Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Flower-like CdSe ultrathin nanosheet assemblies for enhanced visible-light-driven photocatalytic H_2 production

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Experimental Section

Synthesis of flower-like CdSe ultrathin nanosheet assemblies.

All chemicals were of analytical grade and used as received without further purification. Typically, 266.53 mg (1.0 mmol) $Cd(CH_3COO)_2$ and 110.96 mg (1.0 mmol) SeO_2 were added into 40 mL diethylenetriamine in a beaker flask. The mixture was then heated to 55 ^oC and kept for 30 min. After that, the yellow slurry was transferred into a Teflon-lined autoclave. This autoclave was sealed and maintained at a given temperature (120 ^oC, 140 ^oC, 160 ^oC and 180 ^oC) for 16 h and then cooled down to room temperature. The resulting products (referred to as CdSe-120, CdSe-140, CdSe-160 and CdSe-180) were collected and washed with deionized water and ethanol for several times, and then dried under vacuum at 40 ^oC overnight.

Synthesis of CdSe Quantum Dots (QDs).

The CdSe QDs were prepared according to the literature.[1, 2] Typically, 100 mL Na_2SO_3 (3.8 g) aqueous solution was prepared in 250 ml round-bottom flask. Then 800 mg selenium powder was added to the solution. The resulting mixture solution was heated to 100 ^oC and refluxed until the selenium powder was fully dissolved to obtain transparent Na_2SeSO_3 solution (Se^{2-} precursor). Cd^{2+} precusor solution was prepared by mixing of 0.182 g $CdCl_2 \cdot 2.5H_2O$ and 0.1 mL mercaptoacetic acid in 50 ml distilled water at a 100 mL 3-neck round-bottom flask, and its pH was adjusted to 11

with 1 mol/L NaOH. After that, 6 mL 0.1 mol/L Na_2SeSO_3 solution was injected followed by reflux for 30 min with Ar atmosphere protection. The concentration of the as-prepared CdSe QDs ($\sim 6.6 \times 10^{-4}$ M) was calculated based on their UV-Vis absorption spectrum.[3]

Preparation of urchin-like CdSe.

The urchin-like CdSe samples were prepared according to the literture.[4] Typically, 0.1 g SeO_2, 0.24 g $Cd(CH_3COO)_2$ and 20 mL deionized water were mixed with stirring in a beaker flask. 20 mL ethanolamine was then added, and the solution was transferred into a Teflon-lined autoclave. This autoclave was sealed and maintained at 180 ^oC for 16 h, and then cooled down to room temperature. The resulting products were collected and washed with deionized water and ethanol for several times, and then dried under vacuum at 40 ^oC overnight.

Characterization.

The powder X-ray diffractometer (XRD) patterns of CdSe samples were obtained by a Bruker D8 Focus X-ray diffractometer with Cu K_α radiation (λ = 1.5405Å). Scanning electron microscopic (SEM) images were collected on a Hitachi S-4800 scanning electron microscope equipped with an Energy dispersive spectrometer (EDS). UV-Vis absorption spectra and UV-Vis diffuse reflection spectra (DRS) of the samples were collected using a Varian spectrophotometer (Cary 5000). Transmission electron microscopic (TEM) and high resolution TEM (HRTEM) images were collected by using a JEOL-2100F microscope with an accelerating voltage of 200 kV. N_2 adsorption–desorption isotherms were collected by a Quadrasorb SI MP apparatus at 77 K, the samples were degassed in a vacuum at 80 ^oC for 6 h prior to the experiments, and the total specific surface area of the samples was calculated by using the Brunauer-Emmett-Teller method. Valence band X-ray photoelectron spectroscopy (VB XPS) measurements were performed on a PHI Quantro SXM instrument.

Photocatalytic H_2 evolution activity.

The photocatalytic reactions were carried out in a 60 mL quartz vessel sealed with a rubber septum. The photocatalyst powders (CdSe, 5 mg) were dispersed in a 20 mL aqueous solution with 0.35 M Na_2S and 0.25 M Na_2SO_3 as the sacrificial agents. The suspension was dispersed by ultrasound treatment for 10 min, and then deaerated with N_2 for 30 min to remove O_2 and then sealed with a rubber septum. A 300 W Xenon lamp equipped with an ultraviolet cut-off filter (λ > 400 nm) (PLS-SXE300C photochemical reactor, Perfect Light Ltd, Beijing) was used as the light source. The temperature of the reaction system was maintained at room temperature by a flow of water. The amount of evolved H_2

was determined by a Shimadzu GC-2014 gas chromatograph (N_2 carrier gas, molecular sieve 5˚A, TCD detector). The photocatalytic H_2 generation quantum efficiency of CdSe products was evaluated using a 300 W Xe lamp equipped with a 420 nm bandpass filter.

