3C-SiC/ZnS heterostructured nanospheres with high photocatalytic activity and enhancement mechanism

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Among the various semiconductor photocatalysts for pollutant degradation and water splitting, zinc sulfide (ZnS) is one of the most popular and has been studied extensively because it possesses a band structure tunable by doping and the proper negative reduction potential.1–11 Similar to TiO2, bulk ZnS possesses wide bandgaps of 3.72 (zinc-blende) and 3.77 eV (wurtzite),4,5 which hamper efficient use of solar energy. Hence, studies have been carried out to modify/modulate the band structure. One strategy is to dope the materials with metallic or non-metallic ions such as N, Ni, Cu, Pb, and Au4–8 and the other is to incorporate nanocrystalline semiconductors with a narrow band gap or quantum dots such as CeO2, N2O, and CuS.9–11 These modified photocatalysts have been shown to enhance absorption of solar energy by promoting the generation of photoinduced electrons and holes and suppressing direct recombination of charge carriers.

However, the design of efficient ZnS-based hybrid photocatalysts by combining with the suitable narrow-gap semiconductors is challenging. There have been investigations on the use of some appropriate semiconductor quantum dots to facilitate charge separation and photocatalysis. As an important IV-IV non-metallic semiconductor, silicon carbide (SiC) nanocrystals (NCs) have attracted enormous attention because of its high excitation efficiency of electrons and holes under irradiation and widespread applications to biosensors, photocatalysis, and supercapacitors.12–14 To enhance the photocatalytic performance, that is, efficient separation of photogenerated electrons and holes, some composite SiC catalysts such as SnO2/SiC hollow sphere nanochains,15 cubic SiC (3C-SiC)/TiO2 nanocomposites16 have been developed. These catalysts can efficiently separate photoexcited electrons and holes and produce good photocatalytic activity by means of a heterostructure. However, the synthetic methods that have been reported are quite complicated and it is thus important to develop a simple and commercially-adoptable approach to prepare SiC heterostructured catalysts. There have been a few attempts to fabricate hybrid ZnS/3C-SiC NCs17,18 Herein, a one-pot hydrothermal technique to synthesize hybrid ZnS/3C-SiC containing 3C-SiC NCs is described and the
ZnS nanospheres which are surrounded by 3C-SiC NCs exhibit excellent photocatalytic activity. To elucidate the mechanism, a series of ZnS/3C-SiC nanospheres with different amounts of 3C-SiC NCs are synthesized and subjected to microstructural and spectroscopic characterization.

The water suspension with 3C-SiC NCs was prepared according to the procedures described in our previous paper. TEM reveals that the mean size of the 3C-SiC NCs is about 4.0 nm and consistent with the XRD results and please refer to the supplementary material for the XRD patterns acquired from the present samples. In a typical synthesis of the ZnS/3C-SiC nanocomposite, different amounts of 3C-SiC NC suspensions were dissolved in 30 ml of deionized water. Five mmol of zinc acetate dehydrate and 15 mmol of L-cysteine were added to the solution and the pH value was adjusted to 10.0 by adding ammonia. After magnetic stirring for 30 min, the solution was transferred to a 50 ml autoclave and maintained at 100 °C for 6 h to obtain the product. For a more detailed description of the sample preparation, please refer to the supplementary material.

The microstructure and morphology were examined on a Hitachi-3400N scanning electron microscope (SEM, Hitachi Corporation, Japan) and high-resolution transmission electron microscope (HR-TEM, JEOL JEM-4000EX). The ultraviolet-visible (UV-vis) absorption spectra were acquired on a UV-vis spectrophotometer (UV-2550, Shimadzu). X-ray photoelectron spectroscopy (XPS) was performed on a K-Alpha spectrometer (Thermo Fisher Scientific Corporation, USA) with Al Kα radiation and the resolution of the spectrometer was 0.1 eV. X-ray diffraction (XRD) was conducted on the XPERT diffractometer (Philips Corporation, Holland). All the experiments were carried out at room temperature.

SEM reveals that without addition of SiC NCs, the products are made of spherical agglomerates about 100 nm in size as shown in Fig. 1(a). These nanospheres are composed of ZnS NCs 30 nm in size based on TEM (data not shown here). The surface is rough because of the weak interactions between excessive L-cysteine molecules. L-cysteine has the –SH function groups which can bond easily with zinc ions, leading to the formation of the hexagonal wurtzite phase at low temperature (see supplementary material). When SiC NCs are used, the size of the spherical agglomerates increases to about 300 nm. The surface is still quite rough as shown in Figs. 1(b) and 1(c). The size increases due to the addition of 3C-SiC NCs which facilitate nucleation of the ZnS NCs, and the SiC NCs act as binders to make the SiC/ZnS nanospheres bigger (300 nm) than pure ZnS spherical agglomerates (100 nm). Formation of the ZnS/3C-SiC composite nanospheres involves the binding of 3C-SiC NCs with L-cysteine-Zn²⁺ complexes (Cys/Zn) and subsequent hydrothermal decomposition of Cys/Zn produces ZnS NCs surrounded by 3C-SiC NCs as shown in Fig. 1(e). XPS also shows the presence of Si-C and Zn-S bonds attributable to the 3C-SiC and ZnS NCs (see supplementary material).

