



# General strategy for one-pot synthesis of metal sulfide hollow spheres with enhanced photocatalytic activity

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## ABSTRACT

A gas bubble-templating method has enabled synthesis of a diverse portfolio of hollow transition-metal sulfides microspheres (e.g., CdS, ZnS, CuS and Bi<sub>2</sub>S<sub>3</sub>) by a general one-step route. The products were characterized by X-ray powder diffraction, scanning and transmission electron microscopy, high-resolution transmission electron microscopy, energy dispersive spectroscopy analysis, N<sub>2</sub> adsorption and UV–vis diffuse reflectance spectroscopy. The shell of all hollow spheres is composed of single-crystal metal sulfide nanoparticles and the shell thickness can be readily controlled by changing the deposition time. These hollow microspheres are envisioned to have broad applications in catalysis, Li-ion batteries, microreactors, biomedicines, etc. As an example, here, we demonstrate that the prepared CdS and ZnS hollow sub-micrometer spheres are excellent photocatalysts with higher photodegradation efficiency of potential polluting agents than that of commercial CdS, ZnS and TiO<sub>2</sub> P25 under visible light and UV light illumination, respectively.

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## 1. Introduction

Hollow structured micro- or nanoscopic materials have recently attracted special attention due to their superior properties such as lower density, higher specific surface area, similarity to cells and membranes, and better permeability compared to their solid counterparts [1–8]. These outstanding properties make them promising for a series of applications such as drug-delivery systems [9,10], lithium-ion batteries [5,11–13], and catalysts [14–16]. To present, various hollow spheres including carbons, polymers, metals and inorganic materials have been extensively investigated. Transitional metal sulfide hollow spheres are of particular interest for potential applications in the field of optics, electronics, and optoelectronics [17–19].

Traditionally, template-directed methods have included hard templates (e.g., silica spheres, carbon spheres, and metal nanoparticles) [1,5,7,8,14,20,21] and soft templates (e.g., micelles, emulsion droplets, liquid drops, and even bacteria) [22–26] to prepare micro- or nano-sized hollow spheres. However, the following inherent drawbacks greatly restricted their practical application: (i) these template-assisted methods often suffer from difficulty of coating the desirable materials on the template surface due to materials

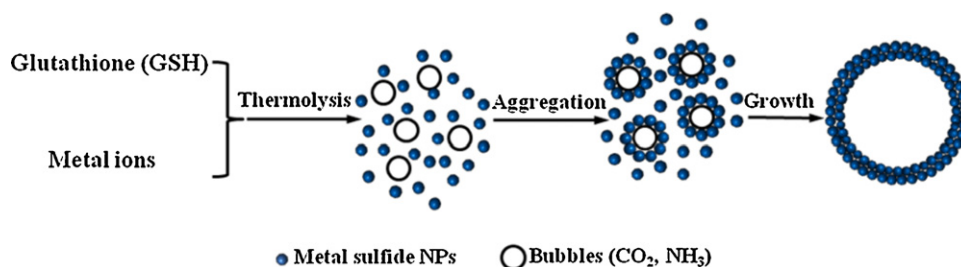
incompatibility issues, thus they are often only suitable for very specific applications; (ii) these template-assisted methods often require large quantities of surfactants and involve tedious operational procedures related to the repeated application of coatings and final removal of the templates; (iii) if the sacrificial template is removed by calcinations or solvent extraction, collapse and high non-uniformity of some fraction of the hollow structures is very likely. Therefore, developing a facile, economic and general synthesis strategy for one-step synthesis of various hollow spheres with no additional core removal step is of great importance and still a major challenge for material scientists.

The in situ gas-bubble template synthesis strategy [27–31] is a new method having the advantage of synthesizing hollow spheres in one-step approach, negating the template removal step in hollow material preparation which may effectively solve most of the above problems. As compared to the other template-synthetic methods, this new method is very simple, convenient and avoids the introduction of impurities. For example, ZnSe hollow spheres were synthesized under hydrothermal conditions using hydrazine as the reducing agent, from which N<sub>2</sub> bubbles were generated and acted as soft template [32]. However, major unsolved challenges for gas-bubble templated methods is improving reproducibility, gaining control of tuning chemical composition, and controlling the interior architecture by a general procedure.

Hierarchical hollow materials are most commonly prepared by use of templates, the removal of which is typically done by

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**Scheme 1.** Schematic illustration of the formation of the transition-metal sulfides hollow sub-micrometer spheres.

calcinations (or chemical etching) often leading to multi-step time-consuming procedures and often non-uniformity of the product. One approach towards more efficient non-sacrificial templating is to use gas bubbles. A gas bubble assisted method may open an exciting perspective for one-step synthesis of hollow materials owing to its efficient, economical and environmentally friendly characteristics. However, a key limitation of this technology thus far is its poor reproducibility and that the chemical composition of the final phase cannot be readily controlled. In this letter, we demonstrate a general one-pot synthesis of hollow sub-micrometer spheres of transition-metal sulfides as summarized in Scheme 1. In our synthesis route, the polypeptide glutathione (GSH), functions as a direct sulfur source for metal sulfide nanocrystal formation and also produces  $\text{CO}_2$  and  $\text{NH}_3$  bubbles during the reaction that are crucial to the formation of the hollow interiors. At an elevated temperature, the primary metal sulfide nanoparticles were formed by thermolysis of metal ions – GSH. Meanwhile, the gas bubbles of  $\text{CO}_2$  and  $\text{NH}_3$  were generated to provide the assembly centers during the reaction. Driven by the minimization of interfacial energy, the fresh-formed crystalline metal sulfide nanoparticles are unstable because of their high surface energy and they are thermodynamically favored to aggregate at the gas–liquid interface between the bubble and water [27–32]. A continuous aggregation process occurs at the gas–liquid interface and ultimately results in the formation of hollow metal sulfide spheres. Here, the energy ( $E$ ) needed for the detachment of a nanoparticle from the bubble interface could be estimated as [33]:

