



Mesoporous $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ microspheres with tunable bandgap and high specific surface areas for enhanced visible-light-driven hydrogen generation



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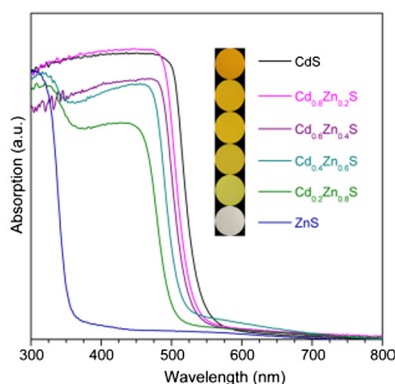
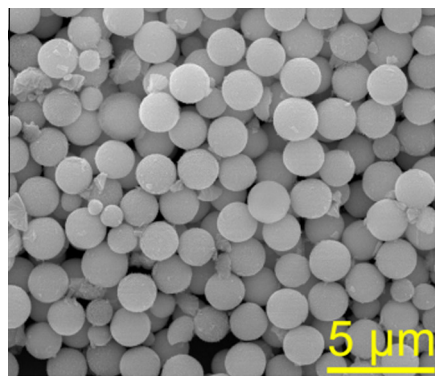
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GRAPHICAL ABSTRACT

Mesoporous $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ microspheres are fabricated via a facile hydrothermal route adopting diethylenetriamine (DETA) as the structure-directing agent and exhibit superb visible-light-driven H_2 production from water.



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ABSTRACT

Visible-light-driven splitting of water using semiconductor photocatalysts is an excellent example of sustainable chemistry. The fabrication of mesoporous photocatalysts with a narrow bandgap into the sunlight region and a high specific surface area is crucial for efficient hydrogen evolution under visible light irradiation. Herein, we describe a facile one-pot hydrothermal approach toward uniform mesoporous microspheres of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ by adopting diethylenetriamine (DETA) as the structure-directing agent. The method is facile, reproducible and allows simultaneously control of the morphology, particle size, bandgaps, as well as the specific surface area of the mesoporous microspheres $\text{Cd}_{1-x}\text{Zn}_x\text{S}$. The photocatalytic activity on H_2 production through the splitting of water without noble metal loading is highly enhanced by the mesoporous structure feature of the products. The optimized $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$ mesoporous microspheres exhibit a specific surface area up to $98.09 \text{ m}^2/\text{g}$ and a H_2 production rate of 3.43 mmol/h g (about 7.62 times higher than that of pure CdS powders) under visible light irradiation. Furthermore, apparent quantum efficiency (QE) of 16.2% was achieved in the as-fabricated $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$ mesoporous

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microspheres under irradiation at 420 nm. This study provides an effective route toward mesoporous microspheres photocatalysts for further investigations and practical applications.

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1. Introduction

Photochemical active semiconductors that can convert light energy into electric energy or fuels have attracted intense recent scientific interests. Numerous research efforts have been focused on the exploration of new materials that can be used directly under solar light to split water into hydrogen and oxygen [1–6]. The desired materials should be low-cost, high-efficiency and exhibit a suitable conduction band for H₂ production and sufficiently narrow bandgap for visible light absorption [2], however, it is not easy to find such a perfect semiconductor. One of the most well-known materials that meet these critical terms is CdS. It has a narrow bandgap of approximately 2.4 eV matching well with the sunlight spectrum and a suitable conduction band position for H₂ reduction, and thus has been used widely for visible-light driven water splitting [7]. To date, the effects to promote the catalytic performance of CdS based materials include: (1) Loading noble metal (such as Pt, Ni) on the CdS surface [8–11]; (2) Coupling with other wide bandgap semiconductors such as TiO₂ [10–14], ZnS [15–18] and metal–organic frameworks (MOFs) [19]; (3) Incorporation of main group elements into the lattice to form a continuous solid solution. Typically, Cd_{1-x}Zn_xS solid solutions have been developed to acquire a larger bandgap than that of CdS and are much more attractive in photocatalytic applications [20–28].

