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Article

Facile synthesis of UCNPs/ $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanocomposites excited by near-infrared light for photochemical reduction and removal of Cr(VI)

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ABSTRACT

Photocatalysis driven by near-infrared (NIR) light is of scientific and technological interest for exploiting solar energy. In this study, we demonstrate a facile hydrothermal process to synthesize core-shell nanoparticles combining upconversion nanoparticles (UCNPs) and alloyed $\text{Zn}_x\text{Cd}_{1-x}\text{S}$, which can be excited using NIR or visible light. Morphologies, phase, and chemical composition have been investigated using field-emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction analysis, and atomic absorption spectroscopy. Moreover, we found that amorphous TiO_2 layers existing in the final samples play an important role in formation of UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ yolk-shell nanoparticles, which bind the as-prepared $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanoparticles tightly to form yolk-shell nanoparticles. The chemical composition of alloyed $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ can be tunable by adjusting the amount of the Cd and Zn source compounds. The photochemical reduction of Cr(VI) in water has been performed to study the photocatalytic performance under irradiation by NIR light or a simulated solar light, showing efficient photoreduction and Cr(VI) removal over the as-prepared UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ yolk-shell nanoparticles. The as-prepared UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ nanoparticles show excellent production of hydroxyl radicals, which are responsible for the photochemical reduction of Cr(VI) to Cr(III). This study will provide an alternative strategy for environmental wastewater treatment, making full use of solar energy.

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1. Introduction

Hexavalent chromium Cr(VI) is a common pollutant in surface and ground water because of its many applications in printing, pigments, leather tanning, polishing, [1–3] etc. Cr(VI) in aquatic systems and drinking water sources poses an in-

creasing threat to the environment and human health because it is non-biodegradable and easily accumulates in living tissues through direct ingestion or food-chain delivery, leading to acute and strong carcinogenic toxicity to most organisms [4–6]. Much effort has been devoted to the treatment of environmental wastewater containing Cr(VI). To this end, many strategies

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including electro-reduction [7,8], microbial reduction [9,10], chemical reduction [11,12], and photochemical reduction [13–16] have thus far been developed for practical applications.

Photochemical reduction methods for detoxifying wastewater make the removal of Cr(VI) by reduction to Cr(III) because Cr(III) is nontoxic and is, in fact, an essential trace metal in the human body [17,18]. In recent years, photochemical reduction has received greater attention because it is carried out under mild reaction conditions, making full use of solar energy. In general, photochemical reduction methods involve using various photocatalysts, including TiO_2 , ZnO, CdS, etc., which are activated by UV or visible light (accounts for ~45% of solar energy) [19–23]. Recently, Yu et al. [24] reported the photochemical reduction of Cr(VI) in the presence of a CuO/ZnO nanocomposite triggered by visible light. Wang et al. [2] reported visible-light-driven photoreduction of Cr(VI) induced by AgI/ TiO_2 . Deng et al. [19] have reported photochemical removal of Cr(VI) and 2,4-dichlorophenol under visible light irradiation in the presence of phosphorus-doped porous ultrathin g- C_3N_4 nanosheets. More recently, photocatalysts excited by near-infrared (NIR) light has drawn intensive research interest owing to enhanced performance towards photodegradation of organic dyes for efficient utilization of solar energy [25–29]. However, the high lattice mismatch between UCNP and semiconductor photocatalysts is a major obstacle for the construction of nanocomposites comprising UCNP and semiconductors.

