

Cite this: *CrystEngComm*, 2011, **13**, 5045

www.rsc.org/crystengcomm

Facile additive-free solvothermal synthesis of cadmium sulfide flower-like three dimensional assemblies with unique optical properties and photocatalytic activity†

Yuming Guo,^a Jinfeng Wang,^a Lin Yang,^{*a} Jie Zhang,^a Kai Jiang,^a Wujv Li,^b Lingling Wang^a and Lili Jiang^a

Received 26th January 2011, Accepted 21st February 2011

DOI: 10.1039/c1ce05132f

Cadmium sulfide flower-like 3D assemblies were successfully prepared through a facile additive-free solvothermal process. It was found that the ethanol played an important role in the formation of the CdS assemblies. Based on the time-dependent experiments, a possible mechanism was proposed. In addition, the CdS assemblies exhibit unique optical properties and potential photocatalytic activity.

Based on biomineralization studies, biominerals with novel morphologies and hierarchical structures can be formed in biological organisms and play the important biological functions, such as the coccoliths with special three dimensional (3D) morphology formed in marine algae^{1,2} and the nacre formed in mollusks.^{3–5} Consequently, the preparation of functionally well-defined ordered hierarchical structures in nano-/microscales *in vitro* has attracted considerable attention and tremendous efforts have been made to prepare these structures, such as multi-armed crystals,⁶ 3D nanoflowers,^{7,8} star-shaped structures,⁹ snowflake-like,¹⁰ and urchin-like patterns.^{11,12} Moreover, the facile and reliable methods to prepare materials with designed chemical components, controllable size and surface chemistry have been widely investigated. However, in addition to the size, compositions and surface chemistry, the special morphologies and arrangements are also important to the properties and potential applications of the materials. Therefore, the preparation of nanostructures in 1 dimension and higher dimensions through facile and controllable self-assembly processes attracts considerable interest. For example, dendritic CuSe and Ag₂Se were successfully prepared through a facile solvothermal reaction in ethanol.^{13,14} As one of the most important and popular semiconductors, cadmium sulfide (CdS) has a large direct band gap of 2.4 eV at room temperature and widely used in various fields because of its excellent non-linear properties. During the past decades, tremendous efforts have been devoted to prepare the CdS nanocrystals, and several novel methods have been

reported to prepare the CdS nanocrystals with controllable size and morphology using organic molecules as templates or additives.^{15,16} However, it is still a great challenge to develop a facile and reliable method to control the morphologies and arrangements of CdS 3D micro-/nanostructures over a wide range.

Herein, a facile, efficient, and additive-free solvothermal process is introduced to prepare the CdS flower-like 3D assemblies of nano-/microcrystals with unique optical properties and photocatalytic activity. A possible formation mechanism is also proposed to account for the formation of the CdS 3D assemblies.

In this work, the mixed solvent of water and ethanol was selected to prepare the CdS flower-like 3D assemblies.¹⁶ However, no template or additive is involved in our method. In the typical experiment, CdCl₂·2.5H₂O and thiourea were dissolved into ethanol/water mixed solvent (2 : 3, v/v) and the pH was adjusted to 5.4. Subsequently, the reaction mixture was transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed, heated at 160 °C for 9 h, and air-cooled to room temperature. Finally, the product was collected by filtration, washed with double distilled water (DD water) and absolute ethanol for several times, and dried under vacuum. For comparison, two different control experiments were also performed. In control system 1, CdS was prepared under similar conditions to typical experiment except that the solvent changed to DD water. In control system 2, CdS was prepared using sodium sulfide as the sulfide source in DD water at room temperature.

