Facile Synthesis of Uniform Zinc-blende ZnS Nanospheres with Excellent Photocatalytic Activity toward Methylene Blue Degradation (Postprint)

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Abstract

Uniform and well-dispersed ZnS nanospheres have been successfully synthesized via a facile chemical route. The crystal structure, morphology, surface area, and photocatalytic properties of the sample were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis, and ultraviolet-visible (UV-vis) spectroscopy. The characterization results indicate that the products are mesoporous zinc-blende ZnS nanospheres with an average diameter of 200 nm, composed of nanoparticles with a crystallite size of about 3.2 nm as calculated by XRD. Importantly, photocatalytic degradation of methylene blue (MB) shows that the as-prepared ZnS nanospheres exhibit excellent photocatalytic activity, with nearly 100% of MB decomposed after UV-light irradiation for 25 min. The excellent photocatalytic activity of the ZnS nanospheres can be ascribed to the large specific surface area and hierarchical mesoporous structure.

Full Text

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ABSTRACT

Uniform and well-dispersed ZnS nanospheres have been successfully synthesized via a facile chemical route. The crystal structure, morphology, surface area, and photocatalytic properties of the sample were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis, and ultraviolet-visible (UV-vis) spectroscopy. The characterization results indicate that the products are mesoporous zinc-blende ZnS nanospheres with an average diameter of 200 nm, composed of nanoparticles with a crystallite size of approximately 3.2 nm as calculated from XRD data.

Importantly, photocatalytic degradation of methylene blue (MB) demonstrates that the as-prepared ZnS nanospheres exhibit excellent photocatalytic activity, with nearly 100% of MB decomposed after UV-light irradiation for 25 minutes. The outstanding photocatalytic activity of the ZnS nanospheres can be attributed to their large specific surface area and hierarchical mesoporous structure.

Keywords: ZnS nanospheres, zinc-blende, photocatalytic activity, methylene blue, degradation

1. INTRODUCTION

With the rapid development of the textile dyeing industry, environmental wastewater pollution from various persistent and hazardous organic pollutants has attracted increasing attention in recent years. Over the past few decades, semiconductor photocatalysts have become increasingly attractive due to their potential advantages such as cost-effectiveness, easy operation, environmental friendliness, high efficiency, wide applicability, and high chemical stability in addressing environmental wastewater pollution issues [?, ?]. Semiconductor photocatalysis is also considered one of the most effective methods for pollutant degradation because of the high reactivity of free radicals such as hydroxyl radicals, which originate from electron-hole pairs created in semiconductor materials through photon absorption [?].

ZnS is an important II-VI semiconducting material with a direct wide band gap. Due to its special electrical and optical properties, ZnS has been widely used in electroluminescence [?], field-effect transistors [?], solar cells [?], gas sensing [?], photocatalysis [?], and other applications. Because of morphology-dependent properties and increasing interest in morphology-controllable synthesis, ZnS materials with various morphologies, such as nanowires [?], nanobelts [?], nanorods [?], two-dimensional nanosheets [?], and three-dimensional flower-like architectures [?], have been fabricated in recent years. For photocatalysts, hierarchical architectures demonstrate superior photocatalytic efficiency, which can be ascribed to their high energy conversion efficiencies and light-harvesting capacities obtained by constructing complex architectures [?]. Therefore, designing photocatalysts with hierarchical structures is of great importance for enhancing photocatalytic efficiency.

In this work, hierarchically uniform and well-dispersed zinc-blende ZnS nanospheres assembled by nanoparticles have been successfully achieved through a facile solution approach. The synthesized ZnS nanospheres can be employed as efficient photocatalysts (with nearly 100% degradation ratio) for the degradation of methylene blue under UV-light irradiation. To the best of our knowledge, there have been few reports on hierarchically uniform zinc-blende ZnS nanospheres composed of secondary nanoparticles with excellent photocatalytic performance.

2. EXPERIMENTAL

2.1 Preparation of zinc-blende ZnS nanospheres and common ZnS

Preparation of zinc-blende ZnS nanospheres: All chemicals were used as received without further purification. In a typical synthesis process, 3 mmol of zinc acetate dehydrate was dissolved in 25 mL of ethylene glycol under stirring to form a clear solution, and then 1 mL of ethylenediamine was added to the solution before heating. When the solution was first heated to 100 °C, a freshly prepared 25 mL ethylene glycol solution containing 4.5 mmol of thiourea was added dropwise into the solution. After the solution was further heated to 150 °C, 1 mL of dodecylamine was quickly injected into the solution. The whole solution was kept at 150 °C for 3 hours. After cooling down to room temperature, the product was centrifuged, washed with ultrapure water and ethanol several times, and then dried at 80 °C for 8 hours under vacuum.

Preparation of common zinc-blende ZnS: In order to gain insights into the structural effect of ZnS nanospheres on photocatalytic activity, common zinc-blende ZnS was prepared by the precipitation method for comparison. 3.6 g of NaS • 9H O (15 mmol) and 4.46 g of Zn(NO) • 6H O (15 mmol) were completely dissolved in 15 mL of deionized water, respectively, and then the two clear and colorless aqueous solutions were mixed together under stirring to form ZnS precipitate at room temperature. The product was centrifuged, washed with ultrapure water several times, and then dried at 100 °C for 8 hours under vacuum.