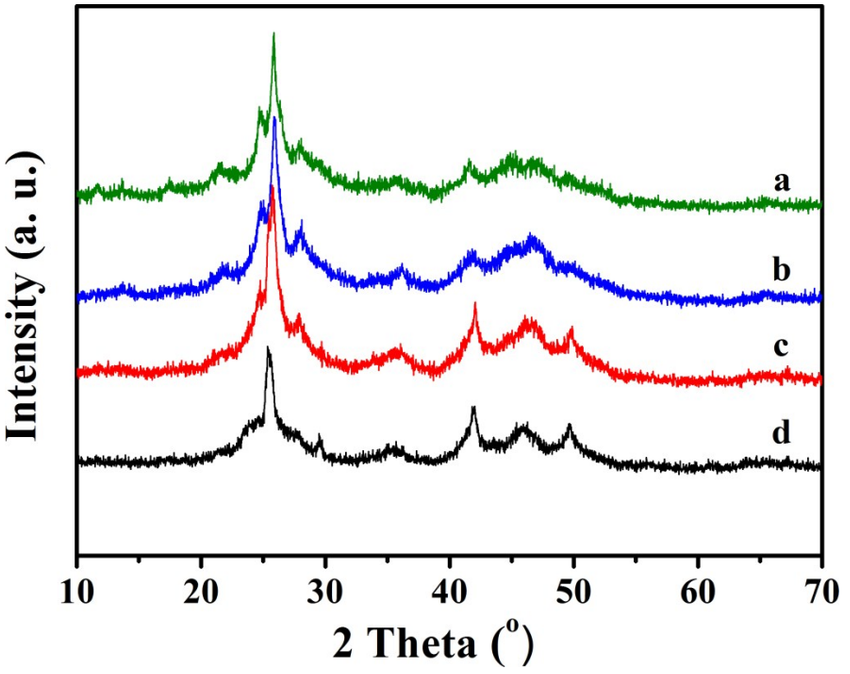
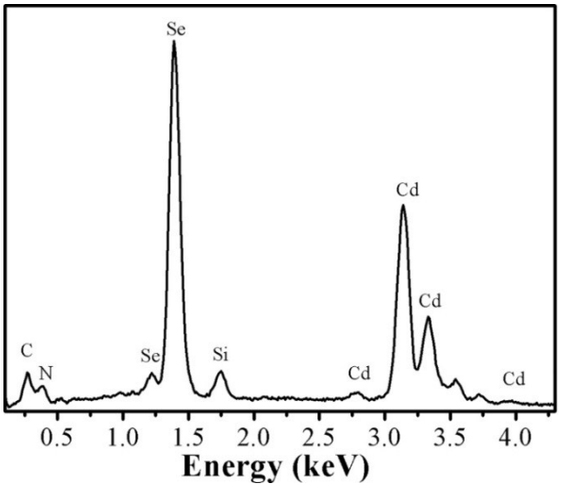


Fig. S1 XRD patterns of (a) CdSe-120, (b) CdSe-140, (c) CdSe-160 and (d) CdSe-180.



Elements	Weight%	Atomics
C K	10.26	37.55
N K	7.03	22.07
Si K	1.99	3.11
Se L	34.55	19.23
Cd L	46.17	18.05
Total	100	

Fig. S2 EDS pattern of CdSe-140.