The size and morphology of the as-prepared CdS were characterized by scanning electron microscopy (SEM, JSM-6390LV, JEOL). High-resolution transmission electron microscopy (HR-TEM) investigations, accompanied by selected-area electron diffraction (SAED), were conducted on a JEOL JEL-2010 transmission electron microscope. The polymorphs of the as-prepared CdS were determined by powder X-ray diffraction (XRD) using a DX-2000 X-ray diffractometer with a Cu-K α radiation source. The UV-vis absorption spectrum of the as-prepared CdS was recorded on a Perkin-Elmer Lambda 17 UV-visible spectrophotometer. A Shimadzu RF-540 PC instrument was used to record the photoluminescence (PL) spectrum of the as-prepared CdS. For photocatalytic activity evaluation, the as-prepared CdS was suspended in organic dyes aqueous solution by sonicating and was stirred in the dark to establish an adsorption-desorption equilibrium. Afterwards, the suspension was exposed to the irradiation of 500 W xenon lamp for

^aCollege of Chemistry and Environmental Science, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang 453007, P. R. China. E-mail: yanglin1819@163.com; Fax: +86-373-3328507; Tel: +86-373-3325999

^bLuohe Vocational Technology College, Luohe 462000, P. R. China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1ce05132f

photocatalysis under moderate stirring. At specific time intervals, the suspension was taken from the reactor and centrifuged. The content of the organic dyes in the supernatant was monitored by UV-vis absorption spectroscopy at 463 nm for methyl orange (MO) and 554 nm for rhodamine B (RhB).

In our experiment, the polymorphs of the as-prepared CdS were determined by XRD analysis and the result is shown in Fig. 1. From the XRD pattern, all the diffraction peaks can be indexed to hexagonal wurtzite CdS (JCPDS no. 41-1049). No obvious diffraction peaks from other impurities were observed. This result indicates that the pure hexagonal wurtzite CdS can be prepared in the experiment. In addition, the samples from control systems showed the similar XRD patterns.

Fig. 2a–c present the SEM images of the as-prepared CdS assemblies, in which Fig. 2a is the low magnification image while Fig. 2b–c are the high magnification images. From Fig. 2a, the CdS assemblies exhibit organized flower-like architectures with the scales of 5–8 μm . As shown in Fig. 2b, each of the CdS assembly is assembled by three flower-like microcrystal architectures with the scales of 3–4 μm , which connect together through “back-to-back” arrangement. It is interesting that the flower-like microcrystal architectures consist of six leaf-like CdS branches, which are arranged with 6-fold symmetry and separated by 60°. The leaf-like branch is composed of a long central stem with the scales of 2–4 μm and two rows of secondary branches. The secondary branches in the same row with the scales of 400 nm to 1 μm are parallel to each other emerging at about 40°–45° with respect to the central stem. From the high magnification SEM image shown in Fig. 2c, the secondary branches are composed of the nanocrystals building units with the scales of 200–400 nm. In addition, CdS was also prepared in absolute ethanol and the morphologies and arrangements are similar to those of the typical experiment shown in Fig. 2.

For comparison, two control experiments were also performed. The powder XRD patterns of the control products are the same as the result of the typical experiment shown in Fig. 1. Fig. 2d shows the SEM image of the product from the control system 1. From the figure, the CdS formed in DD water exhibits irregular arrangement, which is composed of spherical nanocrystals. This is significantly different from the results of the typical experiment. In addition, the product from the control system 2 was mainly composed of irregular nanocrystals and showed severe agglomeration (ESI, Fig. S1).[†] These

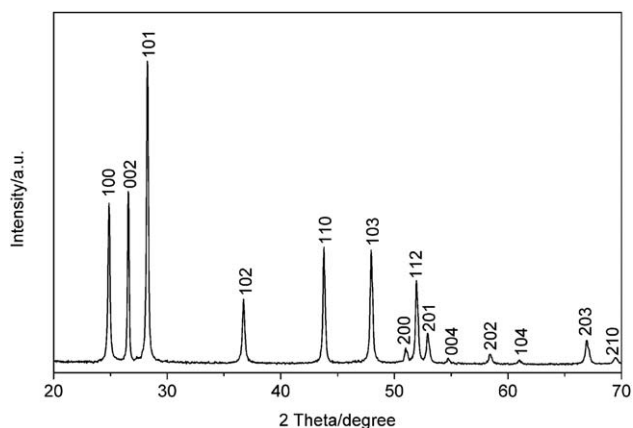


Fig. 1 Powder XRD pattern of the as-prepared CdS flower-like 3D assemblies.

