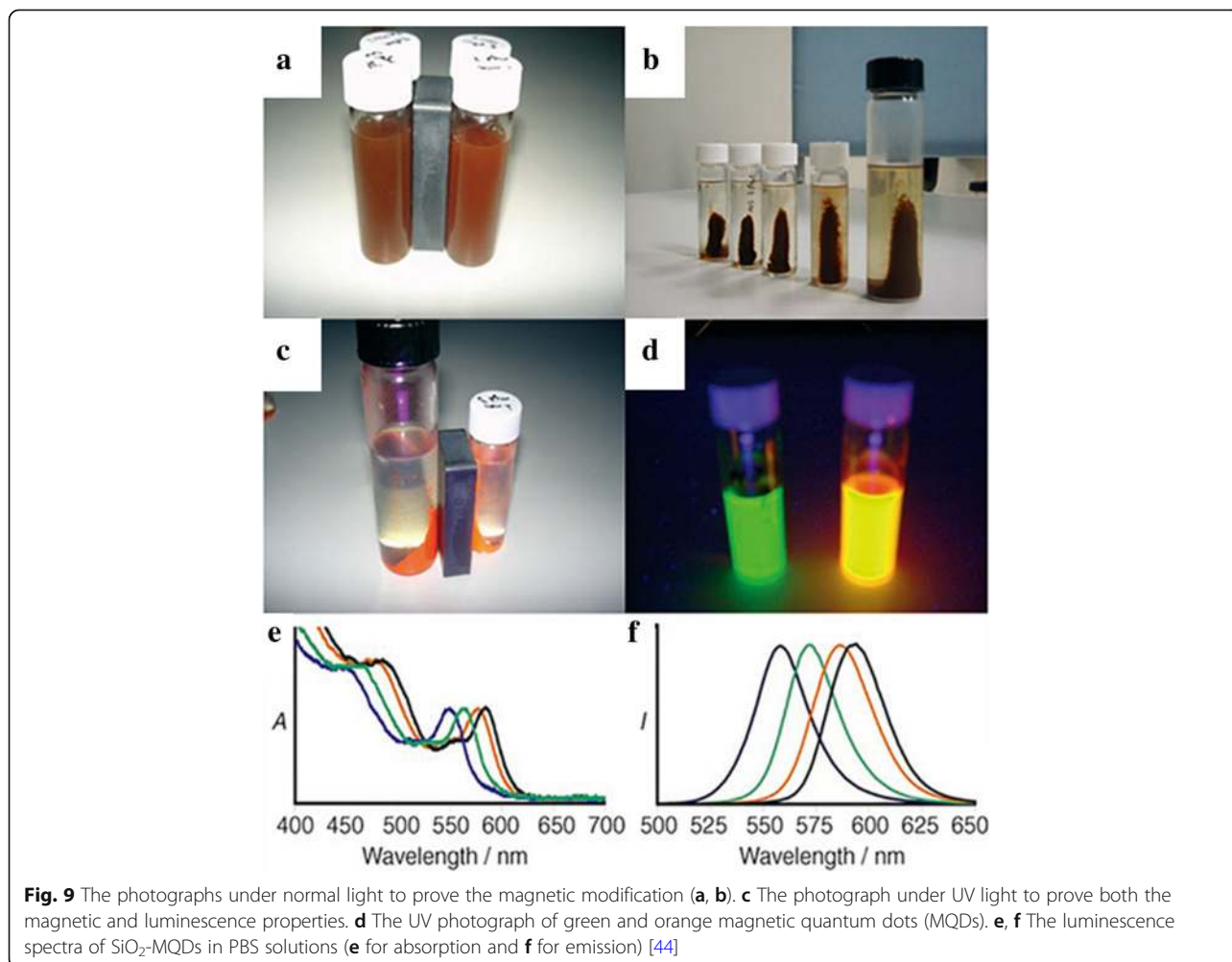
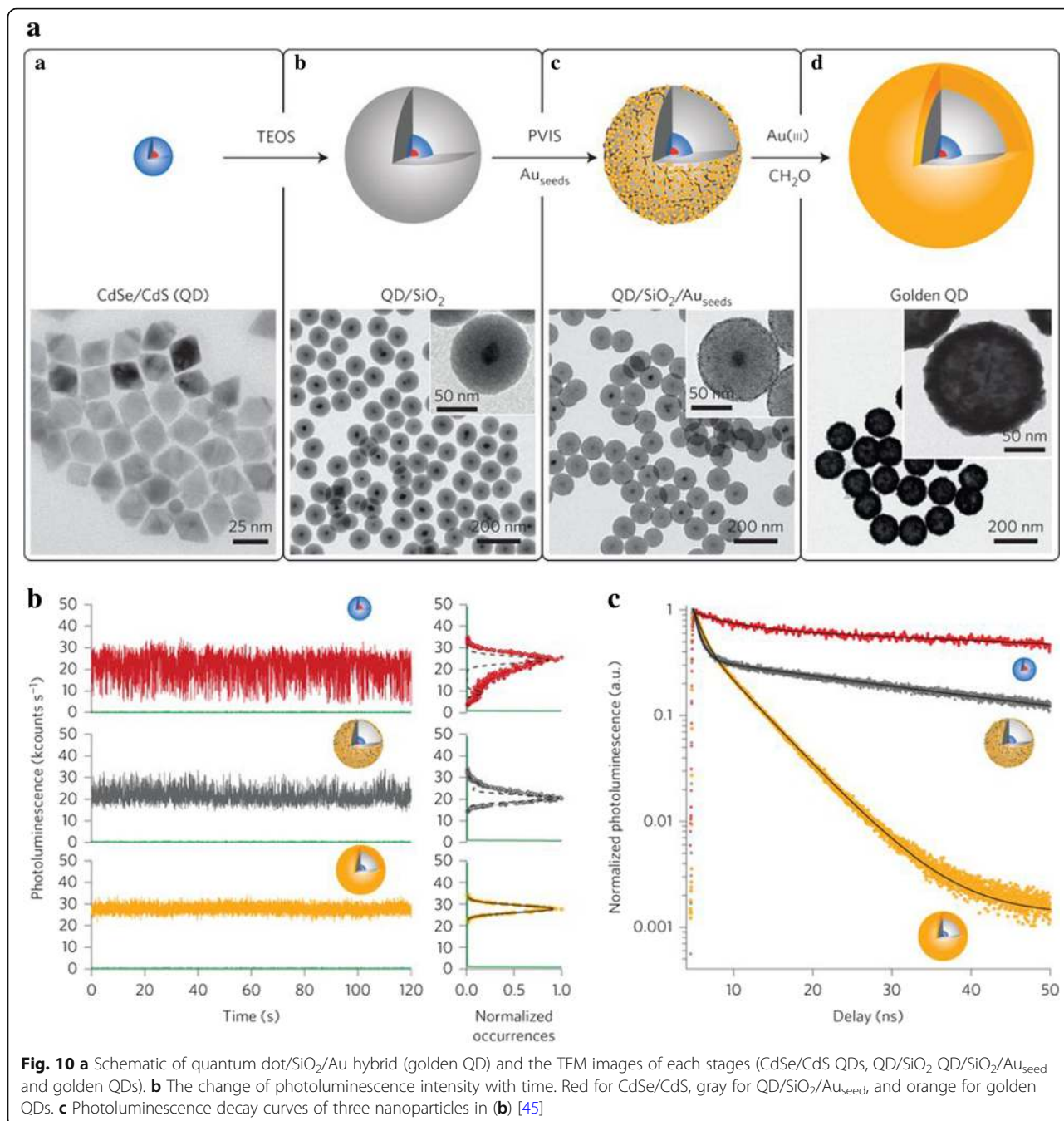


Fig. 10. What is more, the photoluminescence intensity could keep stable for several hours (even 24 h). The luminescence stability test showed that the luminescence of bare QDs would have a dramatic fall after only 1 h. Silica layer improved the performance of QDs slightly but it provided the suitable interval for the next Au layer to show the plasma enhanced effect.