In this study, we demonstrate a facile hydrothermal process to synthesize NIR-light-excited nanocomposites under hydrothermal conditions for removal of Cr(VI). NIR-light-excited lanthanide-doped upconversion nanoparticles (UCNPs) of $\text{NaYF}_4:30\%\text{Yb},0.5\%\text{Tm}@ \text{NaYF}_4:20\%\text{Yb},2\%\text{Er}$ have been cho-

sen as the energy transducer, converting NIR photons to photons with higher energy [30–35]. In the proposed synthetic protocol (Fig. 1(a)), the UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ nanoparticles have been prepared using UCNPs@AA- $\text{Zn}[(\text{OH})_4]^{2-}/\text{TiO}_2$ as hard templates, and cadmium acetate and thiourea have been used as Cd and S sources, respectively. In this work, amorphous layers of TiO_2 are present in the final samples, which combine the as-prepared $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanoparticles and UCNPs tightly together to form yolk-shell nanoparticles [36] and overcome the major obstacle of lattice mismatching between the UCNPs and the semiconductor. The photochemical reduction of Cr(VI) in aqueous solution has been demonstrated under irradiation by NIR light and simulated solar light.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and used without any further purification. Rare-earth chloride ($\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, 99.99 wt%), ammonium fluoride (NH_4F , 98 wt%), titanium butoxide (TBT, 99%), sodium hydroxide (NaOH , 96 wt%) and cadmium acetate dihydrate ($\text{C}_4\text{H}_6\text{CdO}_4 \cdot 2\text{H}_2\text{O}$) were all purchased from Aladdin Industrial Corporation. Methanol (CH_3OH , 99.5 wt%), L-ascorbic acid (AA, 99.7 wt%), hexamethylenetetramine (HMTA, 99.0 wt%), hexadecyltrimethylammonium bromide (CTAB, 99.9 wt%), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.0 wt%), ammonia solution (NH_3), and thiourea (H_2NCSNH_2 , 99.0 wt%) were obtained from Sinopharm Chemical Reagent Co. Ltd. The UCNPs of $\text{NaYF}_4:30\%\text{Yb},0.5\%\text{Tm}@ \text{NaYF}_4:20\%\text{Yb},2\%\text{Er}$ were synthesized via a previously published protocol [37].

Fig. 1. (a) Schematic illustration of the synthesis of UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ nanocomposites; TEM images of UCNPs@AA- $\text{Zn}[(\text{OH})_4]^{2-}$ (b), UCNPs@AA- $\text{Zn}[(\text{OH})_4]^{2-}/\text{TiO}_2$ (c), and UCNPs@ $\text{Zn}_{0.64}\text{Cd}_{0.36}\text{S}/\text{TiO}_2$ (d); (e) HR FETEM image of UCNPs@ $\text{Zn}_{0.64}\text{Cd}_{0.36}\text{S}/\text{TiO}_2$; STEM image (f) and element mappings (g–o) of UCNPs@ $\text{Zn}_{0.64}\text{Cd}_{0.36}\text{S}/\text{TiO}_2$. All scale bars in Fig. 1(g)–(o) are 100 nm.

2.2. Synthesis

The $\text{NaYF}_4\text{:}30\%\text{Yb},0.5\%\text{Tm}@ \text{NaYF}_4\text{:}20\%\text{Yb},2\%\text{Er}@ \text{AA}-[\text{Zn}(\text{OH})_4]^{2-}$ core shell nanoparticles (UCNPs@AA- $[\text{Zn}(\text{OH})_4]^{2-}$) were synthesized via a protocol previously developed by us [38]. Typically, 26.78 mg $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 12.62 mg HMTA were added into a mixture solution consisting of 0.1316 g CTAB, 4.2 mg AA and 1.8 mL of as-prepared hydrophilic UCNPs (~1.8 mg), respectively, to form a clear solution. The temperature of the mixture was increased to 85 °C and then maintained at this temperature for 10 h. The product was collected by centrifugation and washed with de-ionized water and ethanol.

Afterward, the UCNPs@AA- $[\text{Zn}(\text{OH})_4]^{2-}/\text{TiO}_2$ nanoparticles were prepared by hydrolysis of TBT. Briefly, UCNPs@AA- $[\text{Zn}(\text{OH})_4]^{2-}$ nanoparticles (~20 mg) were dispersed in absolute alcohol (25 mL), followed by the addition of ammonia (90 μL). After stirring for 10 min, TBT (200 μL) was added dropwise into the solution. Then the mixture was stirred for 10 h at room temperature. Finally, the product was collected by centrifuging and washed with deionized water and ethanol several times.

UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ nanocomposites were produced via a hydrothermal synthesis method. Typically, UCNPs@AA- $[\text{Zn}(\text{OH})_4]^{2-}/\text{TiO}_2$ (0.12 mmol), cadmium acetate (0.03 mmol) and thiourea (3.8 mmol) were added to 20 mL of deionized water whilst stirring. The resulting mixture was then transferred to a Teflon-lined autoclave with a capacity of 25 mL and kept at 140 °C for 1.5 h. After cooling to room temperature, the final product was collected by centrifugation and washed with deionized water and ethanol several times. For comparison, UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanocomposites with different chemical composition were synthesized using different amounts of cadmium acetate and thiourea, with all other conditions kept the same.

2.3. Characterization

The morphologies of products were detected by transmission electron microscopy (TEM) images, using a high-resolution field-emission transmission electron microscope (HR FETEM; JEM-2100F, JEOL, Japan). The X-ray diffraction (XRD) patterns of products were investigated by an X'Pert PRO MPD X-ray diffractometer (PANalytical B.V., Holland) with graphite monochromated $\text{Cu K}\alpha$ radiation. The X-ray photoelectron spectra (XPS) of UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}@ \text{TiO}_2$ nanocomposites were measured by an ESCALAB250Xi X-ray photoelectron spectrometer (Thermo Scientific, USA). The UV-Visible spectra of these products were obtained with a spectrophotometer (U-5100, Hitachi High-Technology Corporation). The fluorescent spectra of the samples were measured using an FLS980 fluorescence spectrometer (Edinburgh Instruments, UK) with an external 980 nm CW laser. Atomic absorption spectroscopy (AAS) was used to determine the mole ratio of Zn/Cd, which was carried out using AA800 spectrometer (Perkin Elmer, USA).

2.4. Photocatalytic test

Photocatalytic reduction of Cr(VI) was selected as a model to evaluate the photocatalytic activities of as-prepared UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ nanocomposites. The UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ nanocomposites (15 mg) was dispersed in 50 mL of aqueous Cr(VI) solution (20 mg/L) and stirred in the dark for 30 min to reach adsorption/desorption equilibrium. Following that, the Cr(VI) solution was exposed, under stirring, for specific times, to a Xe lamp (1500 mW/cm², emission wavelength range 320–1100 nm) equipped with (or without) a UV-Vis filter. At given time intervals, 2 mL of the Cr(VI) aqueous solution was removed, and the concentration change of Cr(VI) was determined by measuring the characteristic absorption peak of Cr(VI)-complex at 540 nm according to the diphenylcarbazide (DPC) method [13,15].

3. Results and discussion

The morphologies and chemical composition of the as-prepared samples were investigated using TEM, scanning transmission electron microscopy (STEM) and XRD. Fig. 1(c) shows the TEM image of the as-prepared sample, it was obtained from UCNPs@AA- $[\text{Zn}(\text{OH})_4]^{2-}$ core-shell nanoparticles and TBT in presence of ammonia solution. As shown in Fig. 1(c) and Fig. S1 (in the Supporting Information), the as-prepared sample consisted of yolk-shell nanoparticles and thin layers of TiO_2 have been clearly observed, forming on the surface of UCNPs@AA- $[\text{Zn}(\text{OH})_4]^{2-}$ core-shell nanoparticles. Moreover, the shell layers of UCNPs@AA- $[\text{Zn}(\text{OH})_4]^{2-}$ nanoparticles partially dissolved, and have been observed to form yolk-shell nanoparticles. The proposed synthetic procedure is illustrated in Fig. 1(a). UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ ($x = 0.64$) can be obtained from UCNPs@AA- $[\text{Zn}(\text{OH})_4]^{2-}/\text{TiO}_2$ (0.12 mmol), cadmium acetate (0.03 mmol) and thiourea (3.8 mmol) under hydrothermal conditions. As shown in Fig. 1(d), there are many small nanoparticles decorating the surface of the as-obtained yolk-shell nanoparticles. Additionally, the lattice fringes of 3.58 and 3.16 Å from the outmost nanoparticle can be readily assigned to (100) and (101) crystal planes of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$, respectively; which is in good agreement with the previous study [39]. The STEM and elemental mapping images (Fig. 1(f)–(k)) show that Zn, S, Cd, Ti, and O elements distribute homogeneously in the shell layer, verifying the shell composition of TiO_2 and $\text{Zn}_x\text{Cd}_{1-x}\text{S}$. The elemental mapping images in Fig. 1(i)–(o) indicate that the yolk is the UCNPs used herein.