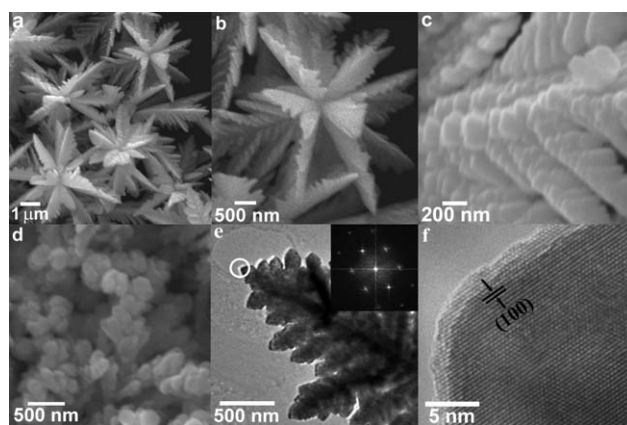


Fig. 2 SEM images of the as-prepared CdS flower-like 3D architectures from a typical experiment (a–c) and control system (d). (e) TEM image of branch of CdS flower-like 3D assemblies, inset: SAED pattern. (f) HR-TEM image of the area marked by the circle in (e). The fringe spacing of 0.3579 nm corresponds to the separation of (100) lattice plane.

results reveal that the ethanol in the mixed solvent is very important to control the formation of the CdS flower-like 3D assemblies.

Fig. 2e presents the TEM image of the CdS flower-like 3D assemblies. The inset shows the SAED pattern. It is obvious that the CdS flower-like 3D assemblies are composed of single crystals. Fig. 2f exhibits the HR-TEM image of the area marked by the circle in Fig. 2e. It reveals that the nanocrystals prefer growth along the [210] direction.

To investigate the formation mechanism of the CdS flower-like 3D assemblies, series of time-dependent experiments were performed. Fig. 3 shows the morphologies of the products at different solvothermal times. From Fig. 3a, irregular organization assembled by the particles with the size of *ca.* 20 nm is formed for 0.5 h. The product of 1 h consists of bowl-like structures with the scale of *ca.* 200 nm through “back-to-back” arrangement (Fig. 2b). When the reaction time is increased to 3 h, the bowl-like structures partially split and changed to flower-like structures (Fig. 3c). When the reaction time extended to 6 h, the branches composed of the flower-like structures also partially split and changed to leaf-like structures

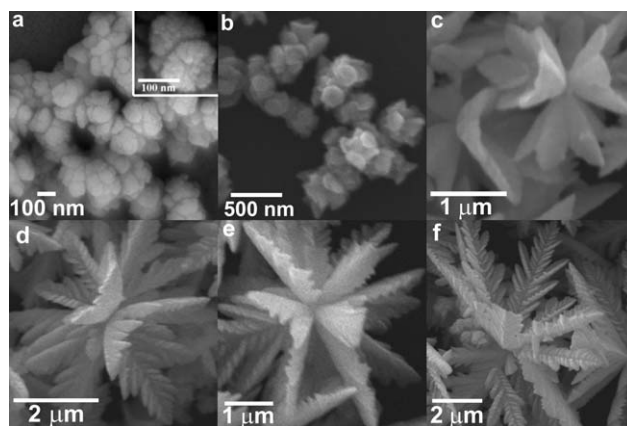


Fig. 3 Morphology-evolution process at different solvothermal times. (a) 0.5 h, (b) 1 h, (c) 3 h, (d) 6 h, (e) 9 h, and (f) 18 h. In all experiments, the other conditions are kept constant.

(Fig. 3d). When the reaction time further increased to more than 6 h, the influence of the solvothermal time on the morphology could be ignored. The extension of the solvothermal times can just affect the size of the as-prepared products. This indicates that the evolution of the morphology of the as-prepared CdS is completed within 6 h.

