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Abstract

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Keywords

nanosheet, light, driven, cus, free, synthesis, hierarchical, photocatalyst, template, microspheres, efficient, natural

Disciplines

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Well controlled nanosheets-based hierarchical microspheres (NSHMS) of pure covellite phase CuS were synthesized using a facile PVP assisted solvothermal process. The reaction conditions were optimized using various amounts of PVP to develop unique hierarchical structured hollow microspheres. CuS hollow structures have a bandgap of ~1.97 eV. These mesoporous structures exhibit excellent photocatalytic activity in degradation of organic dyes (Methylene Blue) under natural light in comparison to other structures of copper sulphide. These photocatalysts show extraordinary reusability with over 96.5% degradation of organic dye after 6th cycle. A “bottom-up” assembly was successfully developed to synthesize hollow microspheres with unique and well defined architectures at large scale, which offer a good opportunity to understand the fundamental significance of unusual and complex hierarchical structures for their potential applications.

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Introduction

It is well known fact that both physical and chemical properties are significantly affected by the structure, size, morphology, composition and crystallinity of materials.¹ Moreover, inorganic micro- and nanostructures with hollow interiors are attracting ever increasing attention owing to their unique properties, such as distinctive morphology, large surface area, void space, good surface permeability, low density, low coefficients of thermal expansion and refractive indexes.^{2–5} Particularly, hierarchically structured spheres stimulate extensive research interest owing to their unusual structural features and extraordinary optical/electrical behaviour which can bring wide potential applications in numerous fields such as catalysts, drug-delivery carriers, sensors, biomedical diagnosis agents, rechargeable batteries and chemical reactors, *etc.*^{6–9} Tremendous interest in the synthesis of nano- or microstructures and hierarchically structured spheres has been aroused. The conventional approaches to preparation of hollow structures with different shapes have involved the use of various removable or sacrificial templates, including hard ones (*e.g.*, metal nanoparticles, silica spheres, and carbon spheres)^{10,11} and soft ones (*e.g.*, liquid drops, micelles, emulsion droplets, and even bacteria).^{12–14} A diverse portfolio of

hollow structures were prepared by template methods and typically physicochemical routes for CuS semiconductor.^{15,16} However, the above-mentioned typical approaches to fabrication of hollow CuS architectures might inevitably increase reaction complexity, suffer tedious synthetic procedures, mostly cause impurities in the products.

Currently, most of the obtained hollow spherical architectures have polycrystalline shells.¹⁷ Therefore the structural and morphological tailoring of the shells of hollow architectures have been an exciting challenge for material design because of the special shape- and structure dependent effects, which would effect significant scientific values and widespread potential applications. Mesocrystals, as a new class of fashionable highly ordered unique superstructures, have been successfully elucidated by Colfen *et al.* for the growth of minerals *via* a non-classical oriented attachment and mesoscale transformation.^{18,19} It is a unique colloid crystal composed of individual nanocrystals as the building units that are aligned in a common crystallographic fashion with notable internal porosity, as well as exhibiting elongated diffraction spots resembling those of a single crystal.²⁰ The study of mesocrystals is not only helpful for constructing the novel morphology by using anisotropic building blocks but also for providing a new opportunity to construct multifunctional materials with potentially unique and exciting properties.

However, to the best of our knowledge, the template free and shape controlled synthesis of hollow and hierarchical mesoporous microspheres, which can exhibit excellent

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physical and chemical properties, have rarely been reported. Consequently, to develop a template free hollow material with hierarchical and unique building blocks is a topic of great interest for researchers.

As a non-stoichiometric p-type semiconductor with unique optical, electric and thermal properties,^{3,4} covellite (CuS) is an important semiconductor material with prospective and numerous applications such as solar cells, optical filters, nanoswitches, thermoelectric and photoelectric transformers, superconductors, gas sensors, lithium-ion batteries and photo catalysis.^{3–5,13,16} Recently, many efforts have been devoted to fabricating covellite CuS in different shapes such as hollow spheres²¹ plates,²² rods,²³ tubes,²⁴ wires,²⁵ flowers,²⁶ *etc.* Therefore, a large number of fabrication methods have been explored including chemical vapor deposition, thermolysis, hydrothermal or solvothermal, ultrasonic and microwave irradiation, as well as microemulsion, electrodeposition and template-assisted methods^{21–29} have also been employed in this regard.