Synthetic Methods of LSNs

For the fabrication of LSNs, selection of phosphors and design of synthetic routes are the core contents. Phosphors determine the emission range of LSNs and synthetic routes establish their structures and functions. All the synthetic routes of LSNs are based on the silica. Sol-gel method, reverse microemulsion method, and





direct micelles assistant method are three major approaches to obtain homogeneous and regular silica spheres which have been used in LSNs. Figure 11 is the schematic diagram of the mentioned methods.

Sol-Gel Method

Sol-gel method, also called Stöber method, is a convenient and feasible method to obtain monodispersed silica nanospheres. It is ideal to synthesize silica nanospheres since Stöber [63] carefully studied the synthesis of

size-specific silica spheres in the range of 50 nm–2 μm with alkoxy silane hydrolyzing under ammonia catalysis. Homogeneous silica spheres with different sizes (10 to several hundreds of nanometers) can be easily obtained by controlling the synthesis conditions such as the ethanol-to-water ratio, the amount of ammonia, and the temperature via sol-gel method. Using Stöber method, Van Blaaderen and A. Vrij Langmuir successfully synthesized dye (FITC)-doped silica by adding (APS) in the reaction system [21]. With the amine group from APS,

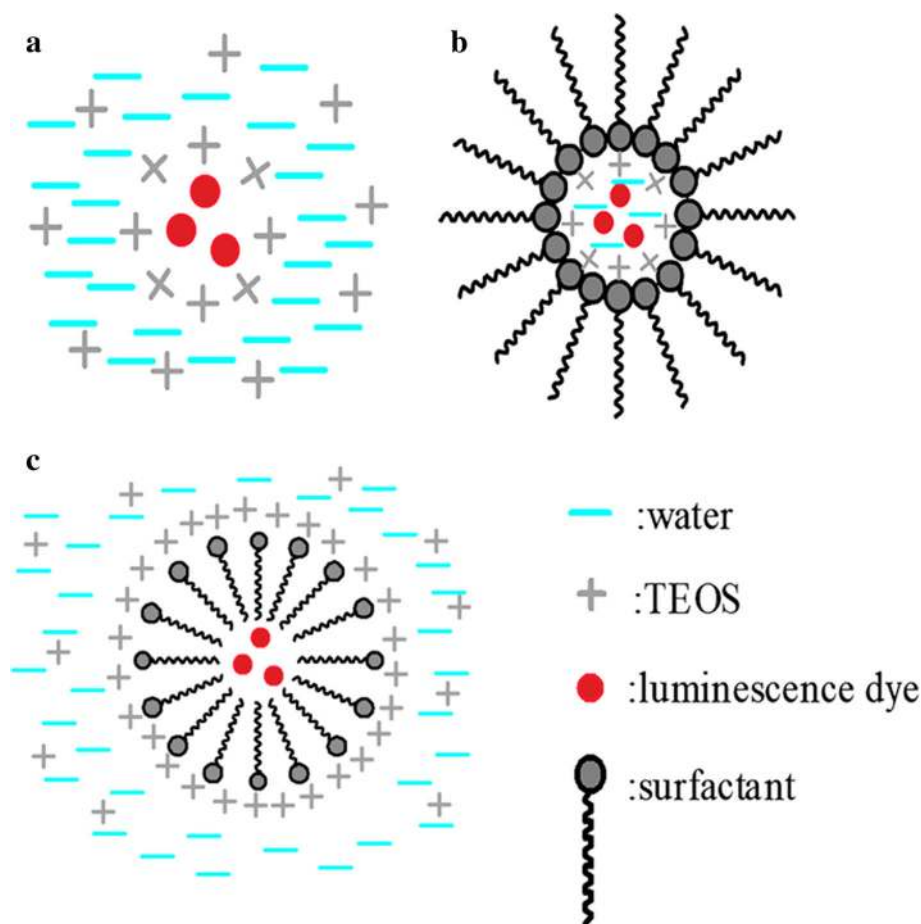


Fig. 11 The schematic illustrations of different LSNs with different methods. **a** For Stöber method, **b** For reverse microemulsion method, **c** For direct micelles assistant method

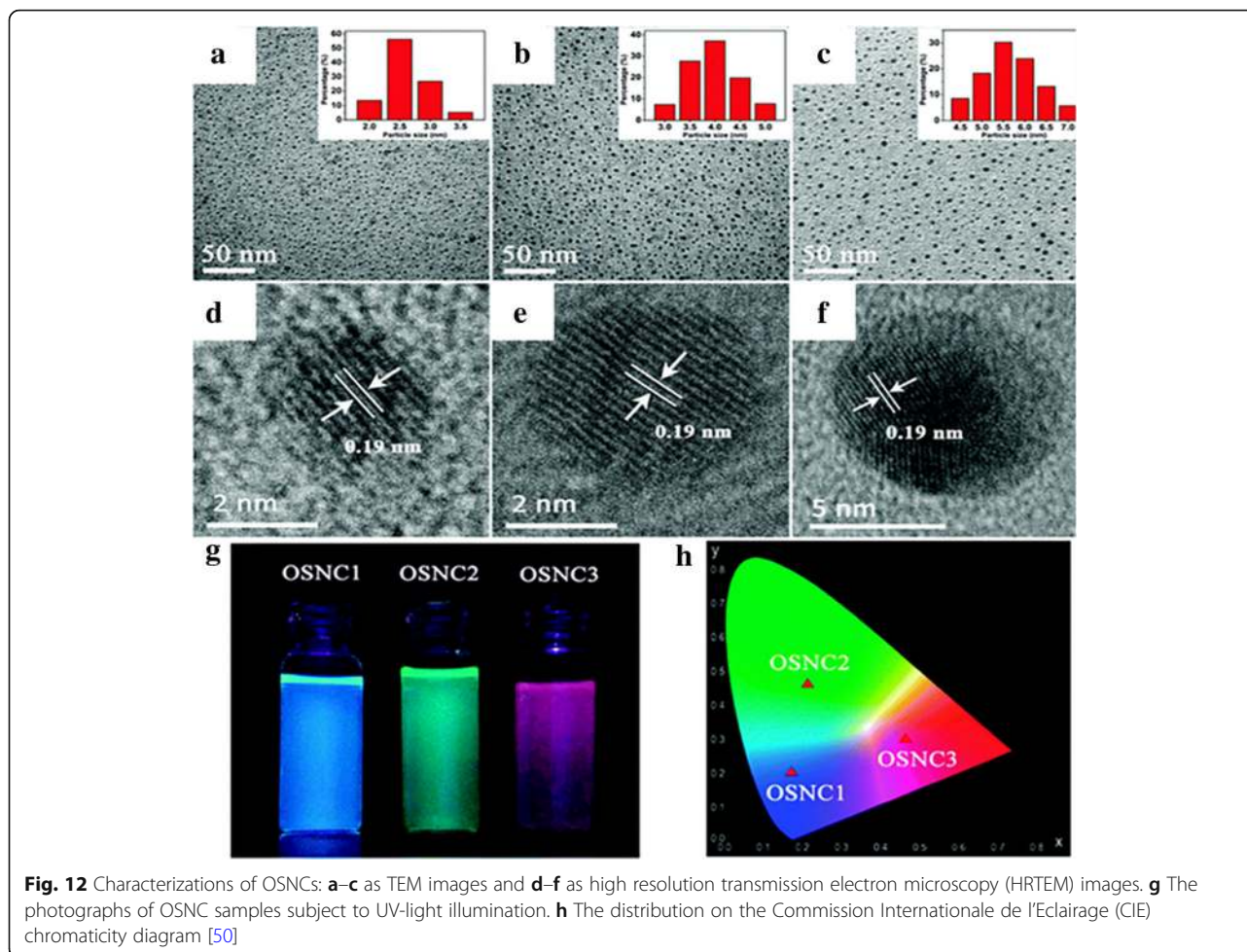
silica spheres caught FITC easily as showed in Fig. 11a. So far, in addition to dyes, many other materials have been linked to silica via Stöber method. Luis M. Liz-Marzan et al. improved the Stöber method and synthesized gold-silica core-shell particles using (3-aminopropyl)-trimethoxysilane (APTS) as the surfactant [64]. Combined with the gold core, APTES provides chemical bond bridging for silica encapsulation. Alkaline condition leads to homogeneous silica spheres as a popular Stöber system and acid catalyzed hydrolysis of alkoxysilane is also a feasible method to encapsulate luminescent dyes into silica [65].