From previous studies, capping agents, *e.g.* organic molecules, played the important roles in the preparation of the inorganic nanocrystals assemblies with 3D morphologies. For example, 3D dendritic CdS nanoarchitectures were prepared using cetylpyridinium chloride as the capping agent,¹⁶ 3D CdS nanocrystals with flower-like structure were prepared using hexamethylenetetramine as the capping agent.¹⁷ Interestingly, in the current study, no any capping agent is involved in the preparation of the CdS flower-like 3D assemblies except for ethanol. Introduction of ethanol in the solvent can change the as-prepared products from irregular arrangement to regular 3D flower-like arrangement, indicating that the introduction of the ethanol is very important to the formation of the CdS flower-like 3D assemblies. Previous studies showed that the hydroxyl groups could spread over the surface of the inorganic nanoparticles, to stabilize, order, and control their spatial arrangement.^{18–21} Therefore, it is proposed that the ethanol in the solvent might spread over the nanoparticles and selectively adsorb onto certain CdS crystal planes and therefore influence the growth of these planes. This leads to the fast growth of some planes and slow growth of other planes, and further results in the formation of the CdS flower-like 3D assemblies.

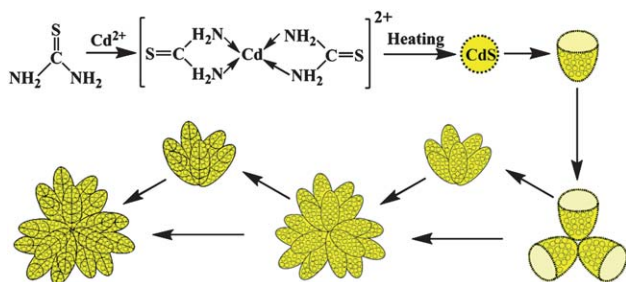
Based on these results, a possible formation mechanism for CdS flower-like 3D assemblies is proposed in Scheme 1. Firstly, the Cd^{2+} and the thiourea might form the complex compound (Cd-thiourea) because of the strong coordinating capacity of the thiourea. With the increase of the temperature during the solvothermal process, the Cd-thiourea complex may tend to decompose to release the active Cd^{2+} and S^{2-} . Then the active Cd^{2+} can react with the active S^{2-} to form CdS seeds.^{22,23} The ethanol in the solvent might spread over and selectively adsorb on certain crystal planes of the CdS seeds for its binding capacity, which might influence the growth rate of these planes and result in the formation of primary nanoparticles with bowl-like structure. These CdS bowl-like nanoparticles can interact each other to form larger aggregates. Subsequently, under the influence of the absorbed ethanol molecules, the bowl-like CdS nanoparticles grow fast along certain directions and slowly along other directions. This leads to the split of the bowl-like structure and the formation of the flower-like structure.

As one of the most important and popular group II–IV semiconductors, CdS has attracted considerable attention over the past decades due to their unique photochemical and photophysical

properties. Therefore, the optical properties of the CdS flower-like 3D assemblies, including the UV-vis absorption and PL spectra, were determined and the results are shown in Fig. 4. From Fig. 4, the as-prepared CdS 3D assemblies show a strong absorption band at 245 nm, indicating the strong photo absorption property. In addition, when excited with wavelength 245 nm, the as-prepared CdS 3D assemblies exhibit a strong emission peak centered about 305 nm, which can be attributed to recombination from the excitonic state in the crystallite interior.^{24,25}

Because of the strong photo absorption property of the as-prepared CdS, the photocatalytic activity to degrade the organic dyes under visible light irradiation were studied and the results are shown in Fig. 5. From the figure, after irradiated with visible light for 90 min in the presence of the as-prepared CdS, 88% of MO and 79% of RhB are photocatalytic degraded (see the ESI, Fig. S2 and S3 for the original degradation spectra of MO and RhB).[†] Because of the weak absorption of the as-prepared CdS in visible light region, it is not the CdS but the dye molecule that is excited by visible light to excited states. Then the electrons would be transferred from the excited dye molecule to the conduction band of the CdS and react with the pre-adsorbed oxygen to form active oxygen species ($\cdot\text{OH}$, O_2^- , *etc.*), which can lead to the photodegradation of the dyes.²⁶ This indicates that the as-prepared CdS own a strong photocatalytic activity under the visible light irradiation and might be potentially used as the photocatalyst candidate to treat the organic dyes in the waste water.

