Supporting Information

Facile Synthesis of $CuInGaS_2$ Quantum Dots Nanoparticles for Bilayer-Sensitized Solar Cells

Jinjin Zhao[†‡¶*], Jiangbin Zhang[†],Wenna Wang[†#], Peng Wang[†], Feng Li[†], Deliang Ren[†‡], Huanyan Si[†], Xiuguo Sun[†] , Fengqiu Ji[†] and Yanzhong Hao[§*]

†School of Materials Science and Engineering, Shijiazhuang Tiedao University, 17 Northeast, Second Inner Ring , Shijiazhuang, 050043, China.

‡College Physics Science and technology, Photovoltaic Research and Development Center, Hebei University, No.180 Wusidong Road. Baoding City, Hebei Province, 071002,China

¶The Key Laboratory for Health Monitoring and Control of Large Structures, Hebei province, 17 Northeast, Second Inner Ring , Shijiazhuang,050043,China.

§ College of Science, Hebei University of Science and Technology, 26 Yuxiang Street, Shijiazhuang 050018, China

#Yingli Energy (China) Co., Ltd.,3399 North Chaoyang Avenue, Baoding 071051, China

E-mail: jinjinzhao2012@163.com; yzhao@hebust.edu.cn

Experimental Section

I. Chemicals

Copper chloride ($CuCl_2$), Indium(III) chloride tetrahydrate ($InCl_3 \cdot 4H_2O$, 39%), Sodium sulfide, Titanium tetrachloride (99.5%), Ethanol (98%), Nitric acid (65%) were purchased from Sinopharm Chemical Reagent Co., Ltd; F127 was purchased from Sigma-Aldrich, Inc. Polyethylene glycol (PEG; 20000 in molecularweight) and Gallium(III) chloride ($GaCl_3$) were purchased from J&K. The sensitizer N719 (Cis-di(thiocyanato)-N,N-bis(2,2'-bipyridyl-4,4'-dicarboxylate)Ru(II)bis-tetrabuty lammonium) electrolyte, surlyn film were purchased from Yingkou Opvtech New Energy Co., Ltd.

II. Synthesis of the TiO_2@CIGS film and fabrication of Quantum Dot-Dye Bilayer-Sensitized Solar Cells (QDBSC)

2.1 Synthesis of TiO_2 nanoparticles

TiO_2 nanoparticles were synthesized as the following method. 2.97g F127 was firstly dissolved in 36.88g ethanol at 40℃ for 30 minutes to form a clear solution. Then 3.4g $TiCl_4$ was added to the obtained solution. The precursor solutions were placed into a Teflon-lined stainless steel autoclave (100 mL in capacity) after stirring 8h under 40℃. The autoclave was placed in an oven at 160℃ for 16h. Subsequently, the products were filtered, washed and dried at 80℃. Finally, the powders were sintered at 610℃ for 10 minutes after being kept at 300℃ for 90 minutes and 500℃ for 240 minutes. During the whole process, the heating rate was kept at a constant of 2℃/min. After sintering, the products were dispersed using deionized water and nitric acid (65%) until the pH of the solution reached to about 2[1]. Then the mixture solution was vigorous stirred at 80℃ for 8 hours to obtain TiO_2 nano particles.

2.2 Preparation of TiO_2@CIGS nanoparticles

In step A, a certain amount of TiO_2 nanoparticles was put into a vessel and subjected to vacuum. After thirty minutes' vacuum, the mixed solution of $InCl_3$/$GaCl_3$ (0.1mol/L) was allowed to enter the system until normal atmospheric pressure was achieved, then the system was held for ten minutes before the mixed solution of $InCl_3$/$GaCl_3$ was removed by evaporation. The precipitate was dried under flowing air at 80℃. After drying, the powder was washed twice with absolute ethanol. Then, the drying under flowing air was took again. Step B and step C were repeated as described step A other than the $InCl_3$/$GaCl_3$ was replaced by 0.2 mol/L $CuCl_2$ aqueous and 0.4mol/L Na_2S aqueous, respectively. after step A, B and C, the samples were calcined in Ar gases at 500℃ for 1h to obtain TiO_2@CIGS nanoparticles.