Herein, we present evidence of the controlled and large scale synthesis of CuS hollow and hierarchical microspheres with unique complex and unusual structures, considerable high specific surface area with entire nanosheets building blocks through a simply PVP derived solvothermal technique. The study has great importance in the “bottom-up” assembly of well ordered CuS hollow hierarchical microspheres, and offers good opportunity to understand the fundamental significance of hollow mesoporous microspheres with nanosheet building blocks, displaying excellent natural light driven photocatalyst properties.

Experimental

Sample preparation

Mesoporous-structure hollow spheres with nanosheet building blocks were synthesized through a surfactant mediated solvothermal pathway and without using any prefabricated template. All reagents (analytical-grade purity) used in this work were purchased from the commercial market, and were used without further purification. In a typical experimental process, 2 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 2 mmol of thiourea were each separately dissolved in 20 mL ethylene glycol (EG), and stirred until they were dissolved totally to obtain a clear solution. Then the two solutions were mixed under stirring. Afterwards, 2.0 g polyvinylpyrrolidone (PVP K-30, $M_w = 58\,000$) was added to the solution under vigorous stirring. The solution was then transferred into a 50 mL Teflon-lined autoclave, sealed and heated at 160 °C for 24 h. The final solid products were collected by centrifugation at 8000 rpm for 3 min and washed more than 6 times with de-ionized water, absolute ethanol and acetone, to dissolve any excess surfactant present, and afterward dried at 80 °C for 6 h in vacuum and collected in the form of dark-blue powder. In comparative experiments, in order to observe the growth mechanism and effect of PVP, the same

experiment was repeated with different concentrations of PVP (PVP = 0.0, 0.5, 1.0, 1.5), different sulfur, copper sources and a variety of solvents, while the precursor ratios and all other experimental conditions were kept the same as the typical experimental process. The as prepared products were then characterized through different characterization techniques, and superior photocatalytic properties of as prepared NSHMS were witnessed.

Characterization

The structure, phase purity and chemical composition of the products were examined by X-ray powder diffraction (XRD, Philips 'XPert Pro MPD) with CuK α radiation ($\lambda = 0.15406$ nm), X-ray photoelectron spectroscopy (XPS), energy dispersive spectroscopy (EDS). The morphologies of the products were examined by scanning electron microscopy (SEM, Hitachi TM-1000). Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analysis were conducted using a FEI Tecnai-T20 electron microscope (FEI, USA) with a 200 kV accelerating voltage. The optical properties of as prepared products were ascertained at room temperature using ultraviolet–visible–near infrared (UV–vis–NIR) transmittance spectrophotometer (U-4100) and photoluminescence spectroscopy (Hitachi FL-4500 Fluorescence Spectrophotometer). The Brunauer–Emmett–Teller (BET) specific surface area of the as prepared powders was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA).

Photocatalytic activity evaluation

Methylene Blue (MB) is a popular probe molecule in heterogeneous catalytic reactions because of being a typical dye resistant to biodegradation and direct photolysis. For the evaluation of catalytic activity, experiments for the oxidation and de-coloration of the MB dye with the assistance of hydrogen peroxide (H_2O_2) were carried out under natural light at ambient temperature. The original solution was prepared by adding 3 mL H_2O_2 (30%, w/w) and 3 mL MB solution (400 mg L^{-1}) in 100 mL of de-ionized water, then 20 mg of the as-prepared CuS mesoporous hierarchical microspheres with nanosheet building blocks was added to the solution to form aqueous dispersion. The solution was magnetically stirred in the dark for 30 min to ensure establishment of adsorption–desorption equilibrium before illumination. Afterwards, the dispersion was irradiated by natural light during continuous magnetic stirring. Then during given time intervals, about 4 mL of the suspension was taken from the reactor and centrifuged to separate the catalyst. The UV–vis absorption spectra were recorded at different intervals and the characteristic absorption peak at 604 nm of MB was monitored to follow the catalytic degradation process using a UV/vis/NIR spectrophotometer (Hitachi U-4100).

