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Supporting Information

Homogenously Hexagonal Prismatic $AgBiS_2$ Nanocrystals: Controlled Synthesis and Application in Quantum Dot-Sensitized Solar Cells

Na Liang,[a] Wenlong Chen,[a] Fang Dai,[b] Xiangyang Wu,[c] Wei Zhang,[c] Zhi Li,[c] Jingmei Shen,[b] Shoushuang Huang,[a] Qingquan He,[a] JiantaoZai,[a] * Nenghu Fang[a] and Xuefeng Qian[a] *

[a] Shanghai Electrochemical Energy Devices Research Center, School of Chemistry and Chemical Engineering and State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai, 200240, P. R. China.
[b] Global Research & Development, General Motors, MI 48090, United States
[c] Shanghai key laboratory of catalysis of poly olefin, Shanghai Research Institute of Chemical Industry, Shanghai 200062, P. R. China.
E-mail: xfqian@sjtu.edu.cn; zaijiantao@sjtu.edu.cn

Preparation of photoanodes: The FTO glasscoated with TiO_2 were purchased from Yingkou OPV Tech New Energy Co. Ltd. The successive ionic layer adsorption and reaction(SILAR) method was available to in situ synthesize CdS and CdSe QDs sequentially on the photoanodes.[1] First, for CdS growth TiO_2 film was alternatively immersed into 0.5 M $Cd(NO_3)_2$ ethanol solution and 0.5 M Na_2S methanol/deionized water (7:3, volume) solution for three cycles. Following each immersion of these two solutions, rinsing wasundertaken for 30 s using dehydrated ethanol and methanol, respectively. After that, the process of CdSe growth is similar to that of CdS, and sodium selenosulphate (Na_2SeSO_3)[2] is used as Se source. The Na_2SeSO_3 precursor aqueous solution is prepared by refluxing 0.3 M Se powder in anaqueous solution of 0.6 M Na_2SO_3 at 70^oC by vigorous magnetic stirring for 7 hours. Other procedure of CdSe SILAR is similar to CdS excepta higher temperature (50 °C) and a longer time are needed forimmersing the as-fabricated CdS-TiO_2-FTO glass into the Na_2SeSO_3 solution. Furthermore, following each immersion ($Cd(NO_3)_2$ and Na_2SeSO_3), rinsing was undertaken using dehydrated ethanol and deionized water for four time, respectively. After finishing the CdS and CdSe SILAR processes, the QD-sensitized TiO_2 electrode was then treated with 2 cycles of ZnS by dipping into 0.1 M $Zn(OAc)_2$ and 0.1 M Na_2S aqueous solutions for 1 min/dip alternately, and following each immersion, rinsing was undertaken using deionized water for 30 s, respectively. The as-prepared photoanodes were dried at 60 ^oC in the vacuum oven.

Material Characterizations.

The as-prepared products were characterized by powder X-ray diffraction (XRD, Shimadzu XRD-6000 with Cu Kα radiation λ=1.5406 Å, X-ray tube current and voltage were set at 30 mA and 40 kV, respectively). The morphology of samples was characterized by field-emission scanning electron microscopy (FESEM, FEI SIRION 200) and transmission electron microscopy (TEM, JEM 100CX and JEOL 2010). X-ray photoelectron spectroscopy (XPS) was performed with a VG Scientific ESCLAB 220iXL X-ray photoelectron spectrometer.

Preparation of $AgBiS_2$ and Pt counter electrodes (CEs): FTO conductive glass were ultrasonically cleaned and then rinsed thoroughly with soap-suds, deionized water and acetone sequentially. The $AgBiS_2$ CEs were prepared by mixing a paste containing 80% active materials powders, 10 % poly (vinyl difluoride) and 10 % acetylene black in a mass ratio of 8:1:1. N-methyl-2-pyrrolidone was used as the solvent to prepare the paste of the above-mentioned mixtures and subsequently the paste was dropped onto an edge of the drilled and washed FTO conductive glass substrate to form the corresponding materials film by the doctor-blade method. Furthermore, the as-prepared $AgBiS_2$ CEs were dried at 60 °C in the vacuum oven. Different from the above $AgBiS_2$ CEs, Pt CEs used the following process: 50 µL of H_2PtCl_6 in ethanol was drop-cast on FTO glass substrates, followed by heat treatment at 380 °C for 30 minutes.[3]

Solar cell fabrication: The CdS/CdSe co-sentisized TiO_2 photoanodes were assembled into solar cell by sandwiching them with CEs ($AgBiS_2$ and Pt). The polysulfide electrolyte consisted of 1 M S, 1M Na_2S and 0.2 M KCl in water/methanol (v/v, 3:7) solution between them. And a 50 µm thickness Surlyn film (3 M) with a square window was used as spacer between the photoanodes and the CEs. The photoanode active area of the cell was 0.4 × 0.4 cm^2.