2.3 Preparation of Mesoporous TiO_2 films and TiO_2@CIGS film

The mesoporous TiO_2 films were prepared by the doctor-blade method. First of all, the TiO_2 paste was made with the TiO_2 nanoparticles synthesized in section 2.2. Briefly, 0.8g TiO_2 was added in a mixed solution of ethanol/ deionized water(3:1) and treated using ultrasonic for 30 minutes after the addition of PEG aqueous which acted as the pore-forming material. Then they were grinded into ropiness in agate mortar. A mask, with a window encompassed by 3M scotch tape, was used to definethe 5mm×5mm area which was used to spread the paste dropped one edge of the window with

a glass slide on the conductive glass (SnO_2:F coated glass, FTO). Subsequently, The as-prepared TiO_2 films were sintered in air with the heating rate of 2℃/min to 300℃ for 30 min, 500℃ for 60 min.

The procedure of synthesis of mesoporous TiO_2@CIGS film was the same as described above.

2.4 Fabrication of Quantum Dot-Dye Bilayer-Sensitized Solar Cells (QDBSC)

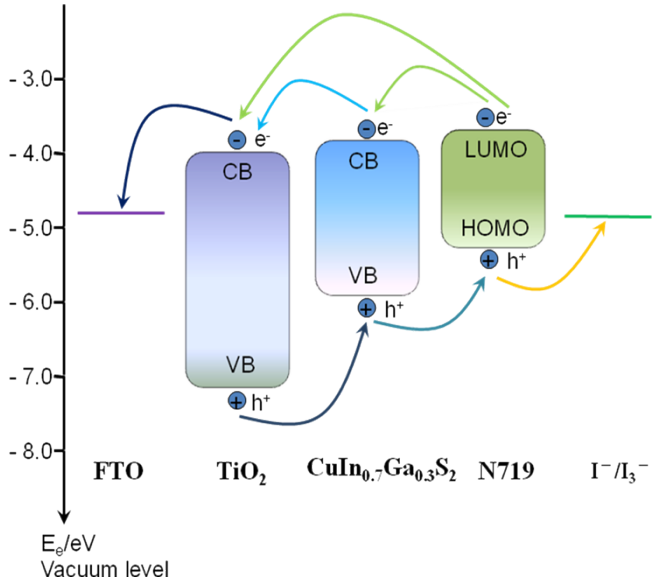
The mesoporous TiO_2 film and TiO_2@CIGS film were sensitized with N719 dye by direct adsorption. Firstly, the as-prepared TiO_2 film and TiO_2@CIGS film were heated to 80℃ and immersed in the N719 ethanol solution（0.5mM）for 24h. After rinsing the film in solution by ethanol and drying, the desired mesoporous TiO_2/N719 film and TiO_2@CIGS / N719 electrodes were obtained.

The photovoltaic cells were assembled with the mesoporous TiO_2/N719 film or TiO_2@ CIGS/ N719 photoelectrode, Pt coated counter electrode, and 60μm thick sealing material (OPV-SN-60). Commercially available electrolyte of I_3^-/I^- was injected into the space between the photoelectrode and counter electrode.