A new kind of LSNs has been synthesized based on Stöber method. Lingang Yang et al. [50] successfully synthesized crystal silica by Stöber method based on the π - π stacking of vinyl groups. A Stöber progress with vinyltriethoxysilane (VTES) as the precursor, neutralization with hydrochloric acid, vacuum distillation to remove the solvent, and extraction using tetrahydrofuran are the whole procedures of organosilica nanocrystals (OSNCs). Three OSNCs had been synthesized with the same

crystal structure but in different sizes as shown in Fig. 12d–f. The sizes of organosilica nanocrystals (OSNCs) are gradually increasing because of the increase of VTES. As a result, they showed different luminescent properties as showed for Fig. 12g, h (blue, green, and red under UV light). OSNCs were characterized to possess good photo-stability and pH stability. The epitaxial growth of vinyl groups in diamond cubic crystal structure are presented due to the π - π stacking. The orderly stacked vinyl groups finally form a large π conjugated system with fluorescence following the quantum confinement. These OSNCs had great potential on the optical fields owing to the characteristics of silica which provided a new approach to get self-luminescence silica materials.

Reverse Microemulsion Method

Stöber method is a simple and convenient method to synthesize LSNs, but reaction conditions and initial particles that are not controlled place restrictions on the luminescent dyes. To overcome such limitations, Bagwe



and Khilar [66] introduced water-in-oil microemulsion system [67] during the synthesis of silver coated with silica nanocomposites (Fig. 11b). The initial alkaline aqueous solution of silver nanoparticles with TEOS was encapsulated in the water drop using surfactants. The hydrolysis progress of TEOS was the same as that of Stöber method. But the whole progress was restricted into water droplets enclosed by surfactants which led to a well-controlled system and monodispersed silica nanoparticles. The size of silica was well controlled by selecting different surfactants, solvents, and changing the ratio of surfactant to water. When the fluorophores are hydrosoluble, it is easy to form a homogeneous silica layer on the surface within the molecules in the droplet. Nianfang Wang et al. [46] synthesized luminescent silica-coated CdS/CdSe/CdS nanoparticles via reverse microemulsion method. Figure 13 showed the TEM images of the synthetic QDs and QDs@SiO₂. The protected QDs showed excellent acid and thermal stability. It provided possibility for further modification to meet special requirements for applications.

Direct Micelles Assistant Method

Reverse microemulsion method require the water-soluble luminescence dyes. Inversely, liposoluble initial micelles are the major features of direct micelle method, and the hydrolysis progress takes place around of the micelles (Fig. 11c). A precursor is indispensable for the agglomeration of silica. As a common progress, the luminescent dye is modified with the silane coupling agent, such as APS, to form the assistant micelles. The initial modified micelles ensure that the TEOS condensation occurs around them. Using Rhodamine B conjugated to APTES as the original micelle, Kumar et al. [26] successfully synthesized Rhodamine-conjugated organically modified silica nanoparticles in oil in water system and modified them with different function groups (such as sulfhydryl, amino, and carbonyl) which can be used as cell fluorescence probe.

The role of the surfactant is not only reflected in the silica synthesis but also in the synthesis of mesoporous silica. A common method of synthesizing mesoporous silica is calcination. Large specific surface area and modifiable surfaces make the mesoporous silica nanoparticles perfect

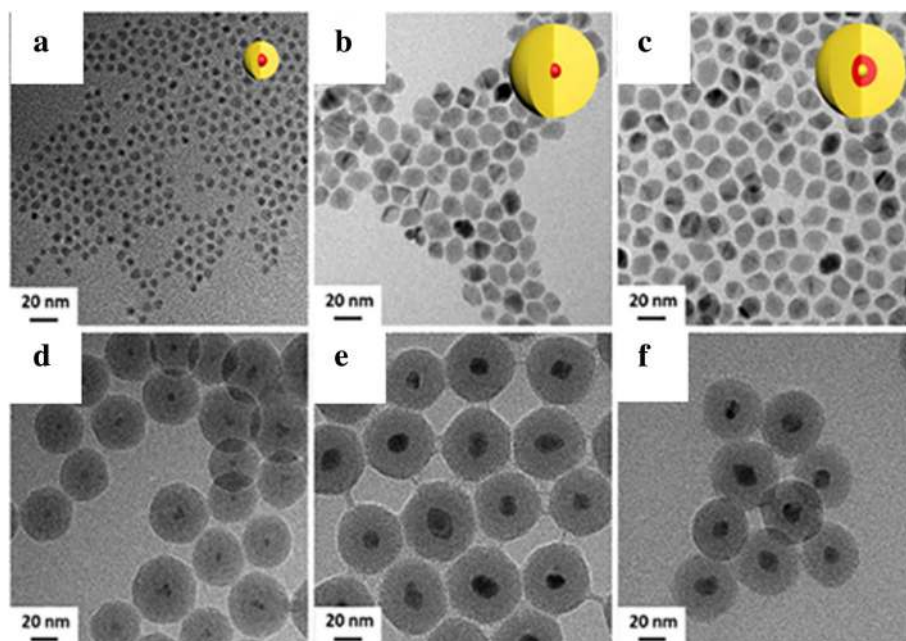


Fig. 13 TEM images of CdSe/CdS core/shell QDs with CdS thin shell (a) and after coating with silica CdSe/CdS@SiO₂ (d); CdSe/CdS core/shell QDs with CdS shell (b) and after coating with silica CdSe/CdS@SiO₂ (e); CdS/CdSe/CdS core/shell QDs (c) and after coating with silica CdS/CdSe/CdS@SiO₂ (f) [46]

carriers. In addition to the known application value in the field of medical drug loading, it also has important application prospects in the field of loading phosphors. Li Wang et al. [68] mixed up CDs with hollow mesoporous silica microspheres with good photochemical stability which can be used for oxygen detection in the whole range. Mesoporous structure makes them unique. Bin Xie et al. [69] incorporated the CdSe/ZnS core-shell QDs into mesoporous silica microspheres by a swelling and evaporation method. Coated with a mesoporous silica layer on the surface of Gd₂O₃:Eu phosphors via modified Stöber method is also feasible according to the Ali Aldalbahi et al. [70]. Because of the encapsulation of silica, the modified Gd₂O₃:Eu nanoparticles showed excellent solubility and biocompatibility.

Other Methods

There are also other methods to synthesize LSNs such as chemical vapor deposition (CVD) [71], hydrothermal method [51], and amino acid-catalyzed seed regrowth technique [72, 73].

Lianzhen Cao et al. [71] synthesized SiC/SiO₂ by CVD and thermal annealing processes. Si was used to coat on the SiC core by thermal CVD and then SiO₂ shell was obtained after oxidizing. The annealed SiC/SiO₂ nanoparticles showed narrow luminescence in the blue-green region. The synthetic method provided a new way to synthesize core-shell nanomaterials.

Chandra et al. [51] synthesized smaller fluorescent silica nanoparticles (1 to 2 nm) with silicon tetrabromide (SiBr₄) and APTS. Heating to 200 °C in an autoclave was the core step of the whole reaction. The final products were obtained after further purification including dialysis and centrifugation. The silica nanoparticles emitted bright blue luminescence with a photoluminescence quantum yield around 34%. It was non-photobleaching and biocompatible at the same time.

Surface modification makes the LSNs more tunable for complex application [74]. Silane coupling agents are the most common chemical methods as it mentions before. Abundant hydroxyl groups provide reaction sites for further modifications. Junqiang Wang et al. synthesized silica modified CeO₂ ammonia sensor with high gas response due to hydroxyl groups [75]. After hydrolysis and condensation, silane coupling agents with different function groups bond on the surface of silica. Superhydrophobic silica was synthesized with the condensation of VTES (-CH=CH₂) [76]. Ming Ma et al. grafted PEGMA and DMEAA on the surface by RAFT polymerization based on the -NH₂ of APTS [77]. Surface modification can enhance their adaptability in complex environments and get improved luminescence properties with appropriate materials.