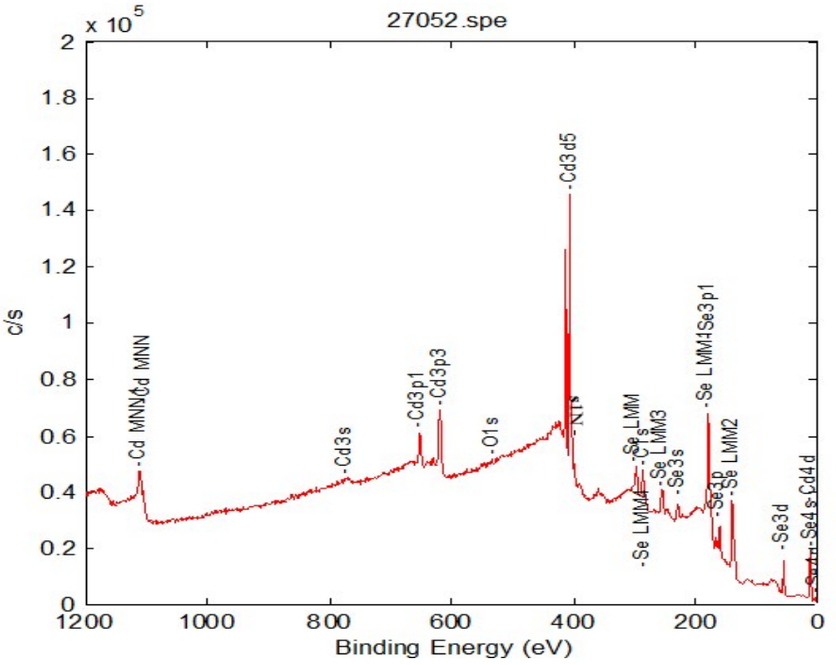


Fig. S3 XPS spectrum of CdSe-140.

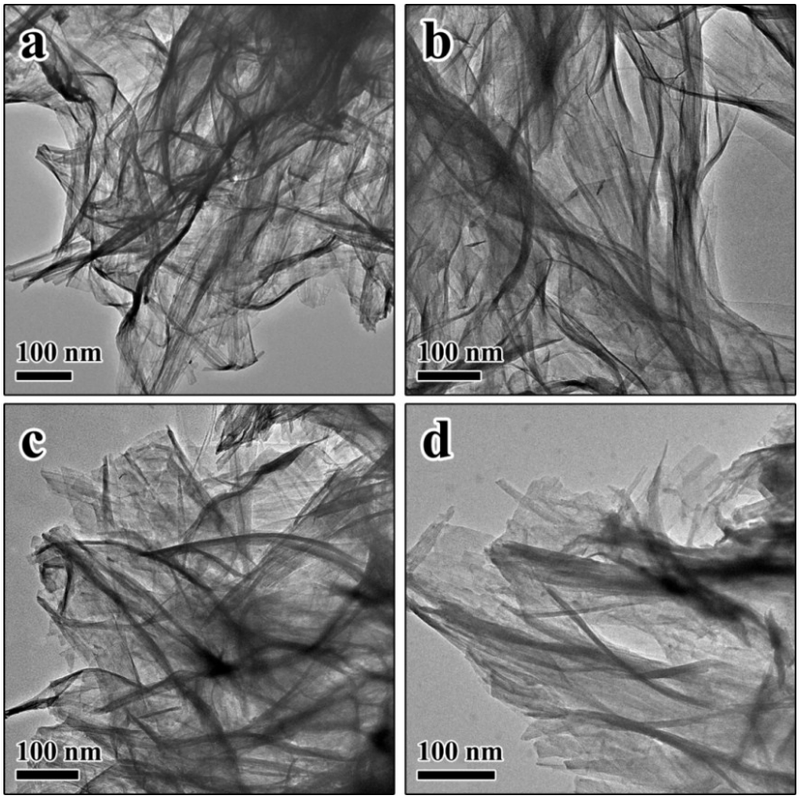


Fig. S4 TEM images of (a) CdSe-120, (b) CdSe-140, (c) CdSe-160 and (d) CdSe-180.

