Water-Soluble and Lowly Toxic Sulphur Quantum Dots

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Here, a new class of quantum dots, that is, sulphur quantum dots (SQDs), which are synthesized by the phase interfacial reaction, is reported. The prepared SQDs are monodisperse with a narrow size distribution (average 1.6 nm in size), excellent aqueous dispersibility, ultrahigh photostability, and lowly toxicity. Because of abundant oxidized sulphur species on the surface of SQDs, the incorporation of TiO_2 with SQDs results in a synergistic effect for the TiO_2-based photocatalysts offering more effective environmental applications. It is demonstrated that SQDs-TiO_2 nanocomposite can enhance the photocatalytic activity of producing hydrogen (enhancement factor for 191) in methanol-water system. The SQDs also can used as fluorescent probe for highly selective quantitative detection Fe^{3+} in an aqueous solution contained various metal ions.

1. Introduction

Quantum dots have attracted much excitement for a variety of promising applications in catalysis, analysis, biology, and medicine.[1–7] Metal-free elemental quantum dots with their low toxicity, excellent solubility, and stable photoluminescence are considered to be next generation green nanomaterials. In contrast to the overwhelming attention given to toxic heavy-metal-based quantum dots, recent efforts in searching for new sensitizer have paid attention to elemental quantum dots, such as carbon quantum dots (CQDs) and silicon quantum dots (SiQDs). However, the preparation of sulphur quantum dots (SQDs) has never been explored, to the best of our knowledge.

Sulphur nanoparticles (SNPs) are widely used as antimicrobial agents,[8–11] lithium sulphur batteries,[12–15] and sulphur-based photocatalyst.[16–18] However, the application of sulphur nanoparticles is limited by their large particle size, poor hydrophilicity, low reactive activity, and toxicity. In order to reduce their toxicity, SNPs should be surface modified.[8]

Herein, we report a facile phase interfacial reaction method to prepare of SQDs with an average size of 1.6 nm, blue photoluminescence, abundant surface functional groups, and excellent water soluble. Significantly, SQDs are used by us as a surface modifier of TiO_2 for hydrogen production in methanol-water system and a fluorescent probe to selectively determine Fe^{3+}.

2. Results and Discussion

The schematic diagram of the synthesized procedure of SQDs is shown in **Scheme 1**. The process can be divided into three steps: physical contact, phase interfacial reaction, and in situ precipitation and dissolution. The metal sulfide quantum dots (MS_xQDs) were fabricated through facile and inexpensive synthetic process.[19] According to the transmission electron microscopy (TEM) image of CdSQDs (seen in **Figure 1**a), the as synthesized CdSQDs were monodisperse and uniform. The diameter of CdSQDs was 2.9 nm. The SQDs were prepared by oil-water phase interfacial reaction. The S^{2-} in the CdSQDs was slowly oxidized to element sulphur in the presence of HNO_3. Because of the dissolving of Cd^{2+}, the diameter of as synthesized SQDs was 1.6 nm (seen in Figure 1b), which was smaller than that of CdSQDs, revealing the forming of quantum dots. Figure 1c,d shows the corresponding size distribution of CdSQDs and SQDs.

To further understand this procedure, the optical properties of as synthesized CdSQDs and SQDs were performed. **Figure 2** a showed the PL spectra of CdSQDs and corresponding SQDs. The PL spectra of CdSQDs performed a excitation at 250 nm and emission at 660 nm, while the SQDs synthesized from CdSQDs displayed a 352 nm of excitation and 428 nm of emission. Moreover, using same exciton (352 nm), the luminescent properties of CdSQDs and SQDs originated from CdSQDs were also shown in Figure S1a. When CdSQDs were converted into SQDs, an obvious blue shift (232 nm) was observed, which indicated a new material (i.e., SQDs) was formed. Figure 2b showed the PL spectra of ZnSQDs and corresponding SQDs synthesized by the same reaction conditions. The optical properties were greatly different between ZnSQDs and SQDs with the excitation wavelength red-shifted and emission wavelength blue-shifted. This result also could be observed in CdSQDs system. A detailed PL study was carried out by using different excitation wavelength to further understand the optical properties of SQDs. The black, red, blue, cyan, pink, and yellow lines were the PL spectra of SQDs obtained from CdSQDs (seen in Figure 2c) for excitation at 300, 320, 340, 360, 380, and 400 nm,