Among these methods, there are two main ideas to fabricate LSNs, namely the luminescent dyes are added directly into the reaction system when the silica resources start hydrolyzing, and that the luminescent dyes

are established chemical bond with silica by other reagents such as silane coupling agents, either before or after silica network set up. It is necessary to select and design an appropriate synthetic route for LSNs with specific structures.

Applications of Luminescent Silica Nanoparticles

Light is the most intuitive tool for people to recognize the world. Luminescent materials with special emission can be directly used in many ways such as lighting, display, and so on. At the same time, changes in fluorescence intensity can reflect some important information. Compared with separate luminescent dyes, LSNs have improved performances in applications, since silica provides a stable matrix for the luminescent dye. It provides an effective way for multifunction at the same time [6]. LSNs with multifunction and tunable surface have great application prospects and development potential in biology, lighting, and sensors.

Biolabeling and Medicine

LSNs have great application value in biology. Non-toxicity is a fundamental requirement for medical field, especially in vivo [78]. The fact that the common luminescent dyes are often toxic limits their clinical application [79]. Silica, a favorite non-toxic modified material, is a good solution to elimination of toxicity. Toxicity of silica nanoparticles (20–200 nm) were also carefully studied by In-Yong Kim et al. [80]. Size, dose, and cell type-dependent cytotoxicity were the issues in their research. Although high dose can cause a disproportionate decrease in cell viability, the silica nanospheres with 60 nm showed their good biocompatibility up to 10 $\mu\text{g}/\text{ml}$. Different cells had different tolerance to silica nanoparticles which indicated that it was necessary to have substantial tests before clinical tests. Although inhalation of silica particles can cause acute and chronic diseases including silicosis [81], silica still has

potential in biological application at the nanoscale. The toxicity of luminescent silica nanoparticles to living cells was studied in detail by Yuhui Jin et al. [38]. From the DNA level to the cell level, the toxicity of RuBpy-doped LSNs were carefully tested. At a certain concentration, the results showed that the dye-doped luminescent silica nanoparticles were non-toxic to the targeted DNA and cells, which indicate that LSNs are a good solution to the non-toxic modification. Xiqi Zhang et al. [27] encapsulated AIE dye (An18, derivatized from 9, 10-distyrylanthracene with an alkoxy endgroup) into the silica nanoparticles via a one-pot modified Stöber method. Coated with silica lead to an enhanced fluorescence intensity, good water solubility, and non-toxicity to living cells which made the An18-SiO₂ NPs had a potential for biomedical application.

LSNs have great application value in diagnosis and biolabeling. For hybrid imaging contrast agents, Dong Kee Yi et al. [48] combined magnetic particles (MPs) Fe₂O₃ with QDs (CdSe) and encapsulated them in silica shell by reverse microemulsion method. The nanostructures of MPs with QDs are clearly showed in Fig. 14. Magnetic resonance imaging (MRI) is an effective method for disease detection, especially for cancer. The advantages of feasible usage, low cost, and accurate diagnosis make it more popular as a diagnostic tool [7]. The nanocomposites can be used as both optical and MRI contrast agents. It is worth mentioning that the presence of CdSe increased the effective magnetic anisotropy of the γ -Fe₂O₃-containing particles. This is a good attempt, but the low quantum yield (SiO₂/MP-QD 1.1% to CdSe 11.4%) limits the actual effect. Willam J. Rieter et al. [39] also synthesized the same multifunctional nanocomposites. What is different is that [Ru(bpy)₃] Cl₂ was chosen as the luminescent core and the paramagnetic Gd complex was coated on the luminescent core by water-in-oil reverse microemulsion method. The nanocomposites were finally embedded in silica in the

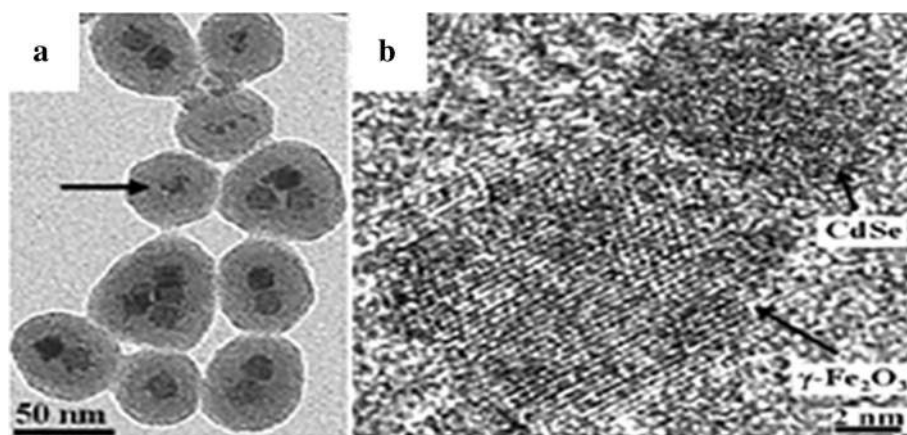


Fig. 14 **a** TEM image and **b** HRTEM image of SiO₂/MP-QD nanoparticles [48]

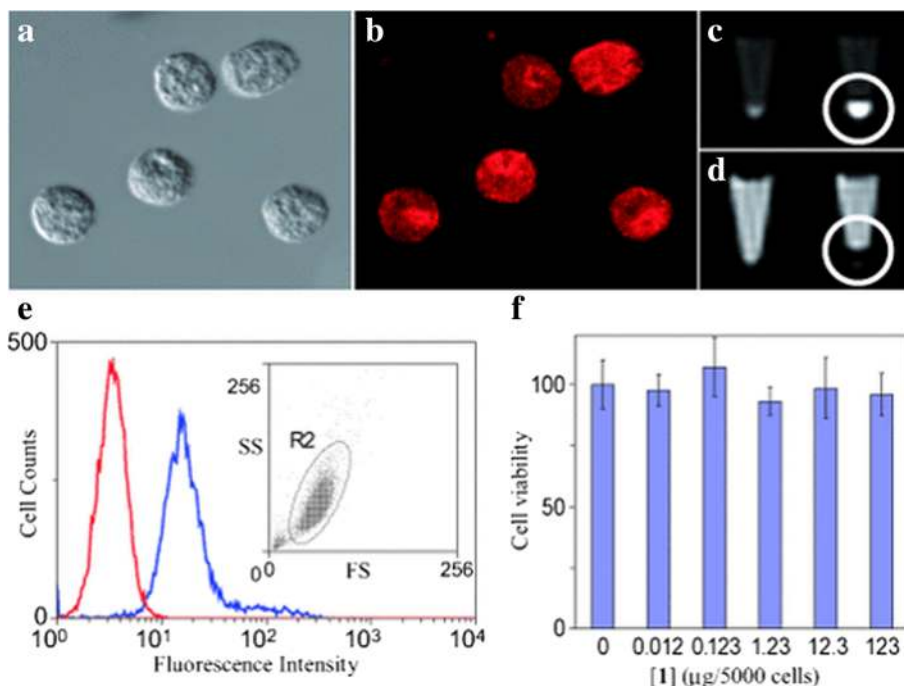


Fig. 15 The imaging results of monocyte cells with **a** optical microscopic, **b** laser scanning confocal fluorescence, **c, d** the images of monocyte cells with MR: left for unlabeled monocyte cells and right for hybrid silica nanoparticles labeled monocyte cells, **e** flow cytometric results of blank and hybrid silica nanoparticles-labeled monocyte cells, and **f** the cell viability with different amount of hybrid silica nanoparticles [39]