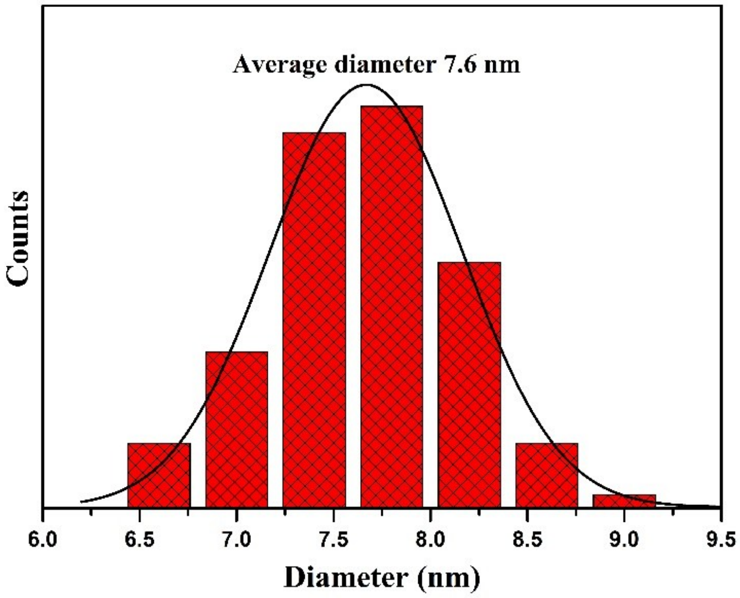

Fig. S1 The size distribution histogram of $AgBiS_2$ nanocrystals.

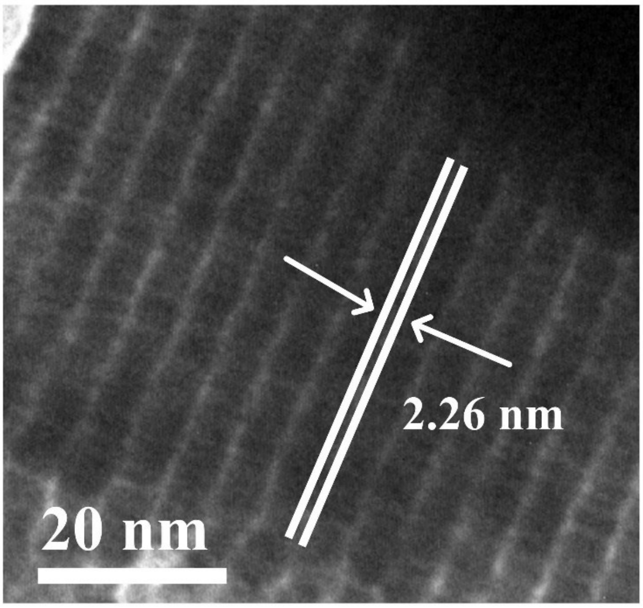

Fig. S2 HRTEM image of the as-prepared $AgBiS_2$ nanocrystals.