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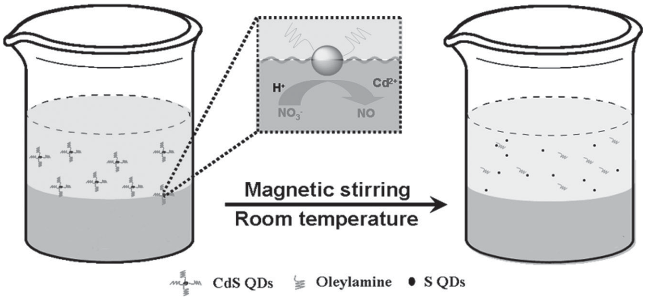
DOI: 10.1002/adfm.201402087



Scheme 1. Schematic diagram of the procedure used to synthesis of sulphur quantum dots.

respectively. Figure S1b (Supporting Information) displays the detailed PL spectra with different excitation wavelength of CdSQDs. CdSQDs and SQDs were excited independently and dependently, respectively. The detailed PL study showed that excitation-dependent PL behavior in SQDs, which was contributed to the complexity of the excited states of SQDs. The photoluminescence quantum yield of the SQDs in water was measured by using the comparative method reported by Chen et al.[20] PL quantum yield of up to 0.549% was obtained relative to the standard of quinine sulfate (QS) in 1 mM H_2SO_4 aqueous solution (Table S 1). The effect of pH for PL intensity was shown in Figure 2d. The PL intensity of the obtained SQDs displayed a pH independent properties at the pH below 7, but was decreased with the increasing of pH value from 7.0 to 9.4. Besides, the SQDs showed excellent stability in water under UV light. Figure 2d shows UV (365 nm) irradiated on the PL intensity of SQDs aqueous solution. Even after UV light irradiation for 180 min, the PL intensity of SQDs showed no obvious change. Fortunately, excellent stability and resistant photobleaching could be applied to analysis and imaging.

The UV/Vis absorption spectra of the SQDs in water displayed a feature at 335 nm which was contributed to the direct band gap transition, as shown in Figure 2a. It could be concluded that the shift direct band gap from the bulk value of 2.79 to 3.7 eV in SQDs was attributed to the strong effect of quantum confinement.[21]

The chemical compositions and structures of the SQDs were investigated. The XPS spectrum of SQDs, there is not signals at 405.4 or 412.3 eV which refers to Cd. **Figure 3**a shows the X-ray photoelectron spectroscopy of S 2p of SQDs. The high-resolution spectrum of S 2p was decomposed into eight different peaks. Three peaks appeared at 161.9 eV, 163.2 eV and 164.3 eV were assigned to the atomic sulphur, in comparison with the previous work.[22] The signals at 159.1 eV demonstrated the presence of unreacted S^{2-}. The oxidized sulphur species (Binding Energy > 166 eV) such as sulfonate were detected by XPS on this samples. The banding energy at 167.9 eV, 168.9 eV, and 170.0 eV which were respectively attributed to the sulphur of SO_2^- ($2p^{2/3}$), SO_2^- ($2p^{1/2}$) or SO_3^- ($2p^{2/3}$), and SO_3^- ($2p^{1/2}$), respectively.[23] Therefore,