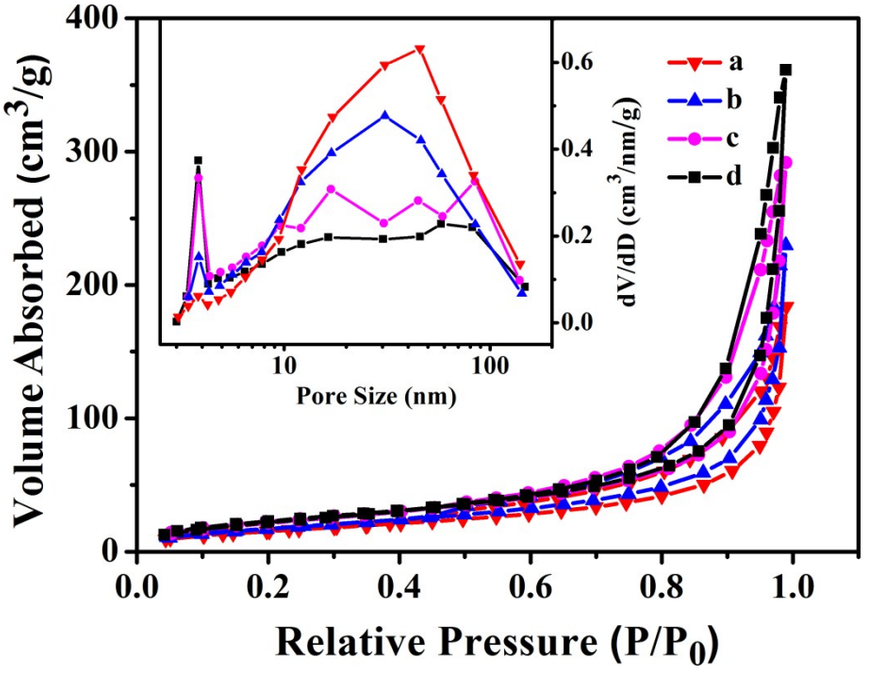


Fig. S5 Nitrogen adsorption-desorption isotherms and the pore size distribution plots (inset) of (a) CdSe-120, (b) CdSe-140, (c) CdSe-160 and (d) CdSe-180.

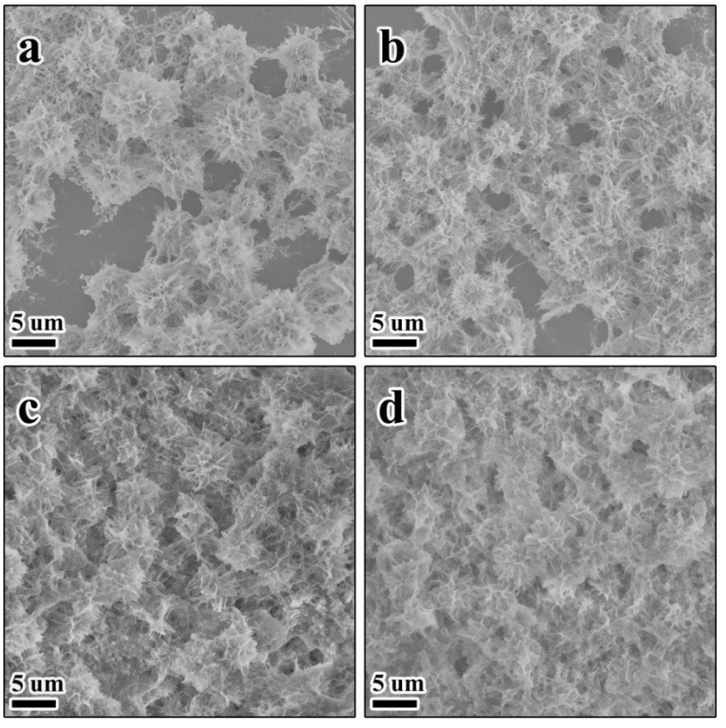


Fig. S6 SEM images of (a) CdSe-120, (b) CdSe-140, (c) CdSe-160 and (d) CdSe-180.

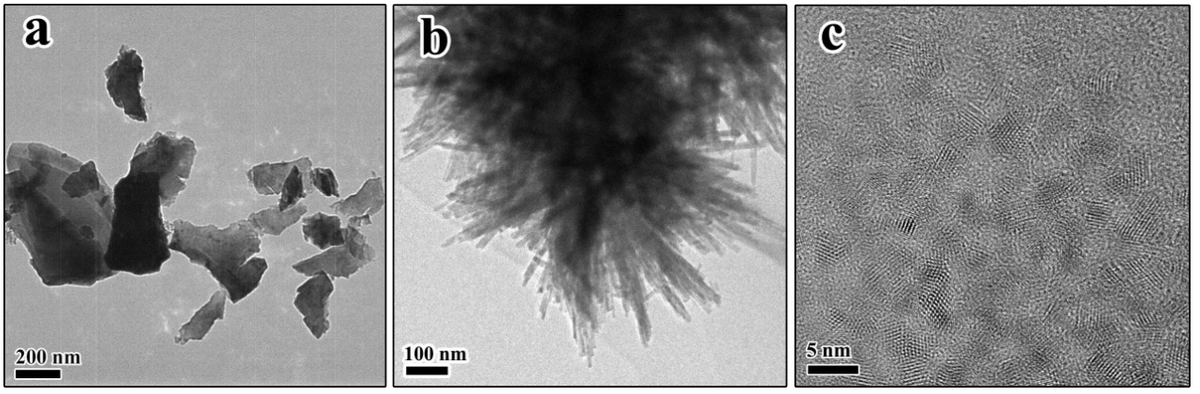


Fig. S7 TEM images of (a) commercial CdSe powders (purchased from Aladdin), (b) urchin-like CdSe and (c) CdSe QDs.