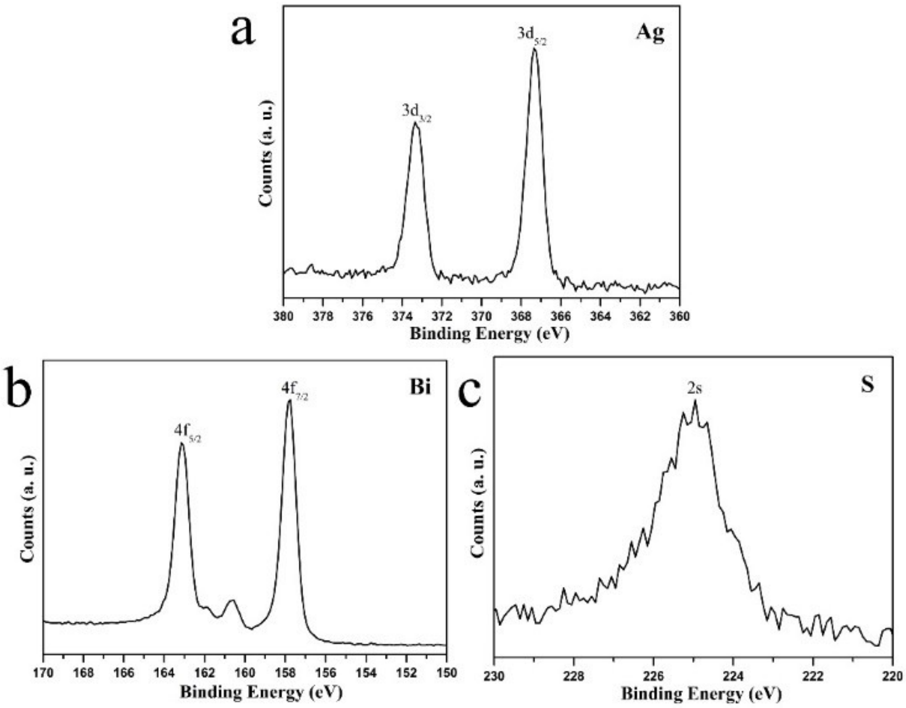

Fig. S3 XPS spectra of the as-prepared $AgBiS_2$ nanocrystals.

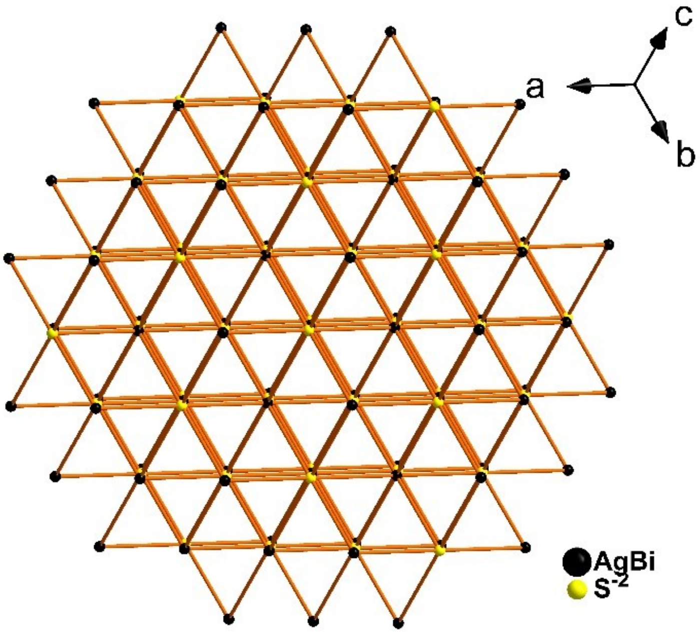

Fig. S4 Three-dimensional network of the as-prepared $AgBiS_2$ nanocrystals.