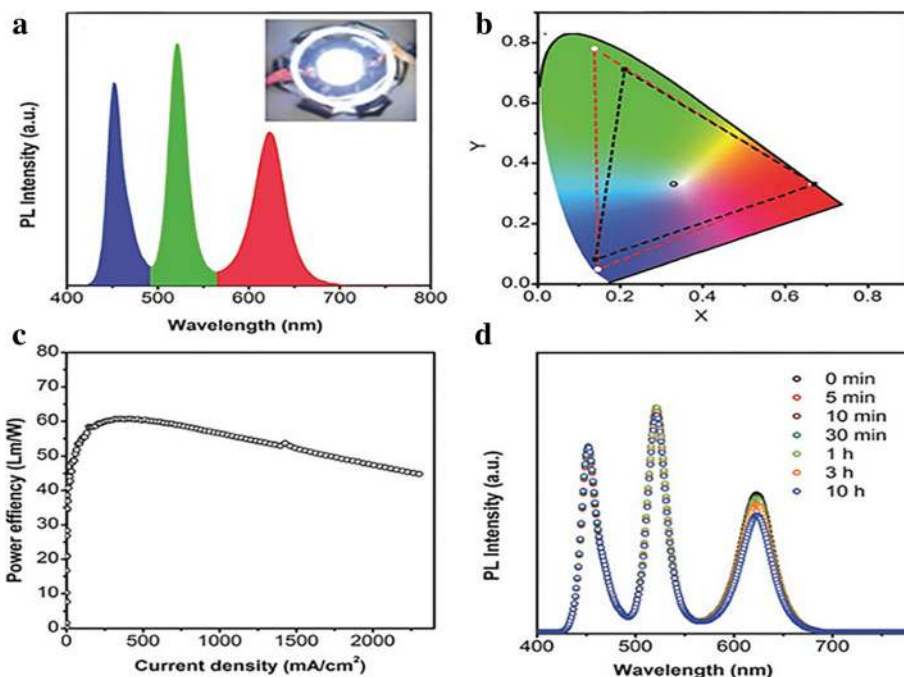
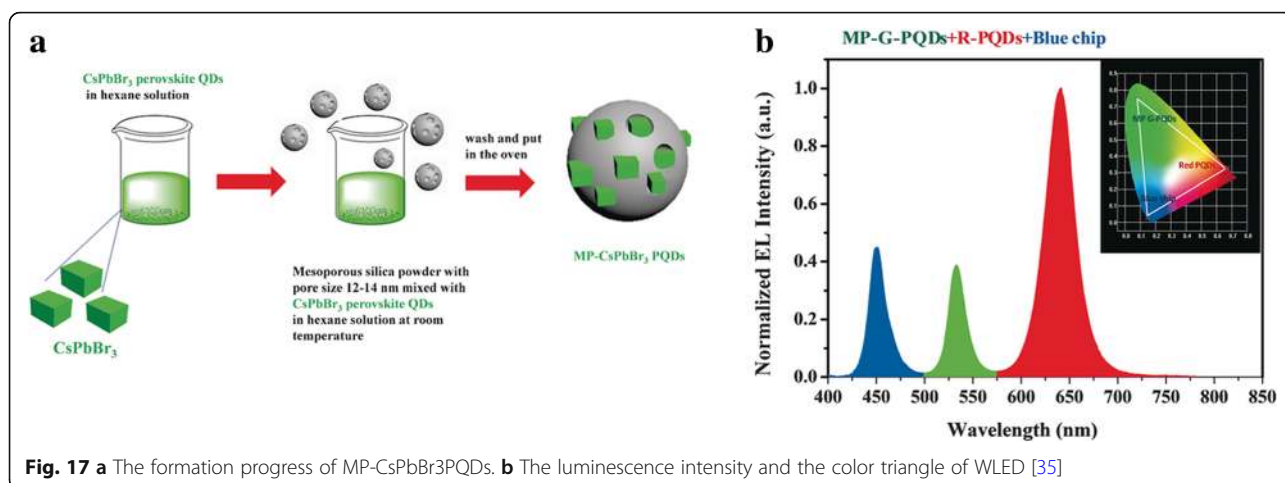


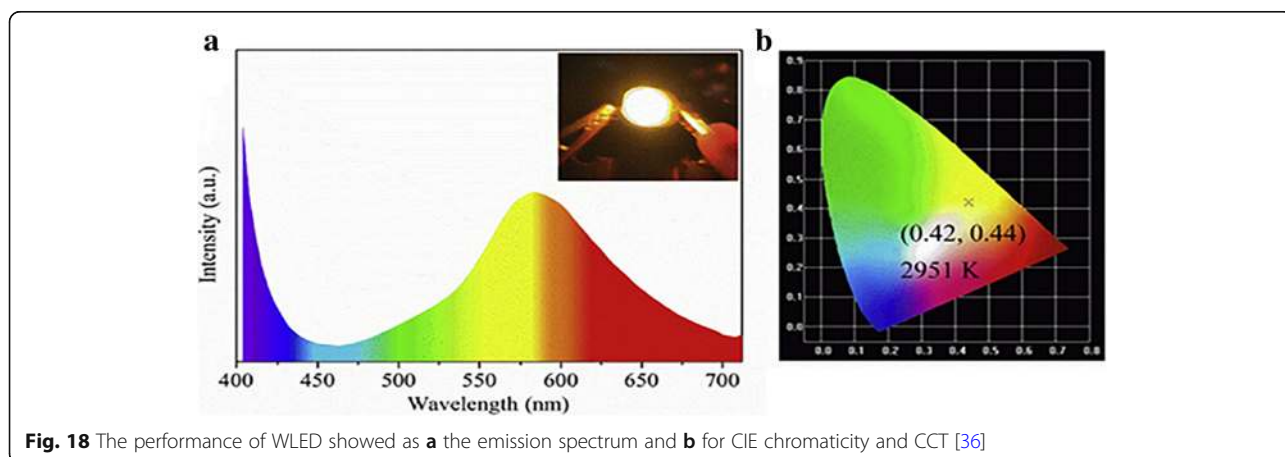
Fig. 16 The optical performances of the WLED: **a** the emission spectra, **b** the CIE color coordinates and the color triangle of WLED (red dashed line) with the NTSC TV standard (black dashed line), **c** the power efficiency, and **d** emission spectra after working for a while [34]



same way. The results of Fig. 15 proved that hybrid silica nanoparticles had good optical and MRI performances in biological imaging. Mesoporous silica nanospheres doped with europium (Eu-MSN) were obtained by Mengchao Shi et al. [32]. Nanoscale size (280–300 nm) and fluorescent property were the basic for an ideal biolabeling material. They found that Eu-MSNs had a positive influence on osteogenesis and angiogenesis-induction. By promoting proper response of macrophages and the expression of relevant genes, the defect of bone replaced by new bone and the healing process of skin wound can accelerate with Eu-MSNs. Besides the function of biolabeling, the LSNs showed the potential in tissue repair. LSNs can achieve the target binding effect by modifying the special group. In Duarte's work [33], organosilane Bpy-Si was chosen as a ligand of Eu complex for the further reaction with silica. SiO₂-[Eu (TTA)₃(Bpy-Si)] nanoparticles were obtained with a uniform size (28 ± 2 nm). With a further modification of an amino acid spacer and an anchor group (anti-*Escherichia coli*, IgG1), the functionalized silica had the specific bonding with *E. coli* bacteria. It was easy to get the distribution of *E. coli* bacteria with luminescence. The

bio-multifunction of LSNs was also carefully studied by Laranjeira et al. [82]. Gadolinium (Gd) composites with unique magnetic properties have potential in MRI contrast agents but Gd³⁺ ions are toxic in humans especially in kidneys and pancreas. GdOHCO₃ nanoparticles were chosen as the MRI contrast core and coated with silica layer via Stöber method. With the silica coating, the Gd composite (SiGdOHCO₃) had the same brightness of MRI contrast images but no degradation at designed pH values (5.5, 6.0, and 7.4). And SiGdOHCO₃ had little effect on human fibroblasts according to the cell proliferation assay which indicated an excellent biocompatibility. Silica provides a more stable environment and further possible modification for GdOHCO₃ without affecting MRI performance. By diverse micelles method, Atabaev et al. [83] synthesized Gd₂O₃:Tb³⁺,Eu³⁺@SiO₂ nanoparticles which can be used as both MRI contrast and fluorescence agents in vivo. The above two examples perfectly reflected the role of LSNs in multifunction with the silica platform.