Fig. 2 shows the XRD pattern of the as-prepared final sample, in which the peaks noted as dots in red can be indexed to the hexagonal phase of NaYF_4 (JCPDS No. 28-1192) [39,40]. The diffraction peaks located at 25.27°, 26.85°, 28.58°, 43.76° and 52.19° can be assigned to the (100), (002), (101), (110) and (112) crystal planes of hexagonal alloyed $\text{Zn}_x\text{Cd}_{1-x}\text{S}$, respectively, because the diffraction angles were bigger than that of pure hexagonal CdS. By contrast, no crystalline TiO_2 has been observed. The composition of TiO_2 in the experiments plays an important role in formation of the yolk-shell nanostructures. As shown in Fig. S2, it is hard to obtain UCNPs@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ yolk-shell nanoparticles in the absence of TiO_2 . Thus, the TiO_2 distribute homogeneously in the total shell layer and bind the

Fig. 2. XRD pattern of the UCNP@Zn_{0.64}Cd_{0.36}S/TiO₂ nanocomposites.

as-prepared nanoparticles of Zn_xCd_{1-x}S at the outer layer of the yolk-shell nanoparticles. The chemical composition of Zn_xCd_{1-x}S nanoparticles can be tuned by adjusting the amount of Cd and S sources, and the accurate mole ratio of Zn/Cd has been determined by AAS and is listed in Table 1.

XPS has been used to investigate the chemical composition and states of the elements in the nanoparticles; the experimental spectra are shown in Fig. 3. The extended XPS spectrum of UCNP@Zn_{0.64}Cd_{0.36}S/TiO₂ shows the co-existence of ele-

Table 1

Tuning of the amount of S and Cd sources and corresponding mole ratio of Zn/Cd in the sample (UCNP@Zn_xCd_{1-x}S/TiO₂) from AAS analyses.

Thiourea (mmol)	C ₄ H ₆ CdO ₄ ·2H ₂ O (mmol)	Zn/Cd
3.8	0.03	0.64/0.36
4.5	0.06	0.48/0.52
6.0	0.12	0.25/0.75

ments, including Zn, Cd, Ti, O, and S. High resolution spectra are shown in Fig. 3(b)–(d), and these verify that the chemical states of the surface composition are divalent metal ions of Zn, Cd and S. In addition, the intensity for the trivalent lanthanide ions including Y³⁺ is relatively weak compared to that of Zn²⁺, indicating that the composition of the yolk is UCNP (data not shown).

Fig. 4(a) and (b) show the fluorescence spectra of the as-obtained UCNP@AA-[Zn(OH)₄]²⁻, UCNP@AA-[Zn(OH)₄]²⁻/TiO₂ and UCNP@Zn_{0.64}Cd_{0.36}S/TiO₂ nanoparticles excited using a 980-nm continuous wave (CW) laser. These show that the fluorescence emissions for the Er³⁺ in the as-prepared UCNP@Zn_{0.64}Cd_{0.36}S/TiO₂ nanoparticles have been greatly quenched, indicating the efficient fluorescence energy transfer occurring between the yolk and shell composition under irradiation of NIR light. UV-Visible spectroscopy has been used to investigate the optical properties for the as-prepared samples. As shown in Fig. 4(c) and (d), it is clear that there is good overlap between the UV-Vis spectra of the final sample and the fluorescence spectra of UCNP, which results in the occurrence of