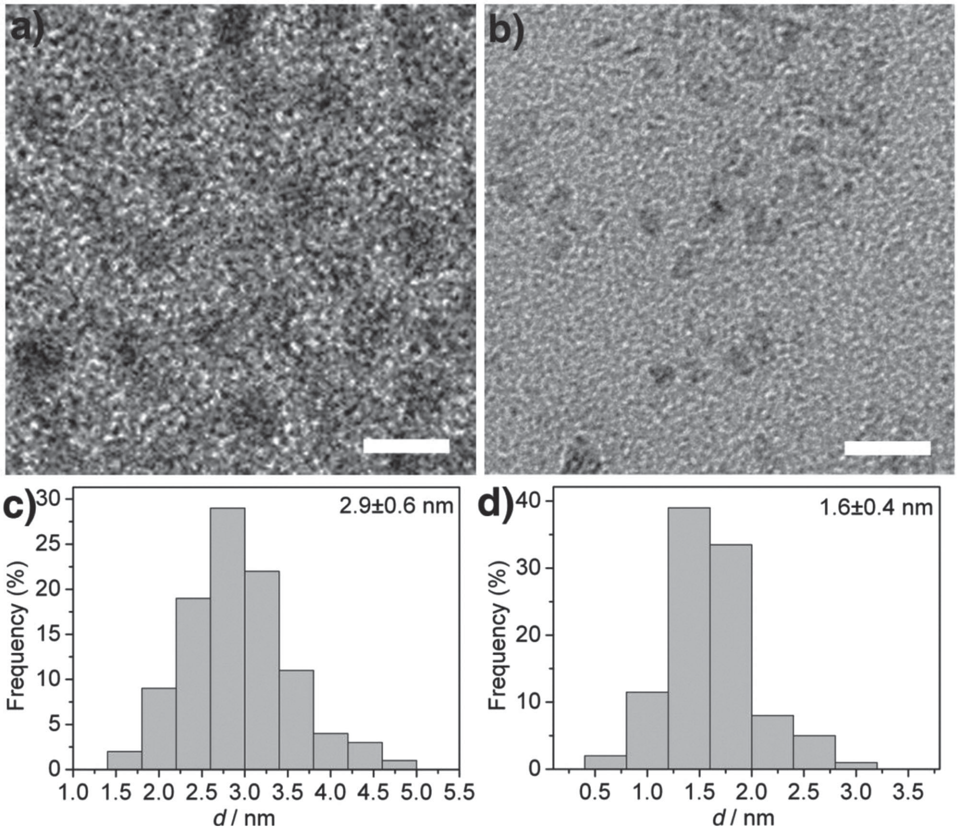


Figure 1. a) TEM image of a large number of CdSQDs. b) TEM image of SQDs obtained from CdSQDs. c) Size distribution of CdSQDs. d) Size distribution of SQDs obtained from CdSQDs. Scale bars in (a,b) are 5 nm.