A facile synthesis method under moderate conditions is desirable for the preparation of catalysts with uniform morphologies. To date, Cd_{1-x}Zn_xS can be fabricated through numerous synthesis routes including co-precipitation method [29], microwave syntheses [25], thermolysis [23], hydrothermal methods [24,26], and etc. Among them, hydrothermal route has attracted considerable attention as an easy approach to acquire Cd_{1-x}Zn_xS nanoparticles with numerous morphologies, and also due to the convenience to perform elemental doping and fabrication of heterostructures [30–33]. For example, Wang and Li et al. [25,34] reported the synthesis of Cd_{1-x}Zn_xS nanorods via solvothermal and microwave route. Biswas et al. fabricated Cd_{1-x}Zn_xS nanowires using an ethylenediamine-assisted solvothermal approach [26]. Wang et al. [27] prepared mesoporous Zn_xCd_{1-x}S nanoparticles via a facile self-assembly route and exhibited excellent photocatalytic efficiencies for the degradation of Rhodamine B. Xu et al. [35] synthesized mesoporous Zn_xCd_{1-x}S nanoparticles through selective leaching of amorphous alumina by sodium hydroxide solution from the Al–Zn_xCd_{1-x}S nanoparticles and the products showed an enhanced photocatalytic performance for degradation of methylene blue. The author also proposed that the unique morphology of the as-made Zn_xCd_{1-x}S catalysts benefited from the generation of hydroxyl radicals which also leads to the high photocatalytic activity. However, to be best of our knowledge, uniform Cd_{1-x}Zn_xS microspheres with simultaneous large surface area and tuneable band gaps has not been described yet.

In this work, we demonstrate a one-pot hydrothermal approach to produce mesoporous Cd_{1-x}Zn_xS solid solutions with uniform microsphere morphology. After contrastive investigations of various organic solvents and different experimental conditions, a reproducible process adopting diethylenetriamine (DETA) as the structure-directing agent has been established to synthesize mesoporous Cd_{1-x}Zn_xS microspheres. The as-obtained Cd_{1-x}Zn_xS materials showed large specific surface area and controllable

bandgaps, endowing them superb visible-light-driven H₂ production from water without any cocatalyst.

2. Materials and methods

2.1. Synthesis of mesoporous Cd_{1-x}Zn_xS microspheres

In a typical synthesis procedure, given amount of Cd(NO₃)₂·4H₂O and Zn(NO₃)₂·6H₂O in different Cd/Zn molar ratios were dissolved in 20 mL aqueous solution with different H₂O/DETA volume ratios, the total amount of Cd(NO₃)₂·4H₂O and Zn(NO₃)₂·6H₂O is 2 mmol, after constant stirring for 15 min at room temperature, 2 mmol cysteine (Cys) was slowly added with stirring for another 15 min. After heated at 180 °C for 24 h, the autoclave was cooled down to the room temperature and the products were collected by centrifugation and washed three times with distilled water and ethanol.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of all the samples were collected at room temperature on a Bruker D8 Advance diffract meter using a germanium monochromatic (Cu K α radiation, 40 kV and 40 mA). The data for phase identification were taken in the 2 theta range between 10° and 60° and with the remaining time of 0.1 s/step. Scanning electron microscope (SEM) images were recorded using a Quanta 250 FEG FEI at 30 kV in gentle-beam mode without any metal coating. Transmission electron microscope (TEM) images and high-resolution transmission electron microscopy (HRTEM) were recorded on a Tecnai G2 20 TEM with an accelerating voltage of 200 kV using a carbon-coated copper grid to obtain detailed insight into the microspheres morphology. The nitrogen adsorption–desorption isotherms and the corresponding Barret–Joyner–Halenda (BJH) pore size distribution curves were studied by N₂ adsorption–desorption measurements (ASAP 2020) at liquid nitrogen temperature. Before analysis, the samples were degassed in vacuum at 200 °C for 6 h. UV–vis diffuse reflectance spectra were measured by using a U-4100 UV–Vis–NIR spectrometer (Hitachi). Fourier transform infrared (FTIR) spectra were obtained on a Thermo Scientific Nicolet iS5 infrared spectrophotometer using KBr discs, with 32 scans average within scan range of 4000–400 cm⁻¹ and a resolution of 4 cm⁻¹. The Cd and Zn contents of Cd_{1-x}Zn_xS photocatalysts were measured by ICP-AES (Optima2000DV, USA). X-ray photoelectron spectroscopy (XPS) data were determined by photoelectron spectrometer using Al K α X-ray sources (Axis Ultra DLD, Kratos).

2.3. Photocatalytic activity tests

The photocatalytic reactions were carried out at room temperature in a closed photoreactor using a 300 W Xe lamp (420 ≤ λ ≤ 780 nm). The rate of H₂ production was measured in an aqueous solution (100 mL) containing 50 mg of catalyst and 40 mM Na₂S + Na₂SO₃. H₂ gas was analyzed by gas chromatograph (TCD, nitrogen as a carrier gas and 5 Å molecular sieve column). To evaluate the stability of the photocatalysts, the sampling and online analyses were conducted at regular intervals (4 h) by evacuating the

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