Fig. 3. XPS spectra of UCNP@Zn_{0.64}Cd_{0.36}S/TiO₂ yolk-shell nanoparticles. (a) Extended spectrum; (b) Zn 2p; (c) Cd 3d; (d) Ti 2p.

efficient fluorescence resonance energy transfer (FRET), as reported by many previous works [39,41]. Moreover, the high energy emissions of Er^{3+} can excite the shell composition of $\text{Zn}_{0.64}\text{Cd}_{0.36}\text{S}$ via an irradiation energy transfer (IET) process. The excited shell composition of $\text{Zn}_{0.64}\text{Cd}_{0.36}\text{S}$, owing to absorption of the energy from the UCNP, should produce photo-generated holes (h^+) and electrons (e^-), which are responsible for causing oxidative and reductive reactions, respectively. As shown in Fig. 5, the hydroxyl radical ($\cdot\text{OH}$) has been con-

firmed in the presence of the as-prepared yolk-shell nanoparticles under irradiation of NIR light and solar light, which can be attributed to the oxidation of H_2O by the photo-generated holes (h^+). Thus, the as-prepared UCNP@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ nanoparticles can be used as photochemical oxidant and reductant thanks to the reducibility of electrons (e^-) and oxidizability of the photo-generated holes (h^+).

In the present study, Cr(VI) was selected as a model to study the photocatalytic properties of the as-prepared samples. Pho-

Fig. 4. (a) Fluorescence spectra of the as-prepared UCNP, UCNP@AA-[Zn(OH)₄]²⁻, UCNP@AA-[Zn(OH)₄]²⁻/TiO₂, and UCNP@Zn_xCd_{1-x}S/TiO₂ nanocomposites; (b) Local enlarged view of (a); (c) UV-Vis absorbance spectra of the as-prepared UCNP@Zn_xCd_{1-x}S/TiO₂ with different mole ratio of Zn and Cd; (d) UV-Vis absorbance spectra of UCNP@Zn_xCd_{1-x}S/TiO₂ nanocomposites (black line) and fluorescence spectra of UCNP (red line).

Fig. 5. Fluorescence spectra of terephthalic acid (TAOH) with the addition of UCNP@Zn_{0.64}Cd_{0.36}S nanoparticles under irradiation of NIR (a) light and visible light (b).

Fig. 6. Photochemical reduction and kinetic curves of Cr(VI) in the presence of different UCNPs@Zn_xCd_{1-x}S/TiO₂ nanocomposites under irradiation of NIR light (a, b) and a simulated solar light (c, d); c_0 and c_t are the concentration of initial solution and the concentration at the irradiation time t (min), respectively.

tochemical reduction analysis of Cr(VI) under irradiation of NIR light and simulated solar light have been investigated. As shown in Fig. 6(a), more than 70% of the Cr(VI) was reduced in 30 min over 15 mg of UCNPs@Zn_{0.64}Cd_{0.36}S/TiO₂ yolk-shell nanoparticles under irradiation of NIR light using a 1500 mW/cm² Xe lamp equipped with an UV-Vis filter. The kinetic curves (Fig. 6(b)) indicate that UCNPs@Zn_{0.64}Cd_{0.36}S/TiO₂ nanoparticles show better photochemical reduction of Cr(VI) than the UCNPs@Zn_xCd_{1-x}S/TiO₂ ($x = 0, 0.25, 0.48$) nanoparticles, triggered by NIR light, owing to the enhanced separation efficiency between the photo-generated electron-hole pairs for the UCNPs@Zn_{0.64}Cd_{0.36}S nanoparticles [43], which is in good agreement with previous studies [39,42]. In contrast, ~99% of Cr(VI) can be photo-reduced and removed under irradiation with simulated solar light from a Xe lamp, which can be attributed to NIR mediated photocatalytic performance, as shown in Fig. 6(c) and (d). Therefore, the as-prepared photocatalysts demonstrated enhanced photocatalytic ability due to photocatalysis triggered by NIR light or visible light compared to that of single counterpart of Zn_xCd_{1-x}S.