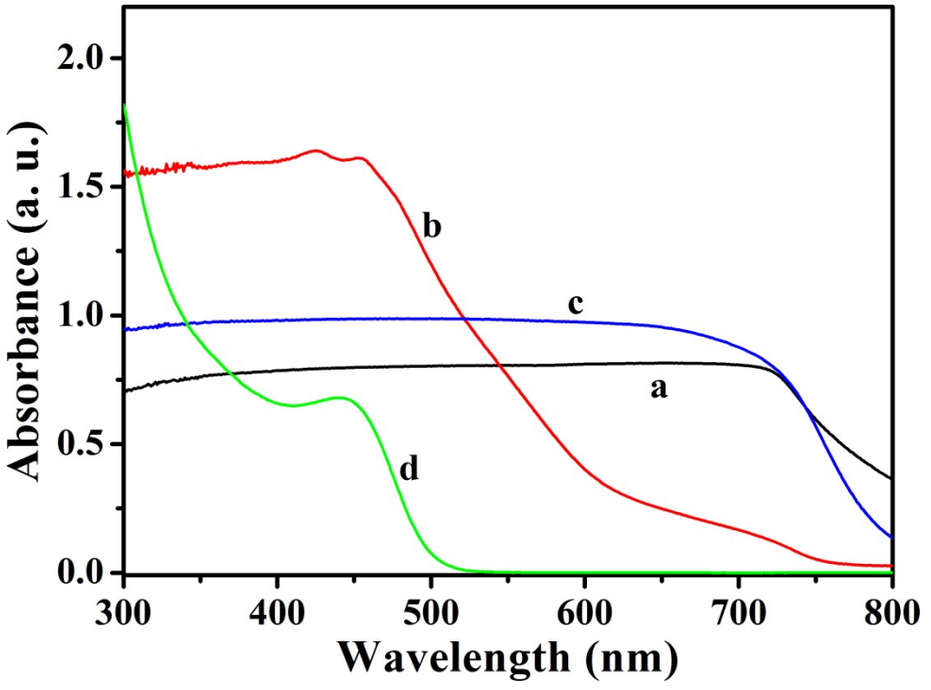


Fig. S8 UV-Vis DRS of (a) commercial bulk CdSe powders (purchased from Aladdin), (b) CdSe-140 and (c) urchin-like CdSe; (d) UV-Vis absorption spectra of CdSe QDs.