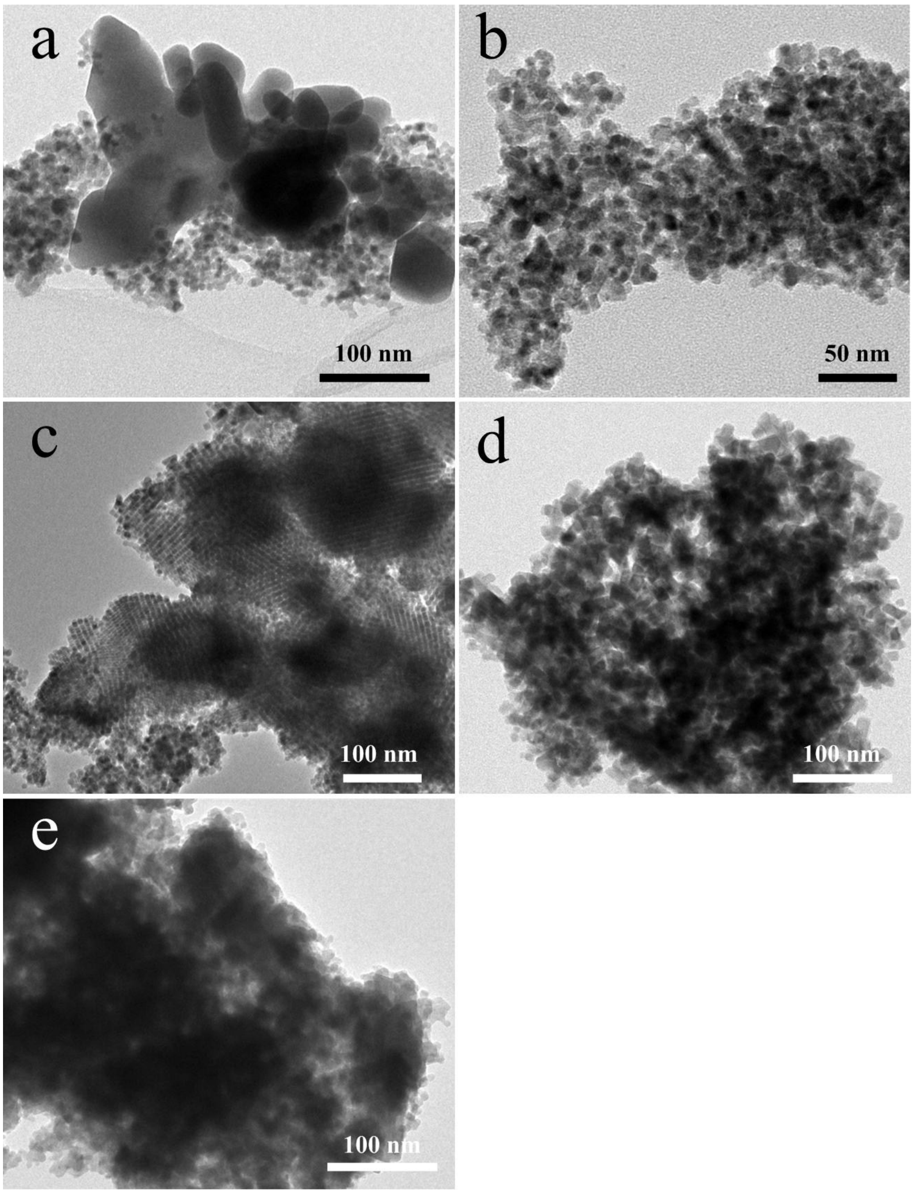

Fig. S5 (a-e) TEM images of as-prepared $AgBiS_2$ prepared in mixed solution of CHA and DCA with different ratio (a) 1:6, (b) 1:3, (c) 1:1, (d) 3:1 and (e) 6:1, respectively.