$$E = \pi r^2 \gamma (1 - \cos \theta)^2 \quad (1)$$

where  $r$  is the radius of the nanoparticles,  $\gamma$  is the surface tension of the bubble interface, and  $\theta$  is the contact angle of the liquid. Theoretical calculation shows that  $E$  is much larger than the thermal energy (the detailed calculation process is well described in Ref. [28]) of the nanoparticle, and thus these aggregated particles have little chance to escape from the bubble surface [28]. As an example, CdS, ZnS, CuS and  $\text{Bi}_2\text{S}_3$  hollow spheres here were taken as model materials to demonstrate the strategy.

## 2. Experimental

### 2.1. Synthesis of metal sulfide hollow spheres

All chemicals were analytical grade (purchased from Aladdin) and were used as received without further purification. In a typical synthesis, 5.5 mmol  $\text{Cd}(\text{NO}_3)_2$  and 5.5 mmol glutathione (GSH,  $\text{C}_{10}\text{H}_{17}\text{N}_3\text{O}_6\text{S}$ ) were dissolved in 250 ml deionized water to form a clear solution after stirring for 30 min at room temperature. After transfer to an autoclave with an inner quartz sleeve, the autoclave was purged with nitrogen for 10 min to eliminate oxygen in the autoclave, and then a pressure of 10 bar nitrogen was introduced into the autoclave. The clear solution was heated to  $200^\circ\text{C}$  and kept for 5–10 h, then allowed to cool to room temperature naturally. The obtained yellow CdS precipitate was washed with absolute acetone

several times, and finally dried at  $60^\circ\text{C}$  for 6 h in a vacuum. The same procedures are applied to synthesize ZnS, CuS and  $\text{Bi}_2\text{S}_3$  hollow sphere samples when zinc nitrate, copper nitrate and bismuth nitrate was used as zinc source, copper source, and bismuth source, respectively.

### 2.2. Characterization

The crystalline structure of the catalysts was characterized by powder X-ray diffraction (XRD) employing a scanning rate of  $0.05^\circ/\text{s}$  in a  $2\theta$  range from  $10^\circ$  to  $80^\circ$ , in a Bruker D8 Advance using monochromatized  $\text{Cu K}\alpha$  radiation.

Scanning electron microscopy (SEM) was performed with a S4800 field emission SEM (FESEM, Hitachi, Japan) at an accelerating voltage of 5 kV. The SEM was linked to an Oxford Instruments X-ray analysis system.

The morphology and particle size of catalysts were analyzed by transmission electron microscopy using a Tecnai G20 (FEI) TEM operated at an accelerating voltage of 200 kV. HRTEM and electron diffraction data are collected using a FEI Titan TEM operated at 300 kV.

The UV–vis DRS were collected using a Shimadzu UV-2450 spectrophotometer from 200 to 800 nm using  $\text{BaSO}_4$  as background.

The nitrogen adsorption measurements were done on a Micromeritics ASAP 2010 physisorption apparatus.

### 2.3. Photodegradation experiment

The photoactivity of the samples was tested by the degradation of Rhodamine B ( $50\text{ ml}$ ,  $1 \times 10^{-5}\text{ mol L}^{-1}$ ) and salicylic acid ( $50\text{ ml}$ ,  $20\text{ mg L}^{-1}$ ) under visible light ( $>420\text{ nm}$ ) or near UV ( $365\text{ nm}$ ) irradiation. In a typical experiment, 50 mg photocatalyst was suspended in RhB or salicylic acid solution, then the mixed solution was oscillated in darkness for 5 h. After reaching adsorption equilibrium, the photocatalytic reaction was initiated by irradiating the system with a 350 W Xenon lamp. At given time intervals, 4 ml aliquots were collected, centrifuged, and then filtered to remove the catalyst particles for analysis. The filtrates were finally analyzed using a UV–vis spectrophotometer (UV-2450). For comparison, the photocatalytic activity of commercial CdS (or ZnS) powders (Aladdin reagent) and Degussa P25 were also tested at the same experimental conditions.

### 2.4. Analysis of hydroxyl radicals ( $\bullet\text{OH}$ )

The production of  $\bullet\text{OH}$  on the surface of vis-illuminated CdS hollow spheres was detected by a photoluminescence (PL) method using coumarin as a probe molecule. Coumarin can readily react with  $\bullet\text{OH}$  to produce highly fluorescent product, 7-hydroxycoumarin (7HC) (umbelliferone) (see Scheme S1 in Supporting information). Experimental procedure was similar to the measurement of photocatalytic activity. In a typical process, CdS hollow spheres (50 mg) and coumarins ( $50\text{ ml}$ ,  $5 \times 10^{-4}\text{ mol L}^{-1}$ ) were mixed under magnetic stirring for 4 h under dark conditions.

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