In conclusion, CdS flower-like 3D assemblies were successfully synthesized *via* a facile solvothermal process without using any templates or additives. It is found that the ethanol in the solvent plays an important role in the formation of the CdS flower-like 3D assemblies. Furthermore, a series of intermediate morphologies were formed during the shape evolution of the CdS flower-like 3D assemblies. Based on the results, a possible mechanism was proposed to explain the anisotropic growth of CdS nanocrystals. This study provides a facile, efficient, and template-free and additive-free solvothermal process to prepare the CdS 3D assemblies of nano-/microcrystals. It also provides useful information for crystal growth, design, and morphology-controlled synthesis. Furthermore, the as-prepared CdS 3D assemblies exhibit the unique optical properties and strong photocatalytic activity and might be potentially used as



Scheme 1 Schematic illustrations of the formation mechanism of the CdS flower-like 3D assemblies.

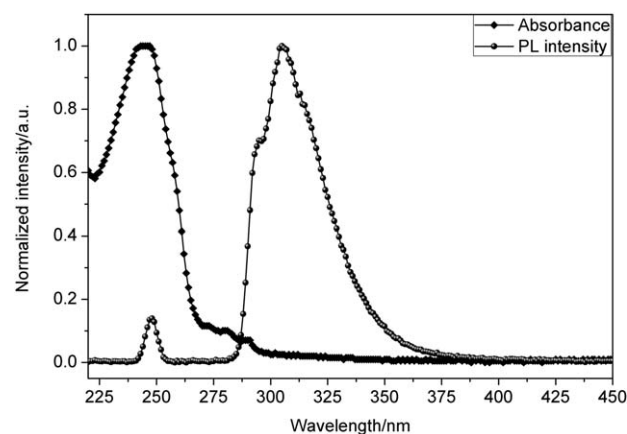


Fig. 4 UV-vis absorption and PL spectra of the as-prepared CdS flower-like 3D assemblies.

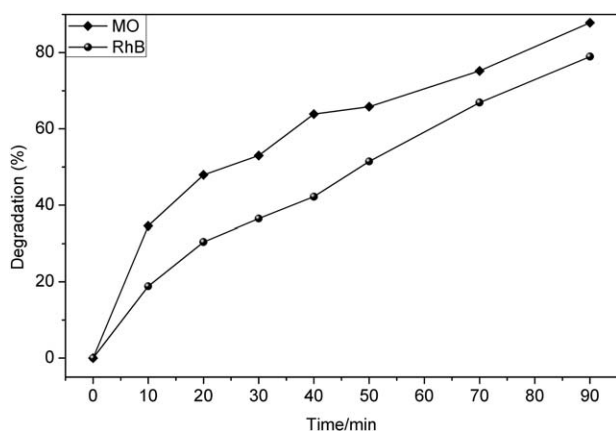


Fig. 5 Photodegradation of MO and RhB in the presence of the as-prepared CdS flower-like 3D assemblies monitored by UV-vis absorption.

the photocatalyst candidate to treat the organic dyes in the waste water.

This work was financially supported by the National Key Basic Research and Development Program of China (grant no. 2009CB626610) and the National Science Foundation of China (grant no. 20771036) and the Innovation Scientists and Technicians Troop Construction Projects of Henan Province and the Natural Science Foundation of He'nan Educational Committee (grant no. 2010A150013).

References

- 1 K. Henriksen, S. L. S. Stipp, J. R. Young and M. E. Marsh, *Am. Mineral.*, 2004, **89**, 1709–1716.
- 2 K. Saruwatari, N. Ozaki, H. Nagasawa and T. Kogure, *Am. Mineral.*, 2006, **91**, 1937–1940.
- 3 G. Falini, S. Albeck, S. Weiner and L. Addadi, *Science*, 1996, **271**, 67–69.