Results and discussion

Structural and morphological characterizations

The phase purity and crystallinity of the as prepared CuS products was characterized using an XRD technique. As shown in Fig. 1, all diffraction peaks match well the standard data of covellite-type CuS with hexagonal lattice parameters of $a = 3.7920 \text{ \AA}$, $b = 3.7920 \text{ \AA}$, $c = 16.3440 \text{ \AA}$ (covellite, syn, JCPDS no: 00-006-0464).

The XRD pattern shows that the products are devoid of any detectable impurities or any other copper sulphide phases such as $\text{Cu}_{1.96}\text{S}$, $\text{Cu}_{1.94}\text{S}$, $\text{Cu}_{1.8}\text{S}$, Cu_7S_4 , and Cu_2S indicating high purity of the obtained products. Moreover the strong and sharp diffraction peaks of NSHMS are obviously due to its much better crystallinity as compared to the other as synthesized products. The energy-dispersive spectra (EDS) analysis of the as prepared product NSHMS are shown in Fig. 3d and demonstrate that the chemical components only consist of Cu and S elements with an atomic ratio ($\text{Cu}:\text{S} = 1:1$), in agreement with the above XRD result.

XPS analysis of NSHMS was carried out to confirm the composition and purity of the as prepared product. The full spectrum, shown in Fig. 2a indicates the presence of Cu, S along with C, N and O peaks. The presence of the C and N peaks is derived from PVP molecules, the peak O may also be due to the absorption of air on the surface of the NSHMS. Fig. 2b represents a high resolution spectrum of Cu 2p and it is obvious that the presence of two strong peaks at 932.6 and 952.5 eV for Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively, separated by 20.0 eV are essentially identical binding energies for the Cu 2p orbital in accord with Cu(II) .³⁰ In addition, a small chemical shift about (0.3 eV) occurs compared to elemental copper. In Fig. 2c, the high resolution survey at the S 2p region shows a presence of two peaks at 162.6 and

Fig. 1 XRD spectra of as prepared CuS products; (a) CuS non-spherical aggregate, (b) hollow microspheres with rough surfaces, (c) NSHMS of CuS.

Fig. 2 XPS spectrum of the as-synthesized CuS NSHMS. (a) XPS spectra of the survey of as-synthesized CuS NSHMS. (b) XPS spectra of close-up survey in the Cu 2p region. (c) XPS spectra of close-up survey in the S 2p region.

163.5 eV, all these peak positions are well matched with literature.³¹ The Cu/S ratio was calculated from the peak areas of Cu and S-cores, the value was found to be 1.04, closely matching the Cu/S value (1.0) estimated from EDS analysis.

Fig. 3 displays typical SEM images of the as prepared NSHMS obtained in the presence of a large concentration of PVP = 2.0 g, at different magnifications. From the low-magnification SEM result (Fig. 3a), it is obvious that CuS microspheres have a high yield, excellent spherical architectures and fully exposed with amazingly unique nanosheets as building blocks at large scale. The images in Fig. 3b clearly indicate all of the spheres are well defined, quite consistent and separately displaced. The presence of microspheres with open structures as presented in Fig. 3b, indicate that microspheres with hollow interior are formed. The inset of Fig. 3b displays a cross sectional view of NSHMS, two partitions of a broken hollow microsphere with curvy interior describes the hollow nature of the NSHMS. And the edges of broken spheres clearly indicate the nanosheets accumulated threading within the entire shell walls of NSHMS. In the corresponding magnified image in Fig. 3c, it can also be ascertained the spheres are threaded identically with nanosheets, hollow in nature and the nanosheets are well

Fig. 3 (a) Large scale SEM image of CuS NSHMS. (b) SEM image of CuS NSHMS (inset is the cross sectional view of CuS NSHMS). (c) High magnification SEM image of CuS NSHMS. (d) EDS spectrum of as prepared NSHMS.

interconnected. The average diameter of the microspheres is about *ca.* 2.3 μm .