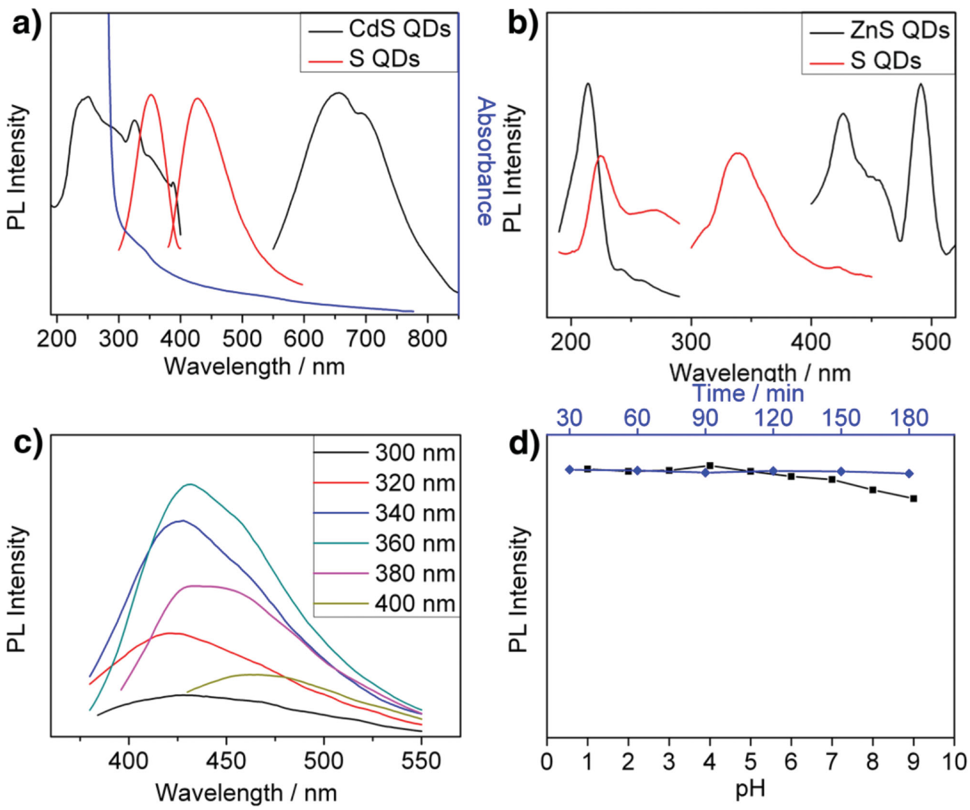


Figure 2. a) PL spectra of CdSQDs (black lines) and the corresponding SQDs (red lines); UV–Vis spectra of SQDs (blue lines). b) PL spectra of ZnSQDs (black lines) and the corresponding SQDs (red lines). c) Detailed PL spectra with different excitation wavelength of SQDs obtained from CdSQDs. d) Effect of pH and UV (365 nm) irradiated on the PL intensity of SQDs.

we concluded that the SQDs prepared by this method were mainly composed of atomic sulphur and abundant sulfite and sulfonyl/sulfonate groups on the surfaces. As we know, elemental sulphur could be oxidized to higher valence state by concentrated nitric acid. Significantly, the surface groups on as synthesized SQDs could improve the hydrophilicity, reactive activity as a surface modifier, and chemical stability as a surface passivating agent of SQDs. Similar to carbon and silicon quantum dots, the photoluminescence from SQDs might be attributed to the presence of surface energy traps and the surface passivation.[24]

Besides the high photostability and excellent water-soluable, low cytotoxicity was important for SQDs as safe nanomaterials. The cytotoxicity of as-prepared SQDs was evaluated using a standard cell viability assay (i.e., 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) assay). HeLa cells (human cervical carcinoma cell) and Chang Liver cells (normal human liver cells) were exposed to SQDs with different concentrations (0–100 μg mL^{-1}) for 24 h and the influence of SQDs on cell viability was tested. As shown in Figure 3b, 80.39% of HeLa cells and 82.04% of Chang Liver cells retained viability after being exposed to SQDs with a concentration of

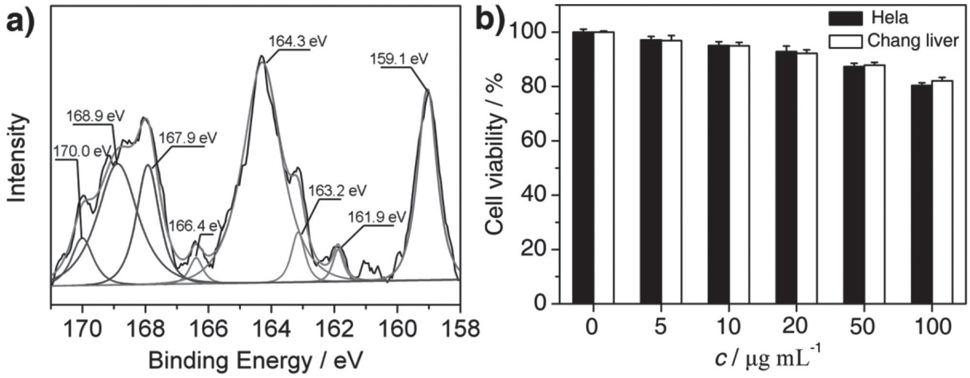


Figure 3. a) The X-ray photoelectron spectroscopy of SQDs; b) HeLa and Chang Liver cell viability after incubating with SQDs for 24 h and quantitative assays by standard MTT method.