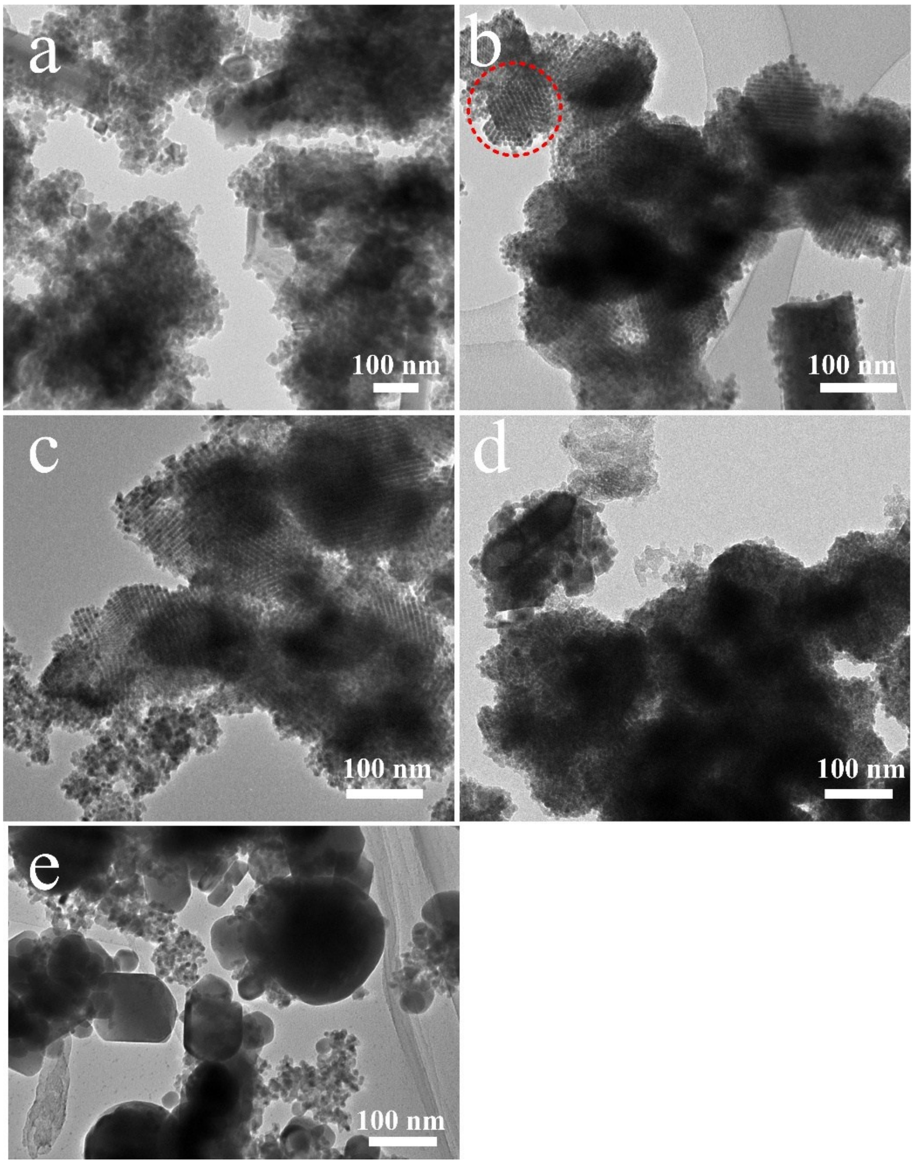

Fig. S6 (a-e) TEM images of as-prepared $AgBiS_2$ prepared at 200 ^{o}C for (a) 3 hours, (b) 6 hours, (c) 12 hours, (d) 16 hours and (e) 24 hours, respectively.

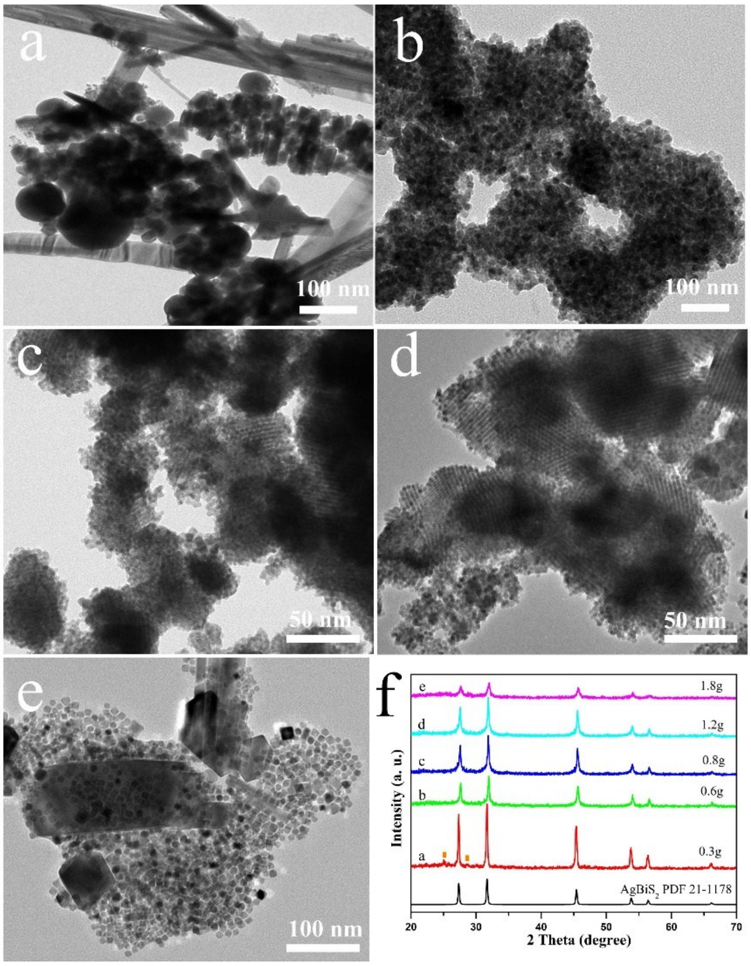

Fig. S7 (a-e) TEM images and (f) XRD patterns of as-prepared $AgBiS_2$ prepared in different mass of OA. (a) 0.3g, (b) 0.6g, (c) 0.8g, (d) 1.2g and (e) 1.8g.

The band gap (E_g) of the as-prepared $AgBiS_2$ nanocrystals can be determined from the absorbance spectra according to the equation:

$\alpha h\nu = A(h\nu - E_g)^n$

where, α, $h\nu$, A and E_g are the absorption coefficient, photon energy, a constant value and band gap energy, respectively. The value of n is assigned to transition, which takes different values for allowed and forbidden, direct (n=1/2) and indirect (n=2) transitions. By the plot of $(\alpha h\nu)^{1/n}$ *versus* $h\nu$, the extrapolation point is obtained. Then value of the as-prepared $AgBiS_2$ nanocrystal is 1/2[4] and the band gap energy is 2.78 eV.

References

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