2.2 Characterizations

The morphologies of the samples were observed by scanning electron microscopy (SEM, JEOL JSM-6700F). The energy dispersive X-ray spectroscopy (EDS) analysis of the sample was measured using a silicon wafer as the substrate on a Field Emission Scanning Electron Microscope (Hitachi SU-8010). Powder X-ray diffraction (XRD) patterns were measured on a glass wafer by a Rigaku MiniFlex 600 diffractometer with a Cu-K X-ray source (= 1.5406 Å). UV-vis spectra were recorded on an Agilent Technologies Cary 60 spectrophotometer. The BET surface areas and pore size distributions of the samples were determined by N adsorption-desorption at liquid nitrogen temperature (77 K), which was performed on a Micromeritics ASAP 2460 after the samples were degassed at 120 °C for 2 hours.

2.3 Photocatalytic experiments

The photocatalytic activities of the ZnS samples were evaluated by the degradation of methylene blue (MB) aqueous solution with an initial concentration of 10 mg/L under irradiation from two 8 W UV-light tubes (= 254 nm). Fifty milligrams of catalyst powder was added to 50 mL of MB solution in a quartz cup, corresponding to a catalyst dosage of 1 g/L. Before UV-light irradiation, the whole system was placed in the dark under magnetic stirring for 60 minutes to ensure adsorption/desorption equilibrium. During UV-light irradiation, approximately 4 mL aliquots were sampled at given time intervals and centrifuged. The clear supernatant MB solution was then analyzed by a UV-vis spectrophotometer (TU-1901, PERSEE, Beijing). The degradation ratio was monitored by measuring the absorption of MB at a wavelength of 664 nm, which was calculated according to the formula: = [(A -A)/A] × 100%, where A is the absorbance of the MB solution with the initial concentration, and A is the absorbance of the MB solution measured after photocatalytic degradation. For comparison, a blank control experiment (pure MB solution without catalyst under UV-light irradiation) was also conducted to establish the effect of photolysis and catalysis on the conversion of MB.

3. RESULTS AND DISCUSSION

3.1 Characterization

The morphology, structure, and composition of the as-synthesized ZnS nanospheres and common ZnS were examined by electron microscopy techniques. Fig. 1a [Figure 1: see original paper] displays a low-magnification SEM image of ZnS nanospheres, indicating that the obtained ZnS sample consists of uniform and well-dispersed nanospheres with an average diameter of 200 nm. The higher-magnification SEM image (Fig. 1b) of ZnS nanospheres shows that the surfaces of the nanospheres are rough, suggesting that the nanospheres are likely assemblies of tiny nanoparticles.

The EDS spectrum (Fig. 1c) indicates that the as-prepared ZnS nanospheres are composed only of Zn and S elements, while the signal for Si originates from the substrate. The atomic ratio of Zn to S in the ZnS nanospheres is approximately 47.42:52.58, close to the stoichiometric ratio of ZnS (1:1). As indicated by the SEM image in Fig. 1d, common ZnS obtained by the precipitation method is composed of nanoparticle aggregates. The sizes of these aggregates are not uniform, being mainly above 200 nm.

The phase compositions of the as-prepared ZnS nanospheres and common ZnS were characterized by XRD. As seen in Fig. 2 [Figure 2: see original paper], all the diffraction peaks of both samples match well with the standard diffraction data for a cubic zinc-blende structure of ZnS (JCPDS, No. 05-0566) [**?**]. No traces of extra diffraction peaks were detected, indicating the formation of a pure-phase structure in both the as-prepared ZnS nanospheres and common ZnS. Three broad peaks are observed for both ZnS nanospheres and common ZnS at 2 = 28.6°, 48.2°, and 56.7°, which are assigned to the (111), (220), and (311) characteristic diffractions, respectively [?]. The typical broadening of the three diffraction peaks indicates that both ZnS nanospheres and common ZnS are comprised of many tiny constituent nanoparticles. The mean crystallite sizes of ZnS nanoparticles for the ZnS nanospheres and common ZnS, estimated by the Debye-Scherrer formula based on the (111) peak, are approximately 3.2 nm and 2.1 nm, respectively, which are much smaller than the sizes of both samples observed by SEM. This demonstrates that both ZnS nanospheres and common ZnS are assemblies of tiny constituent nanoparticles.