100 µg mL^{-1}. The form change of HeLa and Chang Liver cells were no obvious (Figure S3, Supporting Information). The MTT assay revealed no significant cytotoxicity of SQDs even at the highest concentration tested (100 µg mL^{-1}). The results implied that the SQDs are lowly toxic and environmentally friendly nanomaterials.

Semiconductor metal oxides such as TiO_2, ZnO, CeO_2 etc. have widely been used for removing environment pollutions, photovoltaic cells, and spilling water because of their widespread resources and inexpensive.[25–27] However, a major problem to limit its extension lies in the inefficient conversion of light. Recently, researchers have noticed quantum dots sensitized semiconductor photocatalyst can reduce the band gap and greatly enhance the photocatalytic efficiency.[26,27] As the result of a excelled dispersibility, good photostability in water, and band gap, SQDs might be used as a new metal-free quantum dots sensitized photocatalyst for widely application in environment and energy fields. In the view of the optical properties of SQDs and surfaces groups, our previously study indicated that nanosize of TiO_2 could bond with sulfonyl. Therefore, we synthesized SQDs sensitized nanometer TiO_2 by direct mixing. The production of hydrogen in methanol-water system under UV light irradiation was used to evaluate the photocatalytic activity of SQDs sensitized TiO_2, nonsensitized TiO_2, respectively. **Figure 4**a shows the TEM image of as prepared SQDs sensitized TiO_2, the surface of nanoparticles (Figure 4b) decorated with small particles, while no observed in the pure TiO_2 (Figure 4c), The EDX of SQDs sensitized TiO_2 showed that their compositions contain Ti, O and S, indicating SQDs had attached to the surfaces of TiO_2 nanoparticles (Figure S2, Supporting Information). The time vs production of hydrogen for as prepared samples is shown in Figure 4d, from which we could observe that the process of photocatalytic production of hydrogen was efficient. Under above reaction conditions, the produce hydrogen rate of SQDs sensitized TiO_2 was 14.143 mmol h^{-1} g^{-1} at first hour, which was much higher than that of pure TiO_2 (0.074 mmol h^{-1} g^{-1}). The rate of hydrogen production was found to be fairly linear with light irradiation time from 1.0 to 5.0 h. We also tested the SQDs for photocatalytic production of hydrogen at the same conditions, not hydrogen could be determined. The improvement on the photocatalytic activity of SQDs sensitized TiO_2 might be related to the fast separation of the photo-induced electron/hole pairs on the photocatalyst, this results were similar as carbon quantum dots sensitized TiO_2.[28,29] At the light (λ = 365 nm) irradiation, the hydrogen evolution quantum efficiency of SQDs sensitized TiO_2 was 48%, which was higher than other works in similar conditions (Table S2, Supporting Information). So SQDs could be used as a sensitized agent for the design of photocatalysts.

The mechanism of photocatalytic reaction is discussed in **Scheme 2**. When the SQDs sensitized TiO_2 was irradiated under UV light, the electron/hole (e^-/h^+) pairs from TiO_2 were excited and formed. The recombination of electrons and holes in pure TiO_2 was rapid, which resulted in low photocatalytic activity. When SQDs were attached onto the surface of TiO_2, the electrons in conduction band of TiO_2 could transfer into LUMO of SQDs, the charge separation was promoted, and then the photocatalytic activity was enhanced.