LSNs have great application value in drug delivery. Hongmin Chen synthesized luminescent mesoporous silica nanoparticles biofunctionalized by targeting motifs,



which makes them applicable in drug delivery [47]. They first prepared APS-containing mesoporous silica particles, and subjected the products to calcination at 400 for 2 h. They synthesized mesoporous silica by the help of cetyltrimethyl ammonium bromide (CTAB). There were luminescent carbon dots in the silica matrix after calcination. The fluorescence intensity was at the maximum when the particles were excited at 380 nm. The target selectivity of FL-SiO₂ was achieved by surface modification of RGD peptide with the help of APS. They also studied the RGD-FL-SiO₂ loading and release of doxorubicin (Dox). After calcination, fluorescent mesoporous silica (FL-SiO₂) can still load Dox effectively. The porous structure was not affected by calcination. They found that RGD-FL-SiO₂ had good luminescent effect especially around the blood vessels of tumor in vivo imaging studies. Integrin $\alpha_v\beta_3$ of the tumor was the key of the interactions. Although there are many excellent attempts to apply LSNs to medicine but less successful clinical tests in human beings means that there is still a long way to go for the real medicine applications.

Light-Emitting Devices

Due to their special emitting features, LSNs also play a vital role in light emission fields including the field emission- and liquid crystal-based display technologies [84]. WLEDs have received recent attention for their broad applications including general illumination and displays. Tunable color, high color purity, and luminescence

efficiency are in line with the requirements of light-emitting diodes (LEDs) [85]. Quantum dot-based light-emitting diodes (QD-LEDs) have demonstrated recently, and may offer many advantages over conventional LED and organic light-emitting diodes (OLEDs) technologies in terms of color purity, stability, and production cost, while still achieving similar levels of efficiency. In order to improve the performances of polymer dots (Pdots) as WLED phosphors, Kaiwen Chang et al. [49] introduced some Pdots with different emission wavelength into the Stöber system to get encapsulated. The silica-encapsulated Pdots showed the same luminescence properties but markedly enhanced photostability.

To reduce the manufacturing complexity required for achieving full-color displays, it is more desirable to use a common device structure to achieve high efficiency for three primary colors (blue, green, and red). QDs have been widely used in display field because of its unique luminescent properties, such as high luminescent intensity, narrow emission spectra, and tunable emission. Chun Sun et al. [34] synthesized the perovskite QDs, CsPbBr₃, as the light-emitting core of WLEDs. Only the perovskite QDs are not enough for a LED device since photostability and stability are necessary for an optical device under long-time work and elevated temperature. There are anion-exchange reactions between different halide QD nanoparticles which would widen the narrow emission spectrum. QD/silica composite were fabricated in APS to avoid oxidation and decomposition. So they used APTES as the QDs' capping

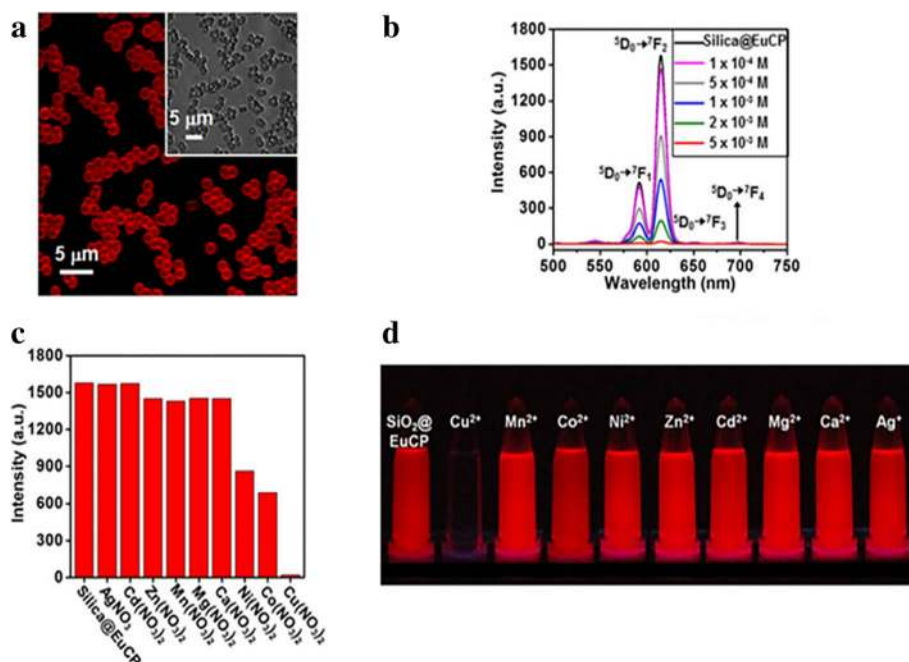
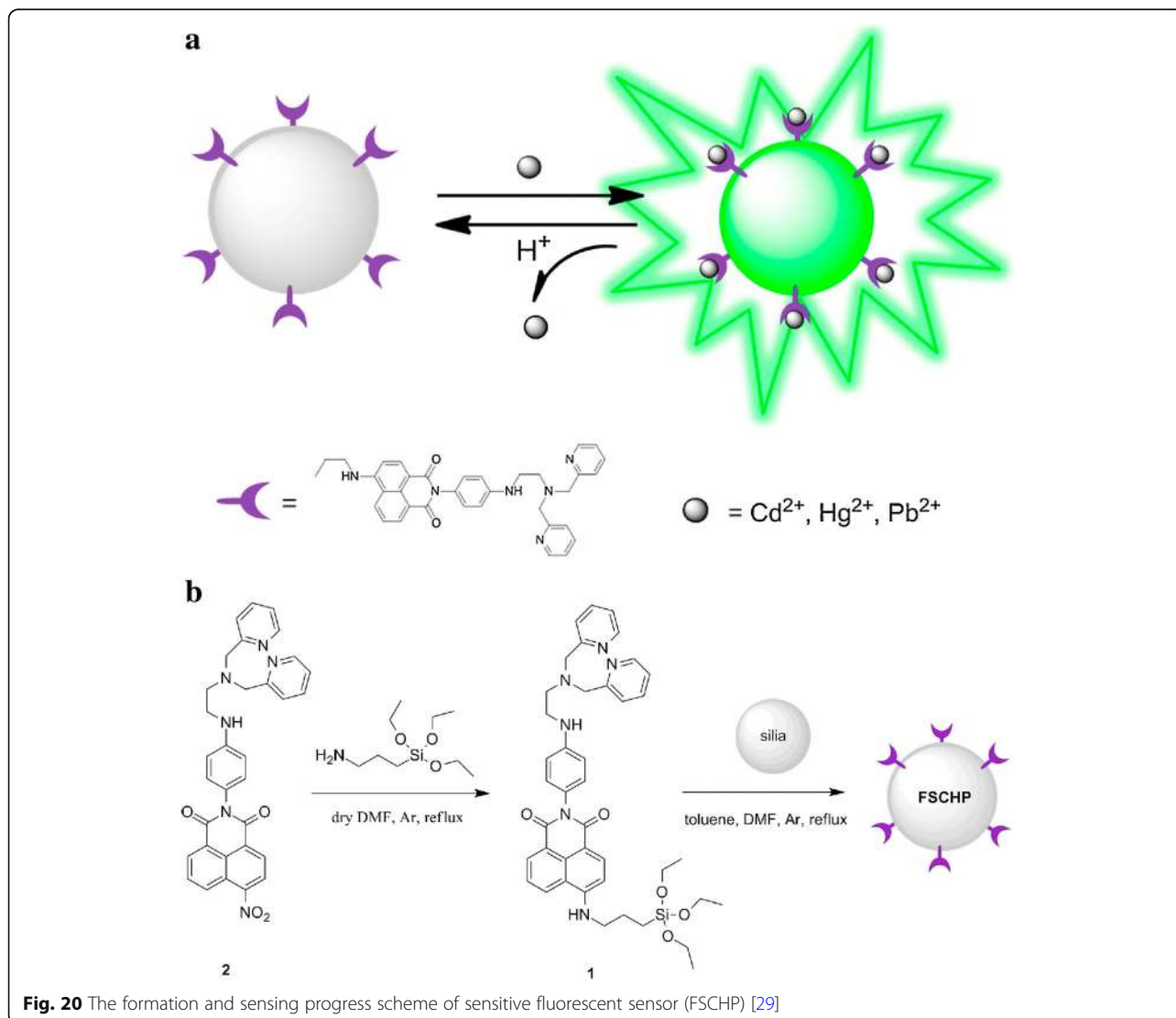


Fig. 19 **a** Confocal microscopy and OM (inset) images of silica@EuCP microspheres. **b** Luminescence spectra with different Cu (NO₃)₂ in MeCN; luminescence intensity changes **(c)** and photograph **(d)** with different metal ion solutions (5 mM) [37]

agent and improved the silica coating process to avoid the decomposition of the QDs. Green and red QD/silica composites were synthesized and a WLED was obtained by the combination of the composites with a blue LED chip. The WLED had good performances with great air stability as depicted in Fig. 16.