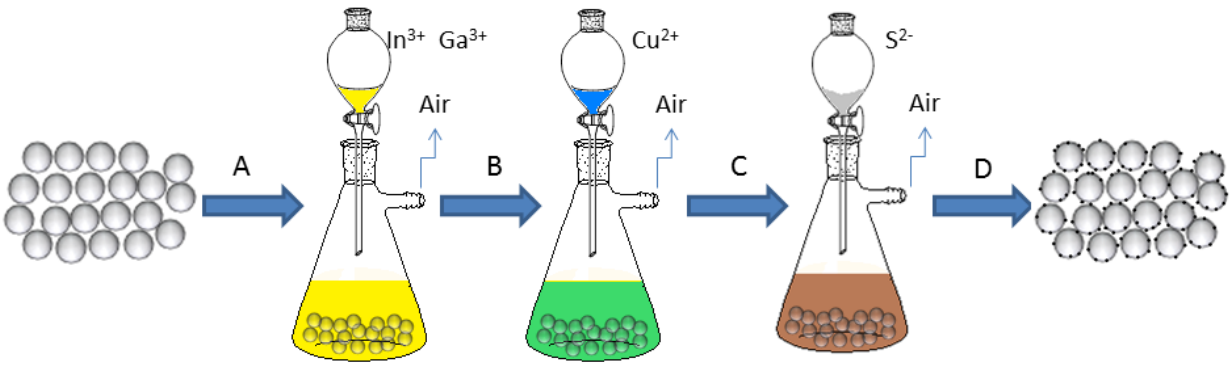
III. Characterization

XRD patterns of powders were obtained using D8 Advance(Germany) diffractometer with Cu Kα radiation (40 kV and 40 mA) with the scanning rate of 4° min^{-1} for wide angle tests. The N_2 sorption measurements were performed using Micromeritics Tristar 3000 for mesoporosity and Micromeritics ASAP 2020 porosimeters and microposity at 77 K , respectively. The mesoporous specific surface area and the pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) methods. SEM (Scanning Electron Microscopy) analysis was performed on a Hitachi-S-4800 electron microscope. TEM (Transmission electron microscopy) images were obtained on a JEOL-2010F electron microscope operated at 200 kV. The UV/Vis absorbance spectra were measured using a Shimadzu UV-2550 spectrophotometer. Photovoltaic measurement (J-V) was recorded with a Newport Oriel class AAA solar simulator (model 92250A-1000) equipped with a class A 300 W xenon light source powered by a Newport power supply (model 69907). The power output of the lamp was calibrated to 1 Sun (AM1.5G, 100 mW/cm^2) using a certified Si reference cell (VLSI standard, S/N 10510-0031). The current-voltage characteristics of each cell were recorded with a Keithley-2400 digital source meter. Photovoltaic performance was measured using a mask with an aperture area of 0.25cm^2. The incident photon-to-current efficiency (IPCE) was measured in DC mode with a 1/4 m double monochromator (Crowntech DK242), a multi-meter (Keithley 2000), and two light sources depending on the wavelength range required (300–600 nm: xenon lamp, 300 W; 600–900 nm:

tungsten-halogen lamp, 150 W). The monochromatic light intensity for IPCE efficiency was calibrated with a reference silicon photodiode. All the measurements were conducted under ambient conditions.