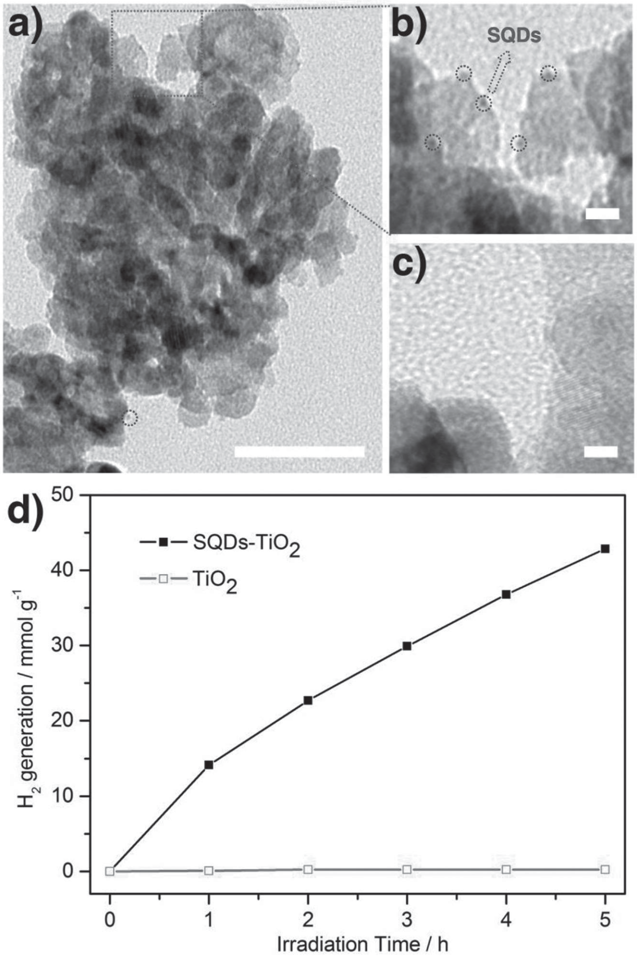
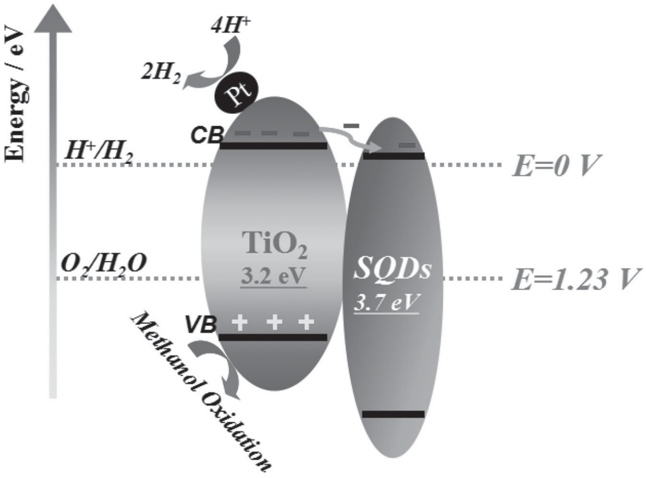


Figure 4. a,b) TEM image of photocatalysts for SQDs sensitized TiO_2; c) TEM image of pure TiO_2; d) UV light photocatalytic hydrogen generation by SQDs sensitized TiO_2 and pure TiO_2 in methanol-water system. Scale bars in (a) is 50 nm; (b,c) are 5 nm.

As mentioned above, the SQDs have fluorescence signal and display excellent stability. The fluorescence of SQDs could be selectively quenched by Fe^{3+} ions and it could be attributed to electron or energy transfer.[30,31] We evaluated the relationship between the concentration of Fe^{3+} and the quenched PL for quantitative and selective detection of Fe^{3+} ions. According to the relationship between the PL intensity and the concentration of SQDs (seen in Figure S4), when the concentration of SQDs was higher than 0.05 mg mL^{-1}, the SQDs PL intensity and peak were relatively sensitive to the change of the concentration of SQDs and the peak shift was happen after the addition of Fe^{3+} ions. Therefore, the concentration of SQDs should be chosen in range of 0–0.05 mg mL^{-1} to avoid the peak shift. Here, 0.01 mg mL^{-1} of SQDs was enough to evaluate this analytical system for quantitative detection Fe^{3+} ions. **Figure 5**a shows the PL intensity of SQDs with varying concentrations of Fe^{3+} ions. The fluorescence intensity ratio $(I_0 - I)/I_0$ against the Fe^{3+} concentration was shown in Figure 5b, the ratio $(I_0 - I)/I_0$ decreased gradually