UV-vis spectroscopy is often applied to investigate the optical absorption properties of semiconductors. Fig. 3a [Figure 3: see original paper] presents the UV-vis absorption spectra of both ZnS nanospheres and common ZnS. Both ZnS samples show a strong absorption edge in the ultraviolet region (310–360 nm), which can be assigned to the optical absorption edge of ZnS. It is observed that the absorption edge of ZnS nanospheres shifts toward a lower wavelength relative to common ZnS. The direct band gap energy (E__g) can be estimated from the UV-Vis spectra via a Tauc plot of (h $)^2$ versus photon energy (h) according to the Tauc relationship [?]: h = A(h -E__g)^{1/2}, where is the absorption coefficient, h is the photon energy, E__g is the direct band gap energy, and A is a constant. As illustrated in Fig. 3b, the estimated band gap energy of ZnS nanospheres is about 3.62 eV, which is larger than that of common ZnS (band gap of 3.54 eV). The observed blue shift in the band gap energy of ZnS nanospheres can be attributed to quantum confinement effects due to reduced particle size [?], which is in agreement with the SEM results.

Since photocatalytic activity is directly correlated with the surface area and pore structure of the photocatalyst, nitrogen adsorption-desorption measurements were carried out. Fig. 4 [Figure 4: see original paper] displays the nitrogen adsorption-desorption isotherms and the corresponding Barrett-Joyner-Halenda (BJH) pore-size distributions of ZnS nanospheres and common ZnS. A typical Type IV isotherm (Fig. 4a) indicates the presence of a mesoporous structure in the ZnS nanospheres stemming from the aggregation of nanoparticles. The inset of Fig. 4a shows a sharp and narrow pore size distribution with pore diameters in the range of 3–4 nm, suggesting uniform internal pore structures of the ZnS nanospheres. A mesoporous structure was also observed in common ZnS, as presented in Fig. 4b. However, the pore size of common ZnS displays a more irregular arrangement from 2 to 20 nm (inset of Fig. 4b). Furthermore, the BET surface area of common ZnS is calculated to be 71.88 m^2/g, which is much lower than that of the as-prepared ZnS nanospheres (107.68 m^2/g).

3.2 Photocatalytic properties

The photocatalytic activities of ZnS nanospheres and common ZnS were investigated by the degradation of methylene blue (MB) under UV-light irradiation, and the blank control experiment (pure MB solution without catalyst) was also evaluated under the same photocatalytic conditions for comparison. Fig. 5a [Figure 5: see original paper] shows the time-dependent UV-vis absorption spectra for the degradation of MB under UV-light irradiation in the presence of ZnS nanospheres as a photocatalyst. It can be seen that the intensity of the MB absorption peak around 664 nm decreases continually with increasing UV-light irradiation time and completely disappears after 25 minutes of irradiation. As presented in Fig. 5b, the degradation ratio of MB shows no significant increase for a long time in the presence of catalyst under dark conditions. A similar result was obtained for the blank control experiment. These results indicate that both light and catalyst are necessary for effective photodegradation of MB dye, and the photoinduced self-decomposition of MB can be ignored in comparison with the photocatalytic degradation caused by the catalyst in the solution. It is worth noting that the as-prepared ZnS nanospheres exhibit remarkable photocatalytic activity toward methylene blue degradation under UV-light irradiation. The degradation ratio of MB can reach up to 99.4% after irradiation for 25 minutes. In addition, ZnS nanospheres show much better activity than common ZnS for the photocatalytic degradation of MB. Compared with common ZnS, the high photocatalytic efficiency of ZnS nanospheres can be ascribed to the larger specific surface area and hierarchical mesoporous structure, which can facilitate the diffusion and mass transportation of MB dye molecules and oxygen-containing radicals during the photocatalysis reaction [**?**].

4. CONCLUSION

In summary, well-crystallized, mesoporous zinc-blende ZnS nanospheres with uniform size were successfully obtained through a simple chemical process. It was found that the as-prepared ZnS nanospheres are assemblies of tiny nanoparticles and exhibit excellent photocatalytic activity with nearly 100% MB degradation efficiency under UV-light irradiation for 25 minutes. The large specific surface area and hierarchical mesoporous structure of the ZnS nanospheres are likely responsible for their excellent photocatalytic activity. The uniform and well-dispersed ZnS nanospheres can be used as a promising photocatalyst and hold great potential for applications in wastewater treatment for the photodegradation of organic pollutants. This work provides insight into designing high-performance photocatalysts by constructing complex architectures.

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Figure Captions

Fig. 1. (a) SEM image, (b) Enlarged SEM image, and (c) EDS spectrum of ZnS nanospheres. (d) SEM image of common ZnS.

Fig. 2. XRD patterns of ZnS nanospheres and common ZnS. Vertical bars at the bottom denote the standard data for a zinc-blende structure of ZnS (JCPDS, No. 05-0566).

Fig. 3. (a) UV-vis absorption spectra of ZnS nanospheres and common ZnS, and (b) Plots of (h)^2 vs. photon energy (h) for ZnS nanospheres and common ZnS.

Fig. 4. Nitrogen absorption-desorption isotherm of (a) ZnS nanospheres and (b) Common ZnS. The insets correspond to the pore size distributions of the samples.

Fig. 5. (a) Time-dependent UV-vis absorption spectra for the degradation of

MB over ZnS nanospheres under UV-light irradiation. (b) Degradation ratios of MB over ZnS nanospheres and common ZnS under UV-light irradiation.

Note: Figure translations are in progress. See original paper for figures.