Further detailed structural characterizations of as prepared CuS NSHMS were performed by TEM and HRTEM. Fig. 4a displays the TEM image of the as prepared NSHMS with a strong contrast between the dark edge and the pale center is an obvious evidence of their hollow nature and cavities within the entire shell walls of the hollow hierarchical architectures. From the high magnification TEM image of NSHMS (inset of Fig. 4a), it is clear that the shell of the hollow microsphere is composed of nanosheets having a thickness of a few nanometers and threaded in a well defined manner within the entire shell walls of NSHMS, being in agreement with SEM results. The HRTEM image conducted on the scattered nanosheets is given in Fig. 4b. From the top view of the HRTEM image, the regular spacing of the clear lattice planes is calculated to be 0.311 nm, which is in good agreement with the interlayer spacing's of (102) crystallographic plane of hexagonal CuS, being consistent with the orientation of the nanoplatelet, reported by Li *et al.*³²

Fig. 4 (a) TEM image of CuS NSHMS, (inset is the high magnification TEM image of CuS NSHMS) (b) HRTEM image of CuS NSHMS (inset is the SAED pattern of CuS NSHMS).

To further investigate the crystallographic features of the as prepared product, the scattered area electron diffraction (SAED) pattern (Fig. 4b, inset) was recorded which displays a clear image of lattice fringes well-matching with XRD results, indicating the good crystalline nature of CuS NSHMS, as having a hexagonal crystal structure. The formation of NSHMS started from a nucleus directed by PVP which acted as a structure directing agent. As soon as the PVP concentration reached the optimized amount, these nuclei started to grow in specific directions to form sheets which then joined together to form highly connected structures by a self-assembly involving bending and aggregation as suggested by Fang *et al.*³³ Furthermore, the well-defined spots in the SAED spectra illustrate the perfect growth of CuS single crystals. Thus, these observations confirmed that microspheres have same crystallographic orientation along the nanosheet axis as a perfect single crystal.

Effect of solvent

To investigate the effect of the solvent on the formation of CuS NSHMS, a series of comparative experiments was carried under similar conditions utilizing a variety of solvents. It was found that the solvent has a significant influence on the morphology of the as-synthesized CuS products, since different solvents have different viscosities, dissolution capability and chemical nature as well, such as ethanol, ethylene glycol and dimethyl formamide.

Fig. 5 depicts the SEM images of the product obtained using different reaction media. Almost spherical and hollow structures have been produced with various sizes and shapes using diethylene glycol (Fig. 5a) as solvent, some of the structures have nearly nanofibers built in within the outer shells and some appear to be in the form of rattle like architectures. Fig. 5b shows the effect of ethylenediamine, the product consists in mixed architectures of spherical and hierarchical

Fig. 5 SEM images of as prepared products using different solvents, under the same typical experimental conditions. (a) Diethylene glycol (DEG). (b) Ethylenediamine. (c) Water (d) dimethyl formamide (DMF).

structures with inconsistency in shape and size. Additionally, the spherical structures also contain randomly aggregated platelets. While the product obtained uses water as the reaction medium (Fig. 5c), it is composed of spherical architectures, randomly displaced particles with inconsistent shape and size. In the presence of dimethyl formamide (DMF) as a solvent, hierarchical architectures were obtained as shown in Fig. 5d. Flower like aggregation of hierarchically aggregated nanoplates was observed, confirming that water is not a good solvent to develop high quality and well defined hollow microspheres.

Overall, no regular architectures were observed and none of the experiments are compatible to produce hollow architectures with well defined building blocks. Therefore, it can be concluded that the reaction medium has a great influence on the morphology and size of the CuS products, and the ethylene glycol solution because having two symmetrical hydroxyl groups seems to be crucial for the formation of symmetrical CuS NSHMS. It is likely that the symmetrical structure of the hydroxyl group creates symmetrical CuS architectures.

Effect of sulfur and Cu^{2+} sources

It is worth mentioning here that copper sources and sulfur sources have different release rates of Cu^{2+} and S^{2-} ions, consequently effecting greatly the final morphologies of CuS. To explore the influence of various copper and sulfur sources on the morphologies of CuS under the same reaction conditions as those of a typical experimental process with the same molar ratios Cu:S (1:2), Cu^{2+} sources with different anions such as cupric sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), cupric acetate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 5\text{H}_2\text{O}$) instead of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and sulfur sources such as sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), thioacetamide (H_3CCSNH_2) were used instead of thiourea.