Scheme 2. Possible catalytic mechanism for SQDs sensitized TiO_2 under UV light.

with the increasing of the concentrations of Fe^{3+} ions from 0 to 30 ppm, a good linearity was obtained with a correlation coefficient of 0.987 (Figure 5b, inset).

Furthermore, we investigated the selectivity of this system for Fe^{3+} analysis by testing the fluorescence quenching effect on other metal ions, including Na^+, K^+, Ni^{2+}, Ca^{2+}, Fe^{2+}, Ba^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Ce^{2+}, Co^{2+}, Pb^{2+}, Hg^{2+}, and Al^{3+}, each at a concentration of 0.01 M under the same conditions as those used with Fe^{3+} ions (Figure 5c). Remarkably, only Fe^{3+} ions could result in a significant fluorescence quenching and no apparent fluorescence signal changes of the solutions could be observed among the other metal ions tested. The selective quenching mechanism of PL by Fe^{3+} might be due to that Fe^{3+} ion has higher affinity with oxygen atoms on the surface of SQDs.[32–34] These results clearly indicated that the SQDs based sensor was highly selective toward Fe^{3+} over the other metal ions.

3. Conclusion

In summary, fluorescent SQDs with an ultrasmall size and narrow size distribution was first synthesized by phase interfacial reaction at room temperature and normal pressure. Because of excellent hydrophilicity free dispersion in water, abundant surface groups, emission dependent optical properties, stability in widely pH range, good photostability and lowly toxicity, SQDs sensitized TiO_2 nanoparticles showed an efficient photocatalytic production of hydrogen in methanol-water system, with a rate of 14.143 mmol h^{-1} g^{-1} and outstanding hydrogen evolution quantum efficiency up to 48% under 365 nm. What's more, the analytical system base on SQDs probe for quantitative detection Fe^{3+} ions showed good linearity ($R^2 = 0.987$) and highly selective. The synthesis of SQDs was easy. SQDs could be used as a new type of fluorescent probes and efficient surface modifier of catalyst for applications in analysis, pollution control, and energy technology.