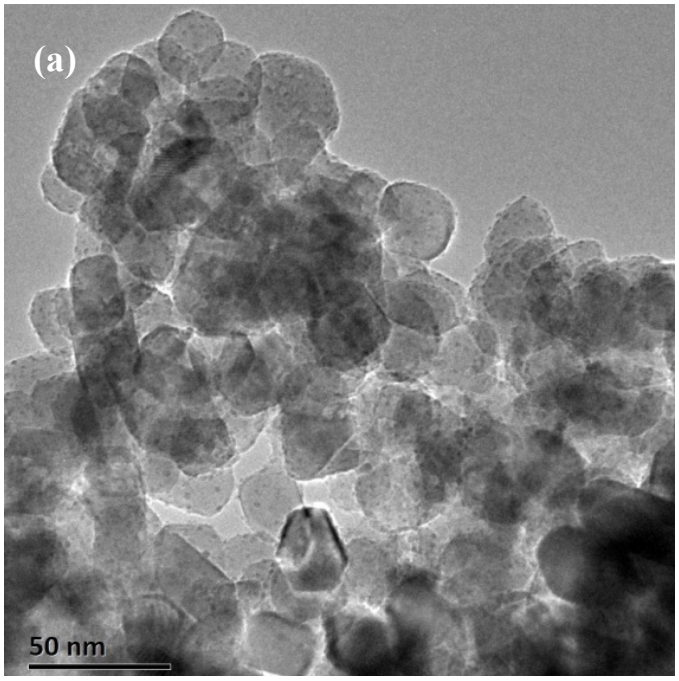


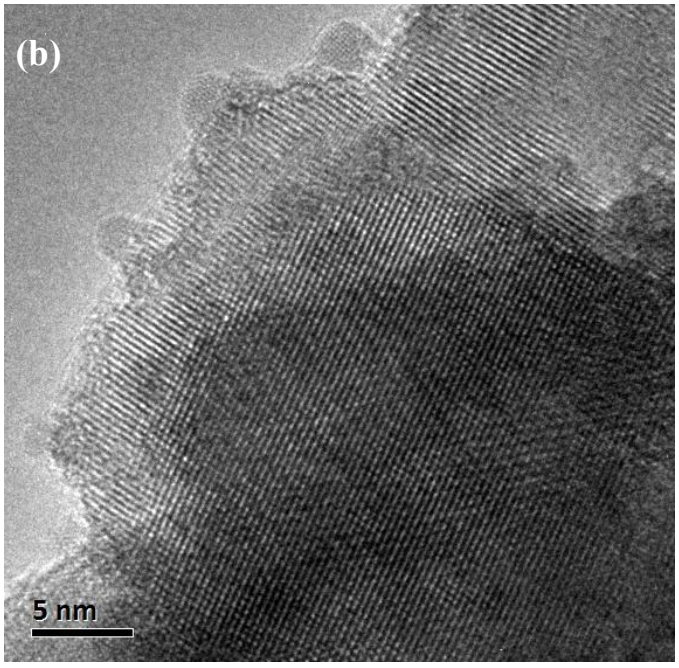
Scheme S1. A schematic showing the relative band energy levels for charge transfer in the FTO/TiO_2/CIGS/N719 electrolyte.



Scheme S2. The schematic process of TiO_2@CIGS nanoparticles in three steps: (A) adding TiO_2

nanoparticles sample and mixed solution of $InCl_3/GaCl_3$ into vessel and vacuumizing; (B) after drying the sample, adding the sample and $CuCl_2$ aqueous into vessel and vacuumizing; (C, D) repeat step B by substituting $CuCl_2$ aqueous and Na_2S aqueous, respectively.





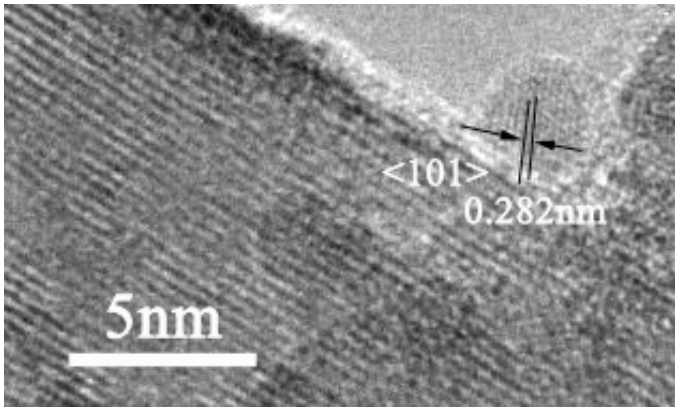


Fig. S1 TEM images (a) and HRTEM image (b,c) of the prepared sample of TiO_2@CIGS