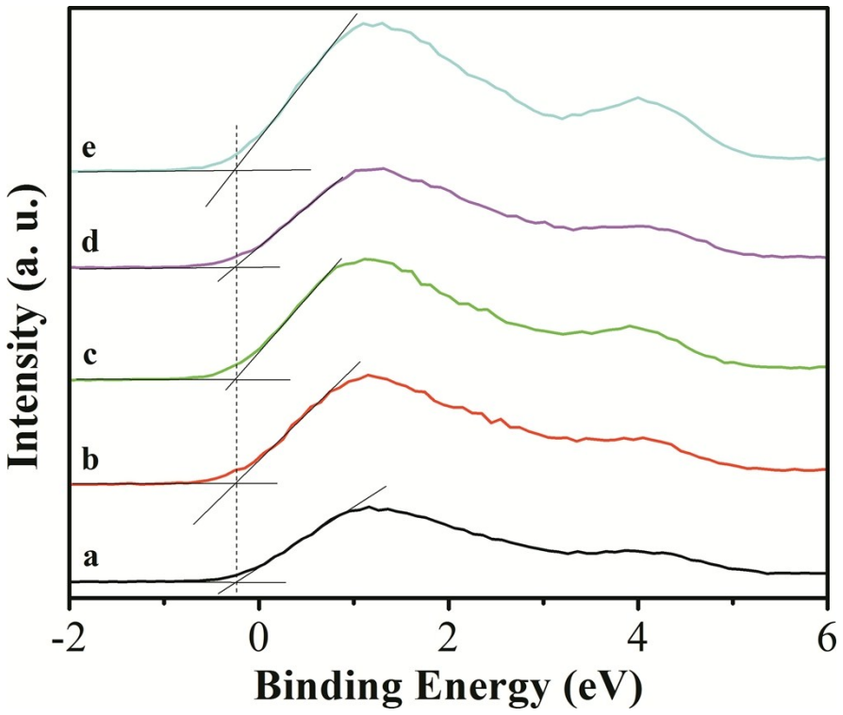


Fig. S9 VB XPS spectra of (a) CdSe-120, (b) CdSe-140, (c) CdSe-160, (d) CdSe-180 and (e) commercial bulk CdSe powders (purchased from Aladdin). It can be clearly seen that the VB positions of flower-like CdSe assemblies are almost no change compared with that of commercial bulk CdSe powders.

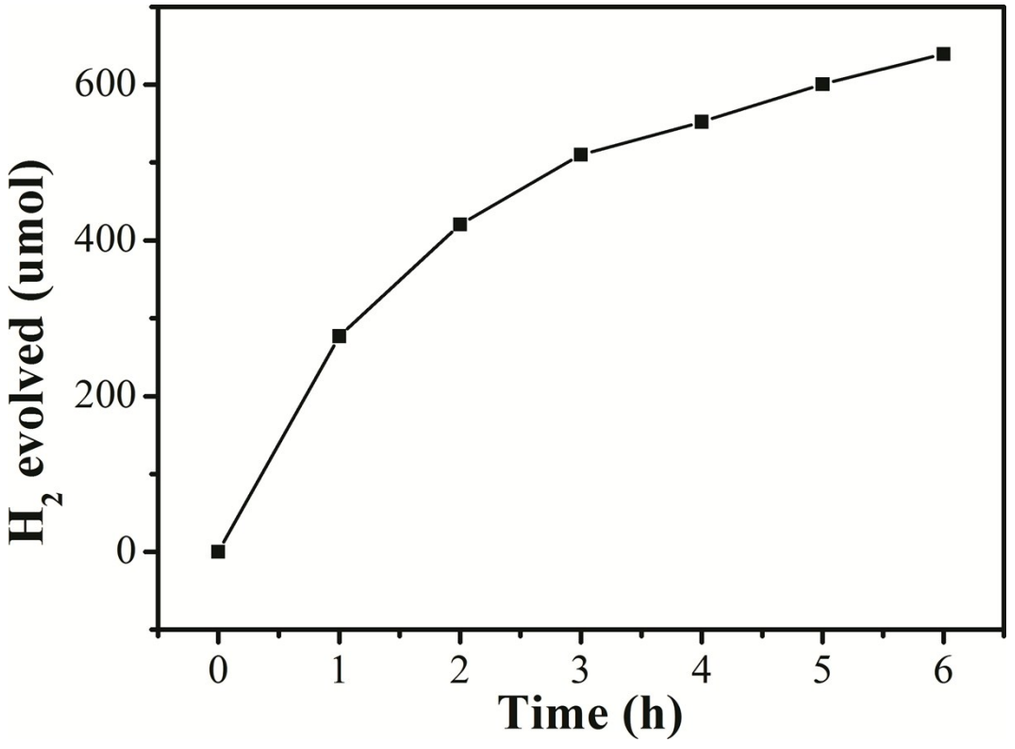


Fig. S10 Photocatalytic H_2 evolution of CdSe-140 under visible light irradiation ($\lambda > 400$nm) for 6 h.

References

1. H. Y. Han, Z. H. Sheng and H. G. Liang, *Mater. Lett.*, 2006, **60**, 3782-3785.
2. Z. J. Li, J. J. Wang, X. B. Li, X. B. Fan, Q. Y. Meng, K. Feng, B. Chen, C. H. Tung and L. Z. Wu, *Adv. Mater.*, 2013, **25**, 6613-6618.
3. W. W. Yu, L. H. Qu, W. Z. Guo and X. G. Peng, *Chem. Mater.*, 2003, **15**, 2854-2860.
4. H. Fan, J. B. Liang, Y. G. Zhang, M. F. Zhang, B. J. Xi, X. Y. Wang and Y. T. Qian, *Solid State Sci.*, 2008, **10**, 901-907.