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Carbon-ensemble-manipulated ZnS heterostructures for enhanced photocatalytic H₂ evolution[†]

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In this paper, we demonstrate a facile design of ZnS-based heterostructures tailored by versatile glucosederived carbon ensembles, including carbon dots (CDs) and thin carbon shells, *via* hydrothermal synthesis. Tuning the content of glucose allows interesting and simple conversion from CDs to carbon shells on the surfaces of ZnS nanospheres. The as-formed ZnS/carbon nanocomposites exhibit an enhanced hydrogen evolution rate, up to 4.9 times over bare ZnS nanospheres, from sacrificial photocatalytic water splitting under solar light. The upconverted photoluminescence properties of the carbon nanomaterials, coupled with favorable electron transfer ability, are responsible for the improved photocatalytic behavior. Additionally, the difference in the hydrogen rates between CDs and the carbon shell was discussed. The inexpensive and convenient strategy may offer new prospects in the engineering of desirable nanostructures with better performance.

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1. Introduction

Photocatalytic water splitting into hydrogen, a clean and sustainable energy of the future, has aroused extensive attention owing to the increasing global energy crisis and environmental concerns.1-3 Several chalcogenide semiconductors, e.g. zinc sulfide (ZnS), have often been reported as good candidates for hydrogen evolution photocatalysts, by virtue of their unique band structure for photogenerated electrons (e⁻) and holes (h⁺).^{4,5} Similar to its counterpart TiO₂, however, ZnS responses mainly in the ultraviolet region (accounting for only 4-5% of the whole solar spectrum) due to its large band gap of \sim 3.66 eV, which remarkably limits its light harvesting capacity, ultimately leading to an impoverished photoactivity.6 To date, considerable effort has been made to improve its efficiency by incorporating ZnS with various materials, including doping by Ni (ref. 7) or In,8 loading with Au (ref. 9) and forming solid solutions, like ZnS-CdS,¹⁰ (AgIn)_xZn_{2(1-x)}S₂ (ref. 11) or ZnS-CuInS₂-AgInS₂.¹² Despite excellent performances, the synthesis approaches in these studies inevitably require complicated procedures, expensive noble metals or even toxic elements, which are undesirable for practical applications. In this regard, it is important to explore the integration of ZnS with

Technology and Research), 3 Research Link, 117602, Singapore † Electronic supplementary information (ESI) available. See DOI: inexpensive, eco-friendly and functional materials in a more scalable and applicable way.

Carbon nanomaterials in diverse dimensions, like carbon nanotubes (1D)¹³ or graphene (2D),¹⁴ have been the state-of-theart because of their appealing electronic and optical properties, which provides new insight into the field of photocatalysis.15 Recently, a novel type of 0D carbon nanomaterial, carbon dots (CDs), has been developed, which holds great promise of enhancing the photocatalytic behavior from their favorable electron transfer ability and upconverted photoluminescence (UCPL) properties.16-18 Kang and his co-workers have first applied CDs to promote the photoelectrochemical water splitting process on TiO₂ nanotube arrays.¹⁹ Our group also presented the in situ generated TiO₂/CD heterostructures from TiO₂/vitamin C complexes to accelerate the hydrogen evolution rate.20 In addition, an alternative carbon form, the thin carbon shell, is noted for its high photoactivity of dye degradation,^{21,22} which is rarely explored for photocatalytic water splitting. We believe that it should be of great interest to tune the ensemble of carbon hybrids from CDs to carbon shells on a host photocatalyst and compare their photocatalytic performances, which might be useful for the design of efficient heterostructured photocatalysts.

In this work, we described a series of ZnS/carbon nanocomposites by manipulating the forms of carbon nanomaterials from CDs to a thin carbon shell on ZnS nanospheres. Hierarchical ZnS nanospheres with a mean size of \sim 200 nm, fabricated from a template-free hydrothermal synthesis, were utilized as the host photocatalyst. The nanospheres were combined with different amounts of glucose, an available, green and cheap carbon precursor, for further hydrothermal

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treatment. The facile tuning of the weight ratio of ZnS to glucose enables the transformation of CDs (3.5 nm in diameter) to the carbon shell (2 nm in thickness). These ZnS/carbon nanocomposites perform a higher hydrogen generation rate over bare ZnS nanospheres, without the assistance of other cocatalysts. The tailoring of the carbon nanoarchitecture coupled sulfide photocatalyst by altering the amount of carbon precursor, to the best of our knowledge, has never been reported before.