To determine the size of the 3C-SiC and ZnS NCs in the composite nanospheres, the HR-TEM and TEM images are depicted in Fig. 1(d) and the inset, respectively. The surface of the nanosphere consists of many small 3C-SiC NCs 3-5 nm in size (white circles). The ZnS NCs are mainly distributed inside the nanospheres and have almost the same size as the 3C-SiC NCs (3.7 nm, red circle). This is verified by Scherrer’s equation and XRD peaks (see supplementary material). Hence, the hydrothermal reaction does not increase the 3C-SiC NC size but only produces spherical agglomerates of ZnS NCs in the presence of SiC NCs. The results indicate that by varying the amount of SiC NCs, the density of SiC NCs to encircle the ZnS nanospheres can be controlled. Here, L-cysteine provides the thiol groups to form stable Cys/Zn complexes and the complex groups on the SiC NC surface bind the SiC NCs to Cys/Zn complexes. Consequent hydrothermal reaction produces SiC/ZnS composite NCs finally leading to the formation of large nanospheres with SiC NCs on the surface (Fig. 1(d)). In addition, L-cysteine as a surfactant prevents the SiC NCs from direct agglomeration (see the size analysis on SiC NCs below).

Therefore, p-n junctions which require direct contact between the different NCs are formed. Increasing the 3C-SiC NC concentration increases the number of p-n junctions and the photoreactivity yield/rate is expected to increase. It should be noted that the amount of 3C-SiC NCs has only a small effect on the nanosphere size in our experiments because these NCs are mainly decorated on the surface of the nanospheres due to the stable Cys/Zn complexes.

The optical properties of the 3C-SiC/ZnS nanospheres are evaluated by UV-vis spectrophotometry and the results are shown in Fig. 2. The steep shape indicates that light absorption is
FIG. 1. SEM images of the 3C-SiC/ZnS composite nanospheres with different SiC concentrations: (a) 0, (b) 2.5, and (c) 20 ml. (d) Surface HR-TEM image of a 3C-SiC/ZnS nanosphere with 5 ml of 3C-SiC NC solution. The interlayer spacing of 0.31 nm is in good agreement with the (002) lattice plane of wurtzite ZnS (red circle) and that of 0.25 nm is equal to the (111) plane of 3C-SiC (white circle). The inset shows the low-magnification TEM image of several nanospheres. (e) Schematic illustration of the synthesis of the 3C-SiC/ZnS nanospheres.

due to the band-edge transition instead of impurities. The band-gap $E_g$ of the synthesized ZnS NCs is estimated to be 3.81 eV (326 nm) according to the absorption edge and equation $(\alpha h\nu)^2 = A(h\nu - E_g)$. Please refer to the supplementary material for the optical absorption spectra. It blueshifts compared to the bulk wurtzite ZnS because of the quantum confinement effect of the small ZnS NCs. The average size of the ZnS NCs can be determined by the effective mass approximation calculation:

$$E_g = E_0 + \left[\frac{\hbar^2}{8\mu_r}\right] - 1.8e^2/\varepsilon_0\varepsilon_r r.$$

Here, $1/\mu = 1/m_h + 1/m_e$ is the reduced mass of the electron hole effective mass and $E_0$ is the band gap of bulk ZnS. The calculated mean size is 3.9 nm and consistent with HR-TEM and XRD results. With regard to pure ZnS nanospheres, the absorption spectrum shows an absorption edge at 326 nm (Fig. 2). However, for the composite nanospheres, a new absorption peak appears and its
FIG. 2. UV-vis absorption spectra of the nanospheres synthesized with different amounts of 3C-SiC NCs: (a) 0, (b) 2.5, (c) 5, (d) 10, and (e) 20 ml. The inset shows the voltammetric curve of the as-synthesized ZnS nanospheres during the oxygen evolution reaction (500 W Xe-lamp illumination, pH = 6) indicating that the ZnS NC is n-type.

intensity increases as 3C-SiC NCs are added. According to our previous investigation,\textsuperscript{26} the absorption peak stems from the band-to-band transition in the quantum-confined 3C-SiC NCs and thus the mean NC size can be estimated to be 3.6 nm which is consistent with our HR-TEM data (Fig. 1(d)). The absorption peak increases with the amount of 3C-SiC NCs added. This is obviously due to the increased light absorption caused by the SiC NCs. To determine the type of the as-synthesized ZnS NCs, the ZnS NCs are spin-coated onto a FTO substrate and photoelectrochemical experiments are performed in a buffer under illumination by a 500 W Xe lamp. According to the voltammetric curve of the oxygen evolution reaction in the inset of Fig. 2, the photocurrent increases with the anode potential indicative of n-type conductivity in a semiconductor.\textsuperscript{27,28} Hence, many p-n junctions are formed to construct heterostructured interfaces between the 3C-SiC and ZnS NCs and the built-in electric field can efficiently separates the photoexcited electrons and holes.