- 4 M. Lai, A. N. Kulak, D. Law, Z. Zhang, F. C. Meldrum and D. J. Riley, *Chem. Commun.*, 2007, 3547–3549.
- 5 F. Nudelman, B. A. Gotliv, L. Addadi and S. Weiner, *J. Struct. Biol.*, 2006, **153**, 176–187.
- 6 H. Chu, X. Li, G. Chen, W. Zhou, Y. Zhang, Z. Jin, J. Xu and Y. Li, *Cryst. Growth Des.*, 2005, **5**, 1801–1806.
- 7 S. Xiong, B. Xi, C. Wang, G. Zou, L. Fei, W. Wang and Y. Qian, *Chem.–Eur. J.*, 2007, **13**, 3076–3081.
- 8 W.-T. Yao, S.-H. Yu, S.-J. Liu, J.-P. Chen, X.-M. Liu and F.-Q. Li, *J. Phys. Chem. B*, 2006, **110**, 11704–11710.
- 9 W.-S. Chae, H.-W. Shin, E.-S. Lee, E.-J. Shin, J.-S. Jung and Y.-R. Kim, *J. Phys. Chem. B*, 2005, **109**, 6204–6209.
- 10 J. Zhang, L. Sun, J. Yin, H. Su, C. Liao and C. Yan, *Chem. Mater.*, 2002, **14**, 4172–4177.
- 11 D. Du and M. Cao, *J. Phys. Chem. C*, 2008, **112**, 10754–10758.
- 12 Y.-X. Zhou, Q. Zhang, J.-Y. Gong and S.-H. Yu, *J. Phys. Chem. C*, 2008, **112**, 13383–13389.
- 13 D. Li, Z. Zheng, Y. Lei, S. Ge, Y. Zhang, Y. Zhang, K. W. Wong, F. Yang and W. M. Lau, *CrystEngComm*, 2010, **12**, 1856–1861.
- 14 D. Li, Z. Zheng, J. Shui, M. Long, J. Yu, K. W. Wong, L. Yang, L. Zhang and W. M. Lau, *J. Phys. Chem. C*, 2008, **112**, 2845–2850.
- 15 L. Dong, T. Gushtyuk and J. Jiao, *J. Phys. Chem. B*, 2004, **108**, 1617–1620.
- 16 D. Wang, D. Li, L. Guo, F. Fu, Z. Zhang and Q. Wei, *J. Phys. Chem. C*, 2009, **113**, 5984–5990.
- 17 F. Chen, R. Zhou, L. Yang, N. Liu, M. Wang and H. Chen, *J. Phys. Chem. C*, 2008, **112**, 1001–1007.
- 18 D. K. Božanić, V. Djoković, J. Blanuša, P. S. Nair, M. K. Georges and T. Radhakrishnan, *Eur. Phys. J. E*, 2007, **22**, 51–59.
- 19 G. Carrot, D. Rutot-Houze, A. Pottier, P. Degee, J. Hilborn and P. Dubois, *Macromolecules*, 2002, **35**, 8400–8404.
- 20 P. Rodriguez, N. Muñoz-Aguirre, E. S. Martinez, G. G. de la Cruz, S. A. Tomas and O. Z. Angel, *J. Cryst. Growth*, 2008, **310**, 160–164.
- 21 S.-W. Yeh, T.-L. Wu and K.-H. Wei, *Nanotechnology*, 2005, **16**, 683–687.
- 22 A. V. Naumov, V. N. Semenov and E. G. Goncharov, *Inorg. Mater.*, 2001, **37**, 539–543.
- 23 V. N. Semenov and A. V. Naumov, *Russ. J. Gen. Chem.*, 2001, **71**, 495–499.
- 24 G. Carrot, S. M. Scholz, C. J. G. Plummer, J. G. Hilborn and J. L. Hedrick, *Chem. Mater.*, 1999, **11**, 3571–3577.
- 25 H. Noglik and W. J. Pietro, *Chem. Mater.*, 1994, **6**, 1593–1595.
- 26 F. Chen, Y. Xie, J. Zhao and G. Lu, *Chemosphere*, 2001, **44**, 1159–1168.