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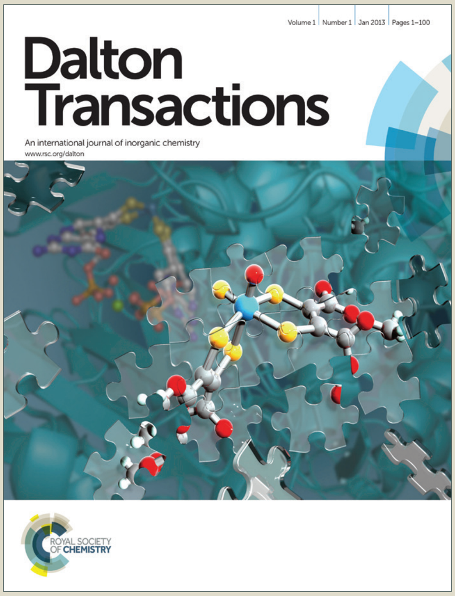

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ARTICLE TYPE

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

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$CuIn_{0.7}Ga_{0.3}S_2$ Quantum Dots (QDs) with particle size of 2-5 nm were directly synthesised by a vacuum one-pot-nanocasting process and homogeneously anchored on TiO_2 nanocrystals (<50nm) for the first time. We further present a $CuIn_{0.7}Ga_{0.3}S_2$ quantum dots and dye bilayer-sensitized solar cells with a power conversion efficiency 36.3% higher than mono-dye sensitized solar cell.

With increasing global energy consumption and environmental issues, the fabrication of low cost and high efficiency photovoltaic cells has attracted intense research interest in recent years[1, 2]. Ternary and quaternary compounds play a key role in the research of novel functional materials with high photoelectric properties and without toxic elements such as Cd, Pb, and Hg.[3-5] Due to the relatively narrow band gaps and high absorption coefficients,[6] chalcopyrite semiconductors show excellent photovoltaic performance in thin film solar cells.[7-10] Furthermore, chalcopyrite semiconductors suffer a large range of off-stoichiometry, such as $CuIn_5Se_8$, $CuIn_3Se_5$, $Cu_2In_4Se_7$, without compromising their performance in optoelectronics as the result of forming deep trap states.[5,33]

It is well konwn that the band gap of semiconductor nanocrystals can be optimized by changing their compositions or sizes [4, 11-15], which makes them very attractive as sensitizers in quantum dot sensitized solar cells (QDSSC).[16-18] $CuInS_2$ is an important representative which has achieved much development in synthesis methods and application in QDSSC.[3, 6, 11, 19-22] In previous work, $CuInS_2$ quantum dots were often synthesized in organic solvent systems with long chains on the $CuInS_2$ QDs, which decreased their photovoltaic performance. By substituting cations or anions with ions of the same oxidation state, CuInSSe[4, 11] and $CuInGaSe_2$[9, 12] can be synthesized.

A different type of approach implemented to expand the spectral response of the system is the co-sensitization of TiO_2 photoanodes with both QD semiconductors and molecular dyes, which have complementary absorption profiles.[25] Herein, we firstly report a facile approach for the synthesis $CuIn_{0.7}Ga_{0.3}S_2$ quantum dots directly and homogeneously anchored on TiO_2 nanocrystals (designated TiO_2@CIGS) for quantum dot-dye bilayer-sensitized solar cells (QDBSC). $CuIn_{0.7}Ga_{0.3}S_2$ QDs with particle size of 2-5nm were attached on the surface of TiO_2 nanocrystals