To investigate the photocatalytic activity of the 3C-SiC/ZnS nanospheres, photocatalytic degradation of Rhodamine-B (RB) is performed under irradiation by a 500 W Xe lamp. Fig. 3(a) depicts the RB absorbance ratios ($C/C_0$) versus irradiation time and $C$ and $C_0$ denote the characteristic absorption of RB at 553 nm after irradiation and initially, respectively. The pure ZnS shows relatively low photocatalytic activity (curve 1) because pure ZnS only responds to the UV part of the Xe lamp spectrum. On the other hand, the ZnS/3C-SiC nanospheres deliver obviously enhanced photocatalytic performance and the photocatalytic activity increases with the amount of 3C-SiC NCs. The nanospheres with 20 ml of SiC NCs exhibits the best photocatalytic activity towards RB degradation and the RB molecules are almost completely degraded within 60 min. It can be inferred that when the concentration of the added SiC NCs reaches a certain value, the surface of the nanosphere may be completely surrounded by the SiC NCs and subsequent addition of SiC NCs no longer increases the number of p-n junctions. As a result, the photocatalytic ability is saturated gradually (see curve 6 in Fig. 3(a)). Moreover, the recycling tests indicate that the efficiency after the third run is almost the same as that of the fresh sample (Fig. 3(b)) suggesting good stability in the photocatalytic process.

The detailed mechanism of the photo-excitation and simultaneous charge transfer process at the interface of the 3C-SiC/ZnS hybrid is described in Fig. 4. Owing to the proper band matching between the two NC materials,\textsuperscript{16,20} the nanosphere photocatalysts absorb photons with energy greater than the bandgap. The electrons in the conduction band of the 3C-SiC NCs are transferred to the ZnS NCs and the holes remain in the valence band of the SiC NCs. Meanwhile, the electrons produced from the ZnS NCs remain in the ZnS NCs and the holes are transported to the 3C-SiC NCs. The photogenerated electron-hole pairs can be effectively separated due to the formation of the p-n junction at the p-type SiC and n-type ZnS heterojunction interface. This results in reduced e-h pair recombination and increased photocatalytic efficiency and the separated electron and holes
FIG. 3. (a) $C/C_0$ versus irradiation time for RB photodegradation with 0.1 g of the photocatalyst: (1) without catalyst, (2) pure ZnS, (3)-(6) heterostructured nanospheres with 3C-SiC NC solutions of 2.5 (3), 5.0 (4), 10 (5), and 20 ml (6). (b) Recycling test performed on the 3C-SiC/ZnS nanospheres for RB photodegradation.

FIG. 4. Illustration of the bandgap and interfacial charge transfer processes occurring between the 3C-SiC and ZnS NCs.
are free to initiate the degradation reaction of the RB on the surface of the photocatalyst.\textsuperscript{29} The electrons (e\textsuperscript{−}) accumulate on the ZnS NCs and are scavenged by oxygen molecules on the surface of the catalyst to form super oxide (O\textsubscript{2}−) radicals. The super oxide radicals react with protons and photogenerated electrons to generate HO\textsubscript{2}− species and eventually produce hydroxyl (OH\textsuperscript{•}) radicals. The autocatalytic effect of the 3C-SiC NCs gives rise to the formation of H and OH species on the surface. Holes (h\textsuperscript{+}) assembled on the 3C-SiC NCs may directly lead to the formation of hydroxyl (OH\textsuperscript{•}) radicals to oxidize the organic species. The mechanism is illustrated below:

\[
\text{Catalyst (3C-SiC/ZnS) + hν → Catalyst (e\textsuperscript{−} + h\textsuperscript{+}),}
\]

\[
\text{Catalyst (e\textsuperscript{−}) + O_2 → O_2^{-\text{•}}},
\]

\[
O_{2^{-\text{•}}} + H^+ → HO_2^{•},
\]

\[
\text{HO}_2^{•} + HO_2^{•} → H_2O_2 + O_2,
\]

\[
H_2O_2 → 2OH^{•},
\]

\[
\text{Catalyst (h\textsuperscript{+}) + H}_2O → \text{Catalyst + H}^+ + \text{OH}^{•}, \text{and}
\]

\[
\text{Dye + OH}^{•} → \text{Dye product.}
\]

Hence, formation of radicals has a positive correlation with the photocatalytic activity. The 3C-SiC NCs not only separate electrons and holes due to the proper band structure but also help to form hydroxyl radicals to enhance the photocatalytic activity.

In summary, nanospheres consisting of both 3C-SiC and ZnS NCs with a mean size less than 5 nm are prepared hydrothermally. The heterostructured catalyst shows excellent and stable photocatalytic degradation ability on RB molecules. The 3C-SiC NCs greatly enhance the catalytic effect of ZnS NCs because the appropriate band structure leads to efficient separation of photogenerated charge carriers and the relatively narrow band gap of 3C-SiC NCs extends light absorption. Besides, the 3C-SiC NCs may increase the -OH concentration due to the surface autocatalytic effect and there is a positive correlation with the formation of OH\textsuperscript{•} radicals. Our results demonstrate the potential of 3C-SiC/ZnS heterostructured nanospheres in high-efficient photocatalysis.

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