LSNs can keep good dispersion, brightness, and photostability of QDs. Hung-Chia Wang et al. [35] provided a new composite method for QDs and silica (Fig. 17). By mixing the QDs with mesoporous silica powder of which pore size was bigger than that of QDs in non-polar solution, mesoporous silica green PQD nanocomposite was obtained after washing and drying. The quantum dot showed better thermal stability and photostability after composited with silica. On the other hand, QDs are a typical kind of aggregation-caused quenching (ACQ) nanoparticles, which means that it is necessary to keep a good dispersion to get a good brightness and photostability. Kai

Jiang et al. [86] synthesized carbon dots with red, green, and blue luminescence with phenylenediamines as precursors to enhance luminescence properties as solution and poly (vinylalcohol) (PVA) film. But it would exist quenching effect as solid-state CDs which was fatal for LED devices owing to aggregation and the result Förster resonance energy transfer (FRET). To avoid the dispersion and the resulting FRET phenomenon, Junli Wang et al. [36] embedded carbon dots into silica matrix (Fig. 18) by dispersing carbon dots into the *N*-(3-(trimethoxysilyl)propyl) ethylenediamine (KH-792) and heating to form a homogenous CD/silica film. A white LED was fabricated by drying the CD/silica solution on the inner wall. By the assistant of silica, CDs were well dispersed with an appropriate distance without quenching which improve the performance as powders. Figure 18 showed the emission spectra and performance in WLED. And the CIE coordinates (0.44, 0.42) and correlated color temperature



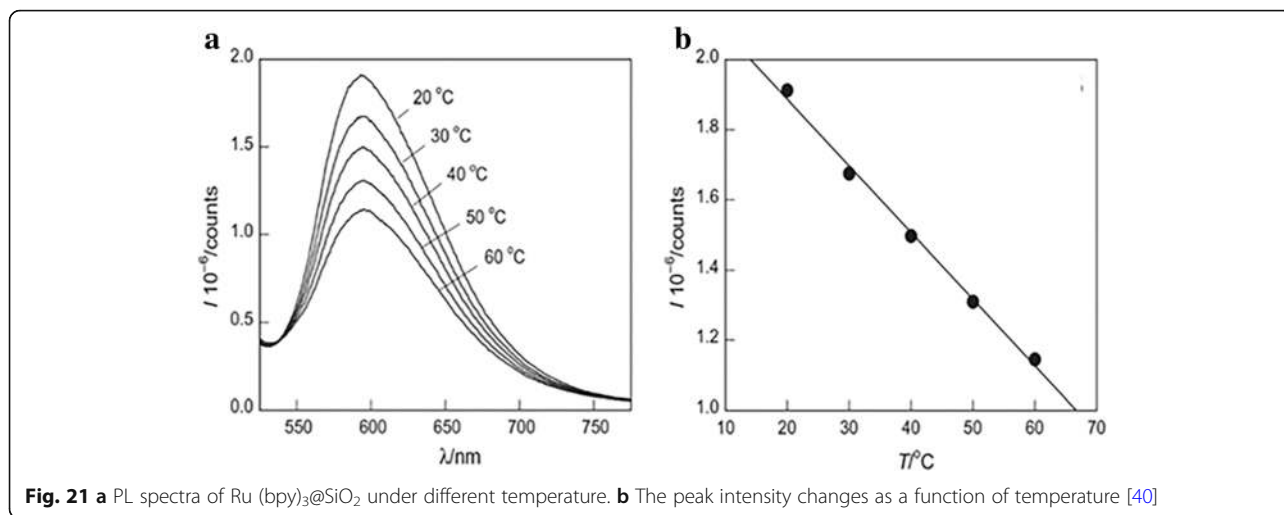


Fig. 21 a PL spectra of Ru (bpy)₃@SiO₂ under different temperature. b The peak intensity changes as a function of temperature [40]

(CCT) (2951 K) suggested that it was suitable for indoor illumination.

Sensors

Luminescent silica showed the excellent performances on static luminescent materials, such as biolabeling and WLED phosphors. All these were based on their unique and stable optical properties. When it came to dynamic luminescent materials, LSNs also display the same wonder [9]. The luminescent sensors of pH [28], ions [87], and temperature [40] are following as representatives.

pH value have great influence on the luminescence intensity which inspires luminescent pH sensor. In the same principle as ref. [22], Atabaev et al. synthesized the same ratiometric pH sensor [28]. FITC was chosen as the pH-dependent luminescence dye and Y₂O₃:Eu³⁺ as pH stable dye. With the Stöber coating of silica, Y₂O₃:Eu³⁺@-SiO₂ with FITC composite NPs were successfully synthesized. The change of pH was reflected by the ratio of fluorescence intensity ($I_{FITC}/I_{Y_2O_3:Eu^{3+}}$). The standard dye

led to a less influence of concentration and a more accurate result.

LSNs can also be used as ions sensors. Based on the changes of luminescence intensity with the measured physical quantity, LSNs have been applied to many sensor fields by the environment-dependent effect of the luminescence. Quenching effect is an effective detective tool to detect the changes of quenching factors such as ions and pH value with external quenching mechanisms such as FRET and photoinduced electron-transfer (PET) [9]. Sensors for metal ions are important fields whether in cells or open system. Won Cho et al. [37] synthesized europium (III) coordination polymer (EuCP) and found the specific quenching effect of Cu²⁺ (Fig. 19). In view of this fact, they synthesized silica@EuCP microsphere which have the same sensitivity on Cu²⁺ with less mass of europium. As an auxiliary material, silica can effectively reduce the amount of sensor materials. Both of them have their unique situations. Besides quenching effect, there are some different effects which can be used in the fields of sensors. 2,2-Dipicolylamine (DPA) and its derivatives have good affinity to heavy ions. And enhanced luminescence