Fig. 6a depicts a SEM image of the product obtained while utilizing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as the copper source, all of the particles

obtained appear to be randomly displaced in irregularly shaped particles and a few of the particles seem to be in the form of spherical shapes, whereas when $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 5\text{H}_2\text{O}$ was adopted as the Cu^{2+} source (Fig. 6b) well organized spherical and hollow architectures were obtained, but still some randomly aggregated structures were also present within the product.

Fig. 6c displays a SEM picture of the product using $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ as the sulfur source. Almost the entire product consists of randomly aggregated particles and none of the hollow and spherical structures are present. Usually, when $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was introduced into EG, it dissociated into Na^+ and S^{2-} immediately, and therefore the formation of CuS nuclei occurred rapidly. Then CuS nuclei grew in an explosive way to form CuS particles, resulting in aggregation, whereas thioacetamide readily releases S^{2-} , but the concentration of S^{2-} is a little lower than S^{2-} released from Na_2S . When thioacetamide was introduced into the reaction system (Fig. 6d), weak anisotropic growth resulted in small nanoparticles as well as hollow structures with rough surfaces. The spherical architectures are inconsistent in shape and size, and some of the structures seem to have attached particles on their surfaces.

Overall, among the comparative experiments, neither the use of other Cu^{2+} sources with different anions such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 5\text{H}_2\text{O}$ nor the use of other sulfur sources such as sodium sulfide and thioacetamide lead to formation of amazingly well-defined hierarchical hollow microspheres.

Effect of PVP and formation of NSHMS

A polyol process, which mainly focused on the use of ethylene glycol (EG) as the reaction medium, has been adopted in the synthesis of mono-dispersed metal powders for more than 2 decades. The polyol not only serves as the solvent for starting chemicals due to their rather high dielectric constants and boiling points, but also acts as a reducing agent. A modified process in the presence of additives such as polyvinylpyrrolidone (PVP) has recently been reported for the shape control of noble metal sulfide nanostructures.^{34,35} PVP is also demonstrated to be a weak reducing agent in addition to a conventional stabilizer.^{36,37} It is notable that the copper-thiourea aqueous system has also been utilized to generate CuS nanomaterials with various forms and compositions.³⁸

In the present work, thiourea (Tu) firstly coordinates with $\text{Cu}(\text{NO}_3)_2$ to produce Tu-copper(II) complexes, which can be observed *via* a simple color change of the solution. After introducing PVP to the reaction mixture, the Cu^{2+} ions are also attracted by PVP to form a copper(II)-PVP complex. Under the solvothermal treatment in the presence of ethylene glycol (EG), Tu in the solution is decomposed at a certain temperature. So S^{2-} ions are then released through decomposition of thiourea and then the dissolved Cu^{2+} ions react with S^{2-} to form CuS nuclei. In a subsequent step, in the absence of PVP these nuclei preferentially grow in the same direction

Fig. 6 SEM images of the as prepared products using different copper and sulfur sources, under the same typical experimental conditions. (a) Cupric sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). (b) Cupric acetate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 5\text{H}_2\text{O}$). (c) Sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$). (d) Thioacetamide (H_3CCSNH_2).

Fig. 7 SEM images of the as prepared products of CuS with different concentrations of PVP. (a) PVP = 0.0 g (CuS non spherical aggregate). (b) PVP = 0.5 g. (c) PVP = 1.0 g (hollow microspheres having rough surfaces, inset is the cross-sectional view). (d) PVP = 1.5 g (inset is the cross-sectional view of hollow microspheres having nanosheet building blocks).

and are further transferred into randomly aggregated microstructures. Fig. 7a shows SEM images of the as prepared product in the absence of PVP, aggregated particles with irregular shape were found with some partially grown microspheres and no spherical hollow structure is present within the entire product.