2. Experimental

2.1 Materials

Zinc acetate dehydrate [Zn(Ac)₂·2H₂O], thiourea, glucose, poly(vinylpyrrolidone) (PVP, $M_w = 300\ 000$) and lactic acid were purchased from standard sources. All the chemicals were used as received without further purification.

2.2 Preparation of ZnS nanospheres

ZnS nanospheres were prepared similar to the reported case.²³ In a typical process, 0.35 g $Zn(Ac)_2 \cdot 2H_2O$ and 3.4 g thiourea were dissolved in 30 mL deionized (DI) water, and stirred vigorously for 30 min under ambient conditions. The as-formed clear solution was then transferred into a 50 mL Teflon-lined stainless-steel autoclave and maintained at 150 °C for 5 h. After cooling to room temperature, a white suspension was obtained, which was centrifuged at 10 000 rpm for 15 min and washed several times with DI water and ethanol. Finally, the precipitate was collected and dried in an oven at 60 °C for 4 h, which is noted as ZnS nanospheres.

2.3 Preparation of carbon nanomaterials

Glucose at different amounts (0.003, 0.01, 0.03 and 2 g) was dissolved in 30 mL DI water, respectively, and stirred for 15 min under ambient conditions. The as-obtained clear solution was then transferred into a 50 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 4 h. After cooling to room temperature, a light yellow solution (0.003, 0.01 and 0.03 g) and a brown suspension (2 g) were obtained, respectively, which were further centrifuged at 10 000 rpm for 15 min. For the light yellow solution, the supernatant was collected and filtered using an ultra-filtration membrane $(0.2 \ \mu m)$ to remove larger particles. The as-formed filtrate is noted as CDs for further characterization. For the brown suspension, the precipitate was washed several times with DI water and ethanol, and then dried in an oven at 60 °C for 4 h. The as-formed powder is noted as carbon nanospheres for further characterization.

2.4 Preparation of ZnS/carbon nanocomposites

0.03 g ZnS nanospheres were dispersed in 30 mL DI water to form a homogeneous suspension. A certain amount (0.003, 0.01, 0.03 and 0.18 g) of glucose was added into the above solution and vigorously stirred for 1 h to ensure the complete dissolution of glucose. In the case of 0.18 g glucose, 1 g PVP was added as the competitive molecule to fabricate a thin carbon layer.²⁴ The mixed suspension was transferred into a 50 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 4 h. The following procedures are similar to those used for ZnS nanospheres. The final product was noted as ZnS/carbon nanocomposites.

2.5 Photocatalytic water splitting

5 mg ZnS nanospheres or ZnS/carbon nanocomposites, 9 mL DI water and 1 mL lactic acid were blended in a quartz vial and stirred until the formation of a homogeneous suspension. These solutions were purged with argon gas for 10 min prior to the photocatalytic water splitting. The measurements of H_2 generation were performed by magnetically stirring under the illumination of a 300 W Xe lamp, in which the readings were taken every 30 min within 2 h.

2.6 Photocurrent test of photoelectrochemical (PEC) cells

The PEC cells were realized by coating a layer of glycol suspensions of pure ZnS nanospheres or ZnS/carbon nanocomposites on a FTO glass (1.5×2 cm) followed by drying at 55 °C. With these samples as working electrodes and Pt as the reference electrode, the amperometric *I*-*t* curves were recorded under the illumination of 300 mW cm⁻² for three 30 s light-on/ off cycles without applied bias.