Photochemical reduction of Cr(VI) in aqueous solution can be illustrated using the following two equations [14]. As discussed previously and illustrated in Fig. 7, the shell compositions absorb energy from the UCNPs under NIR-light irradiation

via FRET and IET processes, or visible excitation light and produce photo-generated holes and electrons. The photo-generated electrons (e^-) in the conduction band (CB) of Zn_xCd_{1-x}S reduce Cr(VI) to Cr(III), and holes (h^+) will be captured by H₂O, leading to the formation of $\cdot OH$, the presence of which was demonstrated by the fluorescence spectroscopy [39].

Besides catalytic ability, chemical stability is another important characteristic of a photocatalyst, allowing for potential important applications. Three recycling photocatalytic experiments have been carried out to illustrate the chemical stability of the as-prepared UCNPs@Zn_{0.64}Cd_{0.36}S/TiO₂ nanoparticles. These show that the as-prepared photocatalysts have excellent chemical capability when excited using NIR light or a simulated solar light (Fig. 8(a) and (b)). The TEM image of the UCNPs@Zn_{0.64}Cd_{0.36}S/TiO₂ nanoparticles after NIR-light irradiation for 30 min has been shown in Fig. 8(c), which shows that the nanoparticles are with similar nanostructures compared to before their irradiation by the excitation light, demonstrating the good chemical stability of our as-prepared photocatalysts. In particular, cell viability of HUVEC cells incubated with the nanoparticles of UCNPs@Zn_{0.64}Cd_{0.36}S/TiO₂ and UCNPs@Zn_{0.48}Cd_{0.52}S/TiO₂ is shown in Fig. 8(d), highlighting

Fig. 7. Irradiative energy transfer (IET) and fluorescence resonance energy transfer (FRET) between UCNP and $\text{Zn}_x\text{Cd}_{1-x}\text{S}$, and the photochemical reduction mechanism of Cr(VI) .

the good biocompatibility of the as-prepared photocatalysts.

Summarizing, the as-prepared UCNP@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ show good photochemical reduction of Cr(VI) excited using NIR light or solar light. In particular, the as-prepared UCNP@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ nanoparticles show excellent biocompatibility, even with concentrations of the nanoparticles was up to 200 $\mu\text{g/mL}$,

which broadens the potential applications in wastewater treatment and nanobiomedicine, including the possibility of its use as a photodynamic agent for cancer treatment. The as-prepared UCNP@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ nanocomposites are therefore definitely an excellent candidate for use as an NIR mediated photocatalyst for wastewater treatment.

Fig. 8. Recycling test of photo-reduction of Cr(VI) using UCNP@ $\text{Zn}_{0.64}\text{Cd}_{0.36}\text{S}/\text{TiO}_2$ nanocomposites under NIR-light irradiation (a) and solar-light irradiation (b); (c) TEM image of the as-prepared UCNP@ $\text{Zn}_{0.64}\text{Cd}_{0.36}\text{S}/\text{TiO}_2$ nanoparticles after NIR-light irradiation for 30 min; (d) The cell viability of HUVEC cells incubated with the UCNP@ $\text{Zn}_{0.64}\text{Cd}_{0.36}\text{S}/\text{TiO}_2$ and UCNP@ $\text{Zn}_{0.48}\text{Cd}_{0.52}\text{S}/\text{TiO}_2$ nanoparticles.

4. Conclusions

In summary, a facile hydrothermal process has been developed to fabricate UCNPs@Zn_xCd_{1-x}S/TiO₂ yolk-shell nanoparticles successfully. The TiO₂ composition plays an important role in the formation of yolk-shell nanostructures, which bound to the as-prepared small nanoparticles of Zn_xCd_{1-x}S together tightly to form the shell structures. Moreover, the composition of Zn_xCd_{1-x}S can be tuned by changing the mole ratio of Cd and Zn sources. The as-prepared UCNPs@Zn_xCd_{1-x}S/TiO₂ nanoparticles can be excited using NIR light or a simulated solar light, demonstrating good photochemical reduction of Cr(VI) to Cr(III) in aqueous solution. This study illuminates an alternative strategy for environmental wastewater treatment, and a potential opportunity for exploiting solar energy.