PVP is a multifunctional polymer in this system, which is used as a stabilizer and a capping agent.³⁹ In the present study, the effect of PVP was explored by adjusting different amounts of PVP and a proposed growth mechanism was shown in a schematic diagram, Fig. 8. Inhomogeneous particles were obtained without PVP, and the product was named CuS non-spherical aggregate, but with addition of 0.5 g PVP into the EG solution the resulted product consists of irregular spherically aggregated microstructure with spherical particles attached on their surface (Fig. 7b). The isolated particles and hierarchical microstructures are absent within this PVP modified product. Fig. 7c depicts the product prepared using 1.0 g of PVP, it consists of a high yield of hollow microspheres having a variable size and shape. A few microspheres are found with hollow interior and opening, moreover the

cross sectional view (inset of Fig. 7c) of a broken hollow microsphere confirms the formation of hollow microspheres with a rough surface. The diameter of these microspheres varies within *ca.* 3–6 μm and no aggregated microstructures are present within this as prepared product.

These results indicate that the PVP acts as stabilizer to prevent agglomeration of the nanoparticles and helps the formation of spherical structures. With further increasing the amount of PVP to 1.5 g the formation of spheres with nanosheet building blocks was achieved, as presented in Fig. 7d. Moreover, the inset of Fig. 6d verifies the hollow interior and nanosheets built in along the entire shell walls of the microsphere. But still some spheres have rough surfaces and inconsistencies in shape and size can also be seen within the product. More increment in PVP results in a more refined morphology, so extending the same process onward and using PVP = 2.0 g, a high yield of hollow microspheres highly consistent in shape and size was achieved. It is noticed that due to an increment of PVP the diameter of the spheres decreased and concentrated threading of nanosheets on the entire shell walls of spheres was produced. The change in diameter and nanosheets threading within the entire shell walls of hollow microspheres may be ascribed to the regulation of viscosity and diffusion coefficient of the reaction system while adjusting the amount of PVP.

Optical properties and BET surface area

Fig. 9a represents an absorption spectrum in the range of 300–850 nm of NSHMS dispersed in ethanol. Increased absorption is ascertained in the near-IR region, which is a characteristic of covellite copper sulfide^{40–42} because of the inter-band transitions (absorptions) from valence states to unoccupied states.^{43,44} According to the equation $\alpha E_p = K(E_p - E_g)^{1/2}$, a plot of $(\alpha E_p)^2$ vs. E_p was based on direct transition as shown in the inset of Fig. 9a. The extrapolated value of E_p at $R = 0$ gives absorption edge energies corresponding to $E_g = 1.97$ eV, which is to some extent larger than the reported value for bulk CuS ($E_g = 1.85$ eV). It can be observed that a larger blue shift absorption profile has occurred, which might be attributed to the quantum size effects, as from TEM images the nanosheets which are the building units of NSHMS, are thinner than 20 nm. So the quantum confinement is obvious in this case.⁴⁵

The photo luminescent (PL) property of CuS is of great interest because of its excellent photoconductive, photovoltaic and rectifying response under illumination. The room temperature PL activity is investigated exploiting ethanolic dispersion of the as-prepared NSHMS of CuS. The PL spectrum (Fig. 9b) showed broad emission peaks in the 462 nm (2.68 eV) region under an excitation wavelength of 370 nm (3.35 eV). Although Jiang and co-workers⁴⁶ reported that there is no emission peak for CuS in the range of 400–800 nm, our result is very consistent with the PL result reported by Ou *et al.*⁴⁷ According to them, various morphologies of copper sulfide may be responsible for this unique phenomenon of

Fig. 8 Growth mechanism for the formation of NSHMS of CuS.

Fig. 9 (a) UV-Visible absorption spectrum of CuS NSHMS. (inset) Band gap energy of NSHMS of CuS. (b) PL spectrum of as-prepared NSHMS of CuS.

PL. However, from the reported literature it can be suggested that the nature of the emission spectrum of CuS depends on the morphology and inherent structure of the samples.^{43,48} Thus, the excitonic emission herein is because of the high optical quality of NSHMS of CuS.