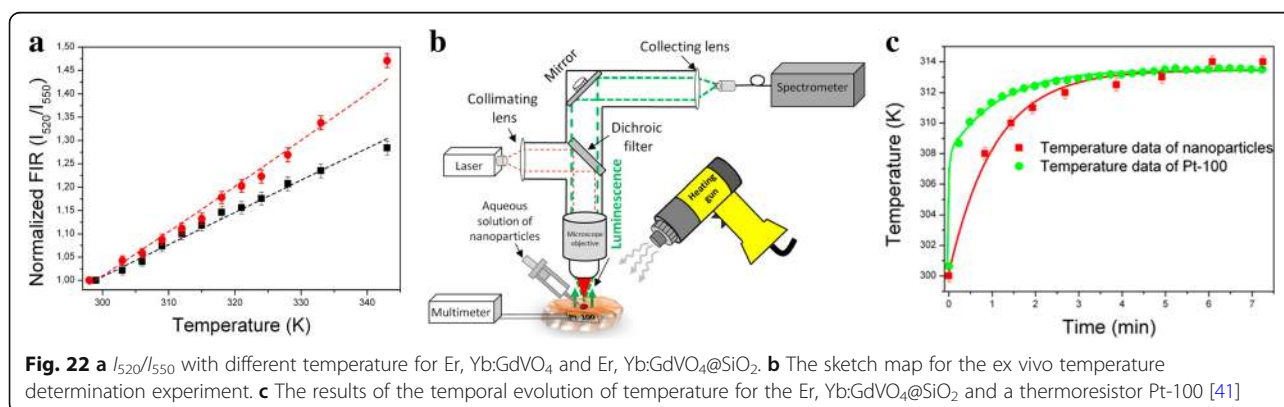


Fig. 22 a I_{520}/I_{550} with different temperature for Er, Yb:GdVO₄ and Er, Yb:GdVO₄@SiO₂. b The sketch map for the ex vivo temperature determination experiment. c The results of the temporal evolution of temperature for the Er, Yb:GdVO₄@SiO₂ and a thermoresistor Pt-100 [41]

effect would happen after chelated with heavy ions. Yu Ding et al. [29] modified silica spheres with N,N' -bis (pyridine-2-ylmethyl)ethane-1,2-diamine (Fig. 20). The concentration of heavy ions (Cd^{2+} , Hg^{2+} and Pb^{2+}) in samples can be determined by the change of fluorescence intensity. The test in real water samples and simulated biological samples confirmed the heavy metal ions-binding ability and the detection which has application prospects in the water monitoring and so on.

Temperature sensors are also important applications of LSNs. Temperature is a basic variable in most science fields. The temperature dependence of radiative and non-radiative transition rates is the core content of temperature sensing which makes it possible for luminescence temperature sensing, with the contactless and large-scale advantages [9]. However, in order to be applied in practice, their stability is crucial as the environment of application is more complex than of that of experiment condition. Silica is an ideal matrix to improve their performance for application. Miranda et al. [40] synthesized silica as the core and then TEOS was hydrolyzed with Ru (bpy)₃Cl₂ to form the Ru (bpy)₃@SiO₂ NPs. The emission spectra of Ru (bpy)₃@SiO₂ NPs (Fig. 21) showed that the intensity of Ru (bpy)₃@SiO₂ NPs decreased linearly as the temperature rising as the result of the activated non-radiative ³d-d state (20–60 °C, $\lambda_{exc} = 463$ nm). The polyethyleneimine (PEI)-modified glass with Ru (bpy)₃@SiO₂ NPs showed the same trend as the NPs which proved that the potential as the temperature sensing. With cycling the temperature between 20 and 60 °C, the relative slope decreased until the seventh cycle which meant that it is necessary to condition to obtain the stable sensing materials. The influence of temperature on probes is complicated. So it is necessary to research the temperature-dependent luminescence of the probes to know how to apply it into temperature sensors. Temperature is a fundamental variable that governs diverse intracellular chemical and physical interactions in the life cycle of biological cells. The change of temperature reflects the level of cell metabolism. GdVO₄ co-doped with Er³⁺ (1 mol%) and Yb³⁺ (1 mol%) has the potential to apply as the temperature sensor. To improve their performance as temperature sensor, Savchuk et al. [41] coated silica shell on the nanoparticles surface by Stöber method. The fluorescence intensity ratio (FIR) of Er, Yb:GdVO₄, I_{520}/I_{550} , had a certain linear relationship with temperature in the range from 297 to 343 K after excitation at 980 nm. And the probes got enhanced thermal sensitivity, high thermal resolution and good stability in different solvents. And the result of the ex vivo experiment to monitor temperature evolution with the special sensor showed in Fig. 22 proved that Er, Yb:GdVO₄@SiO₂

core-shell nanoparticles had a good thermal resolution as the temperature sensor in biomedical applications.

Conclusion

In this article, LSNs with various functions demonstrate that silica is an ideal host material for luminescent dyes. The visualization of related parameters is the most special feature of luminescent dyes. Various luminescent materials have their own advantages but there are still some defects which limit their applications. Improved brightness, photostability, and thermal stability are the advantages of LSNs with the protection of silica. At the same time, it provides phosphors with a versatile platform which makes it possible to become multifunctional and specially modified. Excellent performance, adjustable adaptability, and potential versatility broaden the applications of fluorescent materials. LSNs have great potential in many unmentioned fields such as solar cells and photocatalysts. However, there is still a long way to apply LSNs to the actual species. Poor selectivity and low signal-to-noise ratio in complex conditions are factors that constrain LSNs for the practical applications which need to be further studied. Defined distances between phosphors and LSPR metal deserve more investigations to get the positive effect. Many new luminescent materials with excellent luminescence properties have been developed which means that it is necessary to improve the traditional synthetic methods to obtain LSNs. Silica is a traditional modified material but LSNs still have great potential for development.

Abbreviations

ACQ: Aggregation-caused quenching; AIEgen: Aggregation-induced emission luminogens; AMP: Adenosine 5'-monophosphate; An18: An aggregation-induced emission-based organic fluorogen derivatized from 9,10-distyrylanthracene with alkoxyl endgroup; APS: (3-Aminopropyl)triethoxysilane; APTES: 3-Aminopropyltriethoxysilane; APTS: (3-Aminopropyl)trimethoxysilane; B: Blue; BAM: Bio-anchored membrane; CCT: Corresponding correlated color temperature; CDs: Carbon dots; CDSP: Carbon dot-silica-phosphor composite; CIE: Commission Internationale de l'Éclairage; CLSM: Confocal laser scanning microscope; CRI: Color rendering index; CTAB: Cetyltrimethyl ammonium bromide; CVD: Chemical vapor deposition; DDT: 1-Dodecanethiol; Dox: Doxorubicin; DPA: 2,2-Dipicolylamine; F127: Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol); FIR: Fluorescence intensity ratio; FITC: Fluorescein isothiocyanate; FL-SiO₂: Fluorescent mesoporous silica; FRET: Förster resonance energy transfer; FSCHP: Sensitive fluorescent sensor; FSNP: Fluorescent silica nanoparticle; G: Green; H: The ratio of water/TEOS; HPTS: 8-Hydroxypyrene-1,3,6-trisulfonic acid; HRTEM: High resolution transmission electron microscopy; IgG1: Anti-Escherichia coli; KH-792: N-(3-(trimethoxysilyl)propyl)ethylenediamine; LEDs: Light-emitting diodes; LSN: Luminescent silica nanoparticle; LSPR: Local surface plasmon resonance; MPS: 3-Mercaptopropyltrimethoxysilane; MPs: Magnetic particles; MQDs: Magnetic quantum dots; MRI: Magnetic resonance imaging; MTT: Methyl tetrazolium; NIR: Near-infrared; NTSC: National Television System Committee; OLEDs: Organic light-emitting diodes; OSNC: Organosilica nanocrystal; OTEs: n-Octyltriethoxysilane; PBS: Phosphate-buffered saline; Pdots: Polymer dots; PEI: Polyethyleneimine; PET: Photoinduced electron transfer; PVA: Poly (vinylalcohol); PVIS: Poly (1-vinylimidazole-co-vinyltrimethoxysilane); QD655: A kind of commercial quantum dots; QD-LEDs: Quantum dot-based light-emitting diodes; QDs: Quantum dots; R: Red; R: The ratio of water/surfactant; RBL-2H3: Rat basophilic leukemia mast cells; SEM: Scanning electron microscope;

TEM: Transmission electron microscope; TEOS: Tetraethoxysilane; TPETPAFN: A typical fluorogen consisting of two tetraphenylethylene pendants and an intramolecular charge transfer core; TRITC: Tetramethylrhodamine isothiocyanate; UC: Upconversion; ZRNP: Upconversion nanoparticles; UCNPs@SiO₂@EuTP: NaGdF₄:Yb,Er@SiO₂@Eu (TTA)3Phen; UV: Ultraviolet; VTES: Vinyltriethoxysilane; WLED: White light-emitting diode

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Availability of Data and Materials

Not applicable.

Authors' Contributions

LL read the relevant literature and wrote the manuscript. WW conceived the study and supervised the whole study. All the authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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