2.7 Characterization

Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-7001F field emission scanning electron microscope. High-resolution transmission electron microscopy (HRTEM) images were taken on a Philips CM300 transmission electron microscope. XRD spectra of the powder samples were obtained on a Philips X-ray diffractometer with Cu Ka radiation $(\lambda = 1.541 \text{ Å})$. X-ray photoelectron spectroscopy (XPS) spectra were obtained on a VG Thermo Escalab 220I-XL system. Fourier transform infrared (FT-IR) spectra of ZnS nanosphere and ZnS/ carbon nanocomposite powder were recorded on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. Photoluminescence (PL) spectra and the two-dimensional (2D) PL maps were recorded on a Shimadzu RF-5301 PC spectrofluorphotometer equipped with extra "specget" software under ambient conditions. UV-vis absorption spectra were acquired on a Shimadzu UV-3600 UV-vis spectrophotometer. Hydrogen uptake was measured using the pressure composition isotherm measurement on a Shimadzu GC-2014AT gas chromatograph.

3. Results and discussion

Fig. 1 schematically depicts the fabrication procedures of ZnS nanospheres and the ZnS/carbon heterostructures, including ZnS/CD nanocomposites and the ZnS/carbon core–shell structure *via* hydrothermal synthesis. Initially, ZnS nanospheres were obtained *via* a template-free hydrothermal reaction using zinc acetate and thiourea. Zn^{2+} cations are coordinated with thiourea, followed by nucleation, growth and aggregation under appropriate conditions to produce ZnS nanospheres. After subsequent integration with glucose, ZnS/carbon



Fig. 1 Schematic illustration of the hydrothermal synthesis of ZnS nanospheres from zinc acetate dehydrate and thiourea, and subsequent ZnS/CD nanocomposites and ZnS/carbon core-shell structures obtained at high and low weight ratios of ZnS to glucose, respectively.

nanocomposites were realized. Glucose is a simple monosaccharide commonly found in plants, which can serve as a green precursor to synthesize CDs and carbon micro-/nanospheres.^{25,26} Herein, tuning the weight ratio of ZnS to glucose determines the final carbon architectures on the ZnS nanospheres. At higher weight ratios, CDs were formed at the ZnS surface to yield ZnS/CD nanocomposites, whereas at a lower weight ratio, a thin carbon layer wrapping the nanospheres was formed as a ZnS/carbon core–shell nanostructure.

The morphology of the ZnS nanospheres is displayed in Fig. 2. As shown in the low-magnification SEM image (Fig. 2a), monodisperse nanospheres with a uniform size distribution of \sim 200 nm can be seen. These nanospheres are hierarchically composed of smaller nanoparticles with an average diameter of \sim 25 nm, as evidenced from the high-magnification SEM image (Fig. 2b). From the TEM image, solid nanospheres are observed to be packed closely with nanoparticles (Fig. 2c). A detailed examination of the lattice fringes shows that the interplanar distance of the nanospheres is 0.31 nm (Fig. 2d), corresponding to the (002) facet of ZnS.²⁷ The bottom-up assembly of the template-free construction of ZnS nanospheres is postulated as follows. Firstly, Zn²⁺-thiourea ligands are formed due to the coordination of Zn²⁺ cations and thiourea through Zn-S bonding. Secondly, thiourea can gradually release S^{2-} anions upon heating, which react with Zn²⁺ cations for nucleation. With the hydrothermal process, these ZnS nuclei grow into nanoparticles and further aggregate into larger nanospheres. The diameter of the nanospheres under these conditions is regulated to be around 200 nm, since the excessive thiourea can restrict the growth of nanospheres. The aggregated nanoparticles should markedly increase the specific surface area of the nanospheres, which might benefit the photocatalytic ability of ZnS.

The phase structure and the chemical compositions of ZnS nanospheres were also explored. The XRD spectrum (Fig. 3a) exhibits several diffraction peaks that match well with the hexagonal phase of ZnS (JCPDS card: 01-089-2191), without any characteristic peaks from impurities. The energy-dispersive X-ray (EDX) analysis (Fig. 3b) shows that the nanospheres



Fig. 2 (a and b) SEM and (c and d) TEM images of pure ZnS nano-spheres at low and high magnifications.

predominantly contain zinc and sulphur elements, with a tiny amount of residual carbon. In the XPS spectra (Fig. 3c and d), the binding energy at 1022.1 eV is identified as Zn $2p_{3/2}$, and 162.0 eV and 163.2 eV are ascribed to S $2p_{3/2}$ and S $2p_{1/2}$, respectively. Notably, the absence of a sulphate-related peak at ~168.4 eV suggests that the ZnS nanospheres are chemically stable without photo-corrosive oxidation during the hydrothermal treatment.²⁸ Hence, the successful preparation of ZnS nanospheres is demonstrated.