To be a good candidate for a photocatalyst, its specific surface area is most important. Normally, the larger surface area of the catalyst will result in higher photocatalytic activity⁴⁹ since higher specific surface area can provide more active catalytic sites for photocatalytic reactions. The Brunauer–Emmett–Teller (BET) specific surface area of synthesized CuS products was investigated by nitrogen adsorption–desorption measurements. Fig. 10a shows the nitrogen adsorption–desorption isotherms of as prepared CuS products. The BET surface areas of the CuS NSHMS, CuS hollow microspheres with rough surfaces and CuS non spherical aggregate were measured to be 36, 14.0 and 3.8 m² g^{−1}, respectively. The BET surface area of NSHMS was found to be higher than the other as-mentioned CuS products. Moreover, the spherical architectures appeared to be having double pore size (Fig. 10b). The unique double pore structures along with considerable high surface area make a photocatalyst promising candidate as a catalyst for the degradation of dye pollutions in wastewater.

Photocatalytic properties

To demonstrate the potential application of as-synthesized NSHMS in the degradation of organic contaminants, we have investigated their photocatalytic activities by choosing the photocatalytic degradation of MB dye in the presence of hydrogen peroxide. In our experiments, H₂O₂ yielded highly reactive hydroxyl radicals that could oxidize MB into smaller molecules such as CO₂, H₂O, *etc.* The catalytic property of CuS was found closely dependent on the amount of hydroxyl radicals; furthermore the assistance of H₂O₂ can be in favor of the bleaching of MB.^{50,51} The H₂O₂ alone was found incapable of the degradation of dye solutions without the assistance of catalyst. Meanwhile, it is also observed that CuS catalyst without H₂O₂ is not capable of degrading the MB. However, it is confirmed that the presence of H₂O₂ is necessary to assist the catalytic activity of the CuS.

Fig. 11b shows the optical absorption spectra of MB at different time intervals in the presence of common CuS microspheres having rough surfaces instead of nanofiber building blocks. The intensity of the absorption peak at 604 nm of MB decreased rapidly with the extended exposure time, indicating noticeable photocatalytic degradation of MB, and about 74% of MB (Fig. 11d, panel B) was degraded after 48 min. So

Fig. 10 (a). Nitrogen adsorption–desorption isotherms of the as-synthesized CuS products, (b) pore size distribution curves of as prepared CuS products.

Fig. 11 Absorption spectra of photodegradation of MB by different catalysts under natural light. (a) As prepared non spherical aggregate of CuS + H₂O₂ (b) hollow CuS microspheres with rough surfaces + H₂O₂. (c) CuS NSHMS + H₂O₂. (d) Plot of the extent of photodegradation of MB by different catalysts under natural light. Panel A: non spherical CuS powder; panel B: hollow CuS microspheres with rough surfaces; panel C: the as prepared CuS NSHMS.

the above results indicate that the presence of CuS catalysts can effectively accelerate the degradation of MB, which confirmed the significant role of CuS played in the photocatalytic degradation of MB. Moreover, it was found that the photocatalytic activity of microspheres with consistent shape and size was higher than the non-spherical and randomly aggregated structures (Fig. 11d, panel A). Further experiments were carried out to compare the catalytic activity of as-prepared NSHMS of CuS (Fig. 11c). Interestingly, the intensity of the absorption peak of MB at 604 nm decreased faster than that of the above hollow CuS microspheres with rough surfaces (Fig. 11b) and about 93% of the MB (Fig. 11d, panel C) was degraded after 48 min.

The decomposition of the MB aqueous solution at 48 min in the presence of the above as-prepared samples is as follows: NSHMS of CuS (93%) > hollow CuS microspheres having rough surfaces (74%) > as prepared CuS non spherical aggregate (61%). The relationship between $\ln(C_0/C)$ and time for the as-prepared CuS products is shown in Fig. 12a, where C_0 is the initial concentration of MB and C is the concentration of the dye at time t . The curve for CuS NSHMS is linear, the ratio of $\ln(C_0/C)$ increased at a constant rate with increase in time. A clear demonstration of CuS NSHMS superiority over the as prepared products of CuS is shown in

Fig. 12b in which the first order rate constant ($k \text{ min}^{-1}$) of CuS NSHMS (0.02418 min^{-1}), CuS microspheres having rough surfaces (0.01662 min^{-1}) and CuS non spherical aggregate (0.01081 min^{-1}) are given. The first order rate constant is calculated by the following equation.

$$\ln(C_0/C) = kt \quad (1)$$

The k value of CuS NSHMS shows a significant improvement in photodegradation as compared to other aforementioned as-synthesized CuS products. Moreover, the CuS NSHMS were recycled 6 times for the degradation of MB and the results show its excellent stability and recycling capability (Fig. 12c). In the recycling process, the catalyst was separated by centrifugation and reused after washing for degradation of the same concentration of MB. Almost the same time was taken by CuS NSHMS to degrade MB without any significant loss of efficiency even for the 6th cycle.