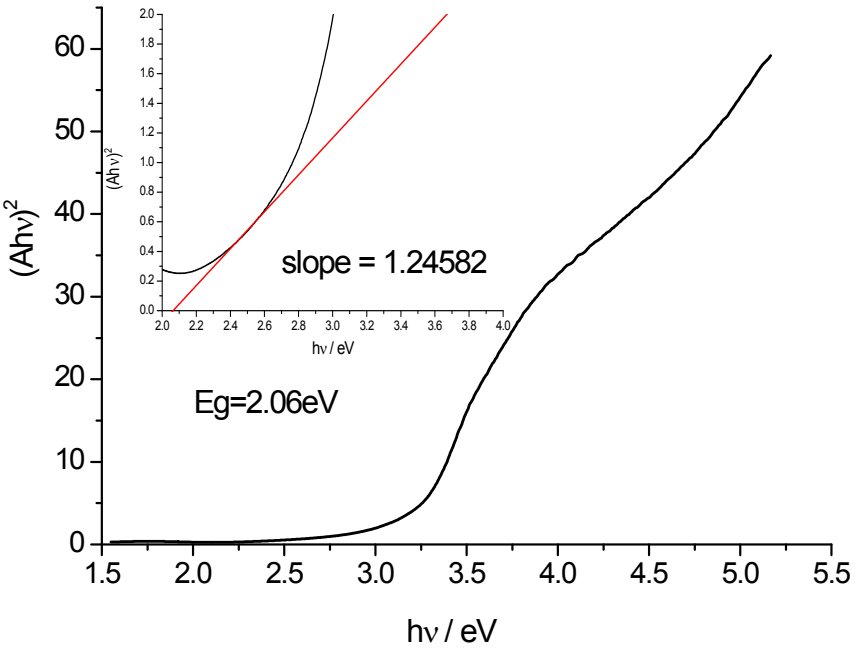


Fig. S2 Plots of $(Ahν)^2$ against the photon energy(hν) for TiO_2@CIGS

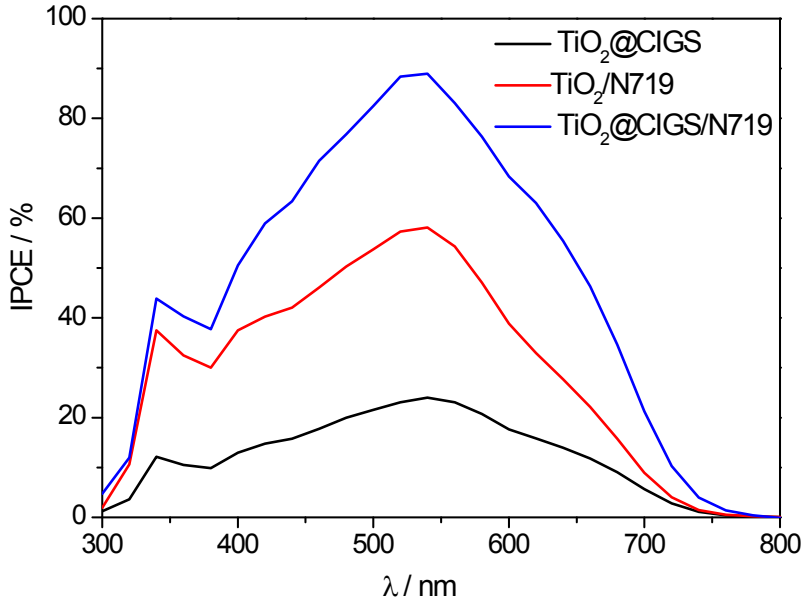


Fig. S3 IPCE spectra of solar cells fabricated with different photo-anode

Table S1 Structural parameters of samples of TiO_2 NPs and TiO_2@CIGS

	BET /$m^2 \cdot g^{-1}$	Mesopore Volume/$cm^3 \cdot g^{-1}$	Mesopore Size/nm
TiO_2 NPs	45.24	0.164	10
TiO_2@CIGS	18.2	0.084	10, 3.5

Table S2 Photovoltaic Parameters of Different Solar Cells

	V_{OC}/mV	**J_{SC}/mA·cm^{-2}**	**η/%**	**FF / %**
TiO_2@CIGS/N719	767	18.44	7.51	53

TiO_2/N719	730	12.28	5.51	62
TiO_2@CIGS	661	6.40	2.38	57

Reference:

1. A. B. F. Martinson, T. W. Hamann, M. J. Pellin and J. T. Hupp, *Chemistry - A European Journal*, 2008, **14**, 4458-4467.