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Graphical Abstract

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Facile synthesis of UCNPs@Zn_xCd_{1-x}S nanocomposites excited by near-infrared light for photochemical reduction and removal of Cr(VI)

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A facile chemical solution approach has been developed to synthesize UCNPs@Zn_xCd_{1-x}S/TiO₂ nanocomposites for removal of Cr(VI) under irradiation of near infrared light.

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近红外光驱动的 UCNP_s/Zn_xCd_{1-x}S 纳米复合结构的化学合成 并用于光化学还原六价铬

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摘要: 近红外光约占入射太阳能的 44% 以上, 为实现太阳能的最大化利用, 近红外光 (NIR) 驱动的光催化技术成为科学研究的热点. 由于上转换荧光纳米材料 (UCNP_s) 是优良的红外能量转换器, 合金半导体 Zn_xCd_{1-x}S 具有较好的化学稳定性以及生物相容性, 本文发展了一种简易的水热法, 将 UCNP_s 和 Zn_xCd_{1-x}S 合金结合, 成功构建了 NIR 与可见光响应的核壳纳米结构. 由于这两种材料的晶格失配度较高, 很难直接外延生长, 我们通过引入非晶 TiO₂ 将形成的催化剂纳米颗粒 Zn_xCd_{1-x}S 紧紧束缚在 UCNP_s 外面形成蛋黄-蛋壳结构, 在 NIR 光照下获得了较高的能量转换效率.

首先, 在 UCNP_s 外面外延生长一层 AA-Zn[(OH)₄]²⁻ 复合物, 形成 UCNP_s@AA-Zn[(OH)₄]²⁻ 复合纳米结构, 然后在其核壳结构外面外延生长薄层的非晶 TiO₂, 以稳定后续要制备的合金半导体 Zn_xCd_{1-x}S; 在水热条件下, UCNP_s@AA-Zn[(OH)₄]²⁻/TiO₂ 与醋酸镉和硫脲反应, 形成 UCNP_s@Zn_xCd_{1-x}S/TiO₂ 复合材料. 在此, 我们选择 β-NaYF₄:Yb(30%),Tm(0.5%)@NaYF₄:Yb(20%),Er(2%) 作为 NIR 的能量转换器. 样品的形貌、物相及化学组成分别采用场发射扫描电子显微镜、透射电子显微镜、X 射线衍射和原子吸收光谱法进行表征.

研究表明, 我们成功制备了具有蛋黄-蛋壳结构的 UCNP_s@Zn_xCd_{1-x}S/TiO₂ 纳米颗粒. 此外, 非晶态 TiO₂ 将 UCNP_s 与 Zn_xCd_{1-x}S 紧密结合, 对最终样品 UCNP_s@Zn_xCd_{1-x}S 核壳纳米粒子的形成起到重要作用. 而且, 合金 Zn_xCd_{1-x}S 的化学组成可通过调整镉源和锌源的用量进行调节. 所制备的 UCNP_s@Zn_xCd_{1-x}S 核壳纳米粒子在 NIR 光线或模拟太阳光照射下显示出高效的光化学还原 Cr(VI) 性能. 溶液中 70% 以上的 Cr(VI) 在 NIR 光照射 30 min 后被还原为 Cr(III). 本研究将为污水处理和太阳能利用提供一种可供选择的策略, 且所制的复合纳米结构在肿瘤治疗、药物释放和能量转换等领域也有着潜在的应用价值.

关键词: 上转换纳米颗粒; Zn_xCd_{1-x}S 合金半导体; 蛋黄-蛋壳结构; 光催化; 水热合成

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