The underlying photo degradation mechanism might involve acceleration in the photodecomposition of H₂O₂ over CuS NSHMS, giving a large number of oxidants. The amount of oxidant is usually determined by the surface active sites of the catalysts.⁵² The relevant chemical reactions include separation of electron-hole pairs due to irradiation and

Fig. 12 (a). $\ln(C_0/C)$ of the as prepared CuS products. (b) First order rate constant k (min^{-1}) of the as prepared CuS products. (c) Stability test of as-prepared CuS NSHMS. (d) Triplet graph among crystallite size, BET surface area and first order rate constant (k) of as-synthesized products.

subsequent scavenging of these electrons and trapping of holes by H_2O_2 molecules, as shown below:

When the as-prepared NSHMS of CuS were irradiated with natural light in the presence of H_2O_2 , the holes present in the conduction band (CB) would be excited to the valence band (VB), with simultaneous formation of electrons in the CB.⁵³ These electrons and holes can be captured by H_2O_2 molecules, so the formations of oxidants (eqn (1)–(4)) have taken place. It has been demonstrated that because of their high oxidative capacities, the photo-generated oxidant species are in favor of oxidizing organic contaminants.⁵⁰

The obtained CuS NSHMS possesses the highest photocatalytic activity among all as-prepared CuS products due to at least the following several factors. Firstly, the NSHMS have the largest surface area ($36 \text{ m}^2 \text{ g}^{-1}$) due to coexistence of hollow interior, hierarchical shell walls with nanosheet building blocks and unique double pore sizes. The as obtained unusual and special complex hollow architectures absorb more MB-molecules, which allowed for more efficient transport of the injected electrons to

them from the excited MB dye, leading to enhancement of the photocatalytic performance.^{54,55} Secondly, the special hierarchical architected shell walls due to cavities within the entire shell walls not only reduce reflection and thus harvest the light well, but also promote transfer of light-generated charge carriers to the reactive surface and allow rapid diffusion of the reactants and products during the reaction.⁵⁶ The crystallinity of CuS NSHMS is better than that of the other as-prepared products, as shown in Fig. 1, since poorly crystallized CuS products lead to fewer defects acting as electron-hole recombination centers in the CuS products. Moreover, the crystallite size (34 nm) of the CuS NSHMS (Fig. 12d) is smaller than the other as-synthesized products; contributing highly to the photocatalytic degradation of organic dye. These results are consistent with the finding by Tian *et al.*⁵⁷ In addition, good dispersing and uniformity can also provide a large active surface area.^{58,59}

Based on the above discussion, it is easily believable that the photocatalytic superiority of as-prepared CuS NSHMS with nanosheet building blocks is attributed to their high specific surface area, unique existence of double pore sizes, wholly exposed nanosheet building blocks, coexistence of hollow interior and hierarchical shell walls, good crystallinity, small crystallite size, excellent dispersing and uniformity. Moreover; it is to be noted that the photodegradation experiment of MB dye was carried out under illumination by natural light. This suggests that the potential application might be quite feasible in practice.

Conclusions

In summary, a facile and well-controlled synthesis of CuS hollow microspheres fully exposed with uniquely well defined nanosheets building blocks was successfully achieved *via* a template free solvothermal method. The photocatalytic superiority of the as-prepared CuS NSHMS was attributed to their high specific surface area, active components and entirely nanosheets building blocks and entirely isolated existence of CuS NSHMS, along with so many influencing factors for enhancing the photocatalytic degradation of MB dye under natural light. The present study not only opens a new horizon for the synthesis of entirely isolated, hollow microspheres based on unique building blocks with fully exposed surfaces for many other chalcogenides, but is also of fundamental importance for the investigation of their potential application in other fields, including sensors, optics, and so forth.

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