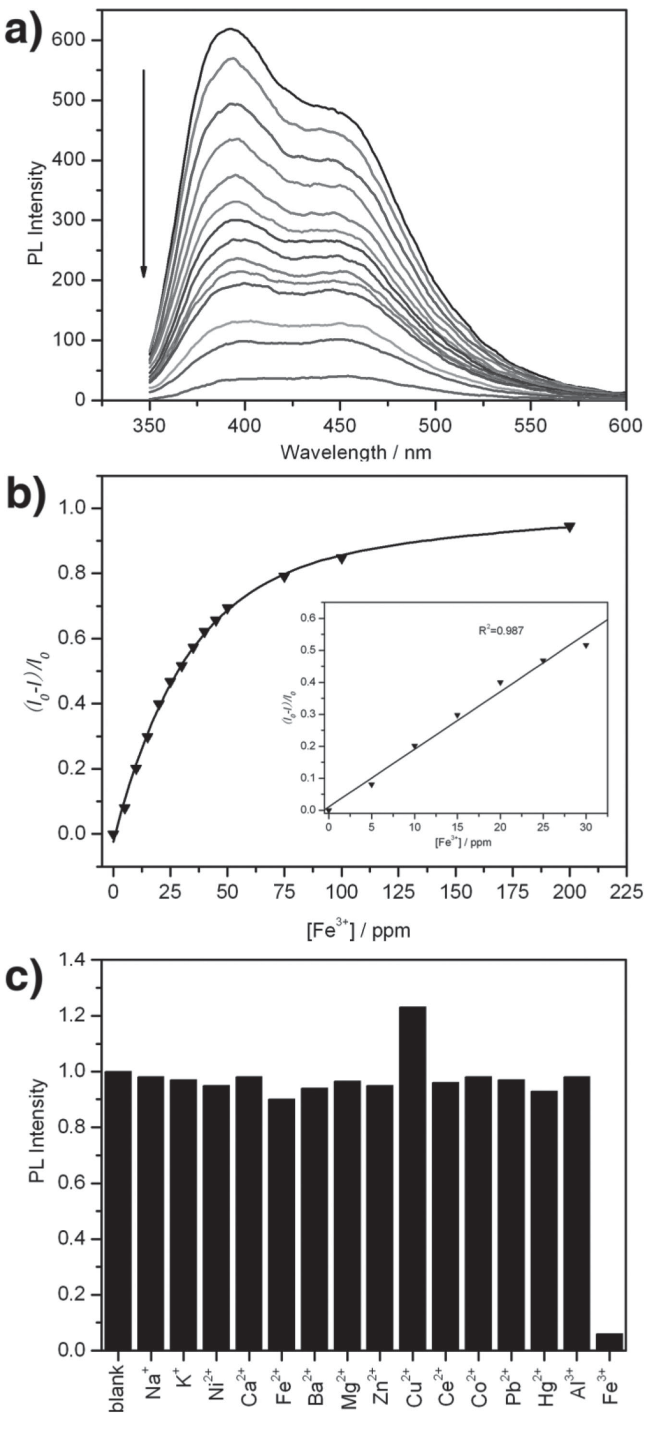


Figure 5. a) Fluorescence quenching of SQDs in the presence of Fe^{3+} ions (0–200 ppm). Downward-pointing arrow shows the trend as the concentration of Fe^{3+} ions increases. b) The relationship between $(I_0 - I)/I_0$ and Fe^{3+} from 0 to 200 ppm. Inset is a linear region. I_0 and I are the PL intensity of SQDs in the absence and presence of Fe^{3+}, respectively. c) Comparison of fluorescence intensities of SQDs after adding different metal ions.

4. Experimental Section

Synthesis of CdSQDs or ZnSQDs: CdSQDs or ZnSQDs were prepared referring to the reported literatures with a little modification.[19] Typically, 1.5 mM of $CdCl_2$ (or $ZnCl_2$) was added to 10 mL of oil acid at room temperature and the resulted solution was heated to 90 °C to generate Cd-oil (or Zn-oil) acid complexes. Then, 0.75 mM of sulphur power in 5 mL of oleyamine was injected into the hot solution and the mixture was heated to 140 °C and aged for 20 h. 50 mL of ethanol was added to precipitate the CdSQDs or ZnSQDs, the precipitate was centrifuged and washed by ethanol for three times, lastly dissolved in 50 mL n-hexane.

Synthesis of SQDs: SQDs was synthesized by phase interfacial reaction method. For the preparation of SQDs, about 5 mL of CdSQDs or ZnSQDs were diluted by 20 mL n-hexane and then sonicated for 30 min to form a homogeneous solution. HNO_3 aqueous solution (20 mL, 0.1 M) was mixed with CdSQDs or ZnSQDs solution with a slowly stirring (500 rpm min^{-1}) for 36 h at room temperature, the organic phase and water phase were separated spontaneously. The resulting white mixture was separated by a funnel, the SQDs which dispersed as a white suspension in hexane in hexane were washed with water three times to remove inorganic ions. Finally, the solution was placed in a vacuum oven and dried at room temperature for 48 h.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20775067, 20977074, and 21175115), the Science & Technology Committee of Fujian Province, China (No. 2012Y0065), and the Program for New Century Excellent Talents in University (NCET-11 0904).

Received: June 24, 2014
Revised: August 5, 2014

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