Alternatively, pure glucose can be transformed into two types of carbon nanomaterials, *i.e.* CDs and carbon nanospheres, by hydrothermal treatment at different amounts. As shown in Fig. S1,† monodisperse CDs with an average diameter of 3.5 nm are demonstrated, as derived from a lower glucose amount (0.01 g). These CDs are well crystallized, with their interplanar spacings of 0.24 nm. Interestingly, the CDs obtained at varied glucose amounts (0.003, 0.01 and 0.03 g) exhibit their PL emission peaks at 442, 450 and 453 nm, respectively. The slight red-shift of the PL emissions, along with the colour change from light yellow to brown, indicates that more CDs are generated upon the increase of glucose content. These CDs present obvious UCPL properties, as typically shown in the twodimensional PL map. The PL emissions range from 330-670 nm upon the excitation of 300-510 nm (shorter wavelengths) and 610-700 nm (longer wavelengths). However, a further increase of the glucose amount to 2 g produces carbon nanospheres with an average diameter of \sim 240 nm (Fig. S2[†]). Several functional groups are found in its FT-IR spectrum, including -OH (3250 cm⁻¹), C=O (1690 cm⁻¹), C-O-C (1300-1500 cm⁻¹) and C-OH (1020 cm^{-1}), which enables good dispersity of the carbon nanospheres in water. Unlike CDs, these carbon nanospheres are devoid of UCPL properties. The yield of carbon nanomaterials from glucose involves dehydration, carbonization and growth processes.²⁹ During the initial stage, glucose is hydrothermally dehydrated into oligosaccharides and some aromatic compounds. The hydrothermal process at higher temperature will result in the carbonization, in which oligosaccharides and



Fig. 3 (a) XRD pattern, (b) EDX spectrum, and (c) Zn 2p and (d) S 2p XPS spectra of ZnS nanospheres.

other compounds will crosslink *via* further intermolecular dehydration. The as-formed carbon nuclei grow either uniformly or isotropically to produce the final carbon nanomaterials in different ensembles. The lower glucose content only allows the realization of CDs, while the higher content would ensure the complete formation of carbon nanospheres.

After combining with glucose at different amounts, ZnS nanospheres were coated with carbon nanomaterials at their surfaces by hydrothermal treatment at 180 °C for 4 h. The weight ratios of ZnS to glucose were set as 10:1, 3:1, 1:1 and

1:6. As displayed in the TEM images of the ZnS/CD nanocomposites obtained at 10:1 and 3:1 (Fig. 4), the ZnS nanosphere structures are well preserved (Fig. 4a and d), indicating that these nanospheres are physically stable. The inner matrix shows the interplanar spacings of 0.31 nm, confirming the ZnS nanospheres (Fig. 4b and e), while the surfaces of the nanospheres are loaded with numerous particles of diameter less than 5 nm. These particles can be verified as CDs, since their interplanar spacings are measured to be 0.25 nm (Fig. 4c and f). Thus, ZnS/CD nanocomposites with ZnS nanospheres



Fig. 4 TEM images of ZnS/CD nanocomposites at the weight ratios of ZnS to glucose of (a-c) 10 : 1 and (d-f) 3 : 1 at low and high magnifications.



Fig. 5 TEM images of ZnS/carbon nanocomposites at the weight ratios of ZnS to glucose of (a and b) 1:1 and (c and d) 1:6 at low and high magnifications.

interior and CDs distributed at the surfaces are successfully achieved.

When the weight ratio of ZnS to glucose is decreased to 1:1, the glucose was also transformed into CDs that are densely accumulated at the ZnS surfaces, forming a quasi-continuous thin layer (Fig. 5a and b). The increase in glucose amount is believed to produce CDs in larger quantities. For a weight ratio of 1:6, some core-shell structures were observed, as typically shown in Fig. 5c. A thin carbonaceous shell of ~ 2 nm is seen to encapsulate the ZnS nanospheres. In contrast to well-crystallized CDs, the carbon shell is observed to be amorphous without any lattice fringes at a higher magnification (Fig. 5d). The formation mechanism of CDs in the nanocomposites is similar to pure CDs that are synthesized from glucose at the amounts of 0.003, 0.01 and 0.03 g. In the case of a high amount, glucose preferably incorporates with ZnS nanospheres to engender the carbon shell rather than isolated carbon nanospheres, as only

rough ZnS nanospheres can be found in the SEM image (Fig. S3[†]).

To confirm their chemical compositions, XPS spectra of the ZnS/carbon nanocomposites in the form of CDs and carbon shells were analyzed. The binding energy of Zn 2p locates at 1021.7 eV, and S $2p_{3/2}$ and S $2p_{1/2}$ at 161.5 eV and 162.8 eV, respectively (Fig. S4†). The slight shift of the binding energy, compared to pure ZnS nanospheres, should be attributed to the loading with CDs or encapsulating by the carbon shell. Fig. 6a and b show the C 1s peaks of ZnS/carbon nanocomposites, in which C–C/C=C (285.0 eV), C–O (286.5 eV) and C=O (288.1 eV) groups can be detected, suggesting that the carbon nanomaterials have been successfully coupled at the ZnS surfaces.

The ZnS nanospheres and ZnS/carbon nanomaterials were employed for hydrogen production from sacrificial photocatalytic water splitting, with their hydrogen generation performances shown in Fig. 7. Bare ZnS nanospheres are able to produce hydrogen at a rate of 198.0 μ mol g⁻¹ h⁻¹, while all ZnS/ carbon nanomaterials show an enhanced hydrogen rate. The hydrogen rate of ZnS/CD nanocomposites (10:1) is 630.6 µmol g⁻¹ h⁻¹, 3.2 times over bare ZnS, implying that the heterostructuring of CDs makes a difference to the water splitting process. The hydrogen rate, however, drops to 518.4 and 229.3 μ mol g⁻¹ h⁻¹, respectively, when the weight ratios of ZnS to glucose decline to 3 : 1 and 1 : 1. The decreased rate is related to the amount of CDs at the ZnS surfaces, in which the overloading of CDs from a higher glucose amount will shield the inner ZnS nanospheres from light irradiation,²⁰ thus giving rise to reduced photocatalytic activity. The ZnS/carbon core-shell structure shows the highest hydrogen rate of 969.6 μ mol g⁻¹ h⁻¹ that is 4.9 times over bare ZnS. The water splitting of the ZnS/CD nanocomposites (10:1) was carried out for another two cycles, in which a relatively stable hydrogen evolution rate without dramatic fluctuation is observed (Fig. 7b).

To explore the difference between CDs and the carbon shells in the hydrogen evolution rate, the PL emission maps and UV-vis spectra were obtained. The ZnS/carbon nanocomposites display obvious UCPL properties that can transfer from longer wavelength (690 nm) to shorter wavelength centring at ~430 nm (Fig. 8), a suitable wavelength for the photocatalytic behaviour of ZnS. As a result, better light absorption is attained in the composites than bare ZnS nanospheres for a higher hydrogen



Fig. 6 XPS spectra of ZnS/carbon nanocomposites at the weight ratios of ZnS to glucose of (a) 10 : 1 (CDs) and (b) 1 : 6 (carbon shell).



Fig. 7 (a) H_2 production from different samples of ZnS and ZnS/ carbon nanomaterials at different weight ratios. (b) Stability test of ZnS/ carbon dot nanomaterials (10 : 1) for three cycles.

rate. The intensity of the PL emission increases with the weight ratios (10 : 1, 3 : 1 and 1 : 1) as more CDs are loaded at the ZnS surface. Interestingly, the ZnS/carbon core–shell structure (1 : 6) also shows UCPL properties, unlike the carbon nano-spheres, which is probably due to its thin carbon layer of only \sim 2 nm. The excitation ranges of the core–shell structure red-shift to over 690 nm, beyond the limit of the fluorospectrometer, which infers that the carbon shell can upconvert longer wavelength than CDs. In the UV-vis spectra (Fig. 9), all the ZnS nanospheres and ZnS/carbon nanocomposites exhibit absorption peaks at approximately 335 nm. The absorption in the visible light region is greatly improved in the ZnS/carbon



Fig. 9 UV-vis absorption spectra of bare ZnS nanospheres (black) and ZnS/carbon nanocomposites at different weight ratios of ZnS to glucose of (red) 1:1 and (blue) 1:6.



Fig. 8 PL maps of ZnS/carbon nanocomposites at different weight ratios of ZnS to glucose of (a) 10:1, (b) 3:1, (c) 1:1 and (d) 1:6.

nanocomposites, especially in the ZnS/carbon core-shell structure (blue line), which may partially contribute to the enhanced H_2 generation rate.

The photoresponses of bare ZnS nanospheres and ZnS/ carbon nanocomposites over time were also conducted (Fig. 10). The two-electrode photoelectrochemical (PEC) cells were fabricated using ZnS nanospheres or ZnS/CD nanocomposites as the working electrode while Pt as the reference electrode. As shown in their amperometric I-t curves, the photocurrent densities of all samples remain steady without obvious decay in three 30 s light on/off cycles. The photocurrent density of bare ZnS nanospheres is ca. 10 nA cm^{-2} , which is enhanced to 28 nA cm $^{-2}$ for ZnS/CD nanocomposites and 69 nA cm $^{-2}$ for the ZnS/carbon core-shell structure. The higher photocurrent over bare ZnS suggests better electron transport and more effective separation of the e^{-}/h^{+} in the ZnS/carbon composites,³⁰ which is more beneficial for the hydrogen generation. Moreover, the ZnS/carbon core-shell structure possesses better charge transfer properties over ZnS/CD nanocomposites. The amorphous carbon is reported to modify the electronic properties of some metal oxides, like ZnO,31 resulting in a higher hydrogen rate than that of ZnS/CD nanocomposites as shown above.

The mechanism of the improved hydrogen generation rate is discussed below. Firstly, the large surface area, originated from smaller nanoparticles, makes it possible for favourable water splitting of ZnS nanospheres under solar light. Secondly, CDs and the carbon shell possess unique UCPL properties, in which the PL emissions centring at the optimal wavelength (430 nm) for the photocatalytic behaviour of ZnS were greatly enhanced. Along with the enhanced absorption in the visible light range, better light harvesting of ZnS is realized, hence beneficial towards the hydrogen generation. Thirdly, carbon nanomaterials, either CDs or the carbon shell, possess rapid electron transfer properties, as manifested from the photocurrent tests. Indeed, CDs can serve as electron acceptors and donors, in which photoinduced electrons can transfer from CDs to ZnS surfaces and the redundant electrons on ZnS return to the CD particles.³² All these features enable the ZnS/carbon



Fig. 10 Photocurrent responses of the PEC cells using ZnS nanospheres, ZnS/CD nanomaterials and ZnS/carbon core-shell nanostructures as working electrodes for three 30 s light-on/off cycles.

nanocomposites to perform better than bare ZnS nanospheres in the photocatalytic water splitting process.

4. Conclusions

In summary, we have designed two carbon architectures, including the 0D CDs and a thin layer of the carbon shell, on ZnS nanospheres to yield a series of ZnS/carbon nanocomposites by hydrothermal synthesis. The conversion from CDs to the carbon shell is realized by simply governing the amount of glucose and the precursor of the carbon nanomaterials. Compared to bare ZnS nanospheres, these ZnS/ carbon nanocomposites show 3.2- and 4.9-fold higher hydrogen production rates for ZnS/CD nanocomposites and the ZnS/ carbon core–shell structure, respectively. The enhanced hydrogen rate should be associated with the UCPL properties and better charge transport performances of CDs and the thin carbon layer. The facile tailoring of carbon nanomaterials may offer valuable opportunities of constructing green and effective nanocomposites for enhanced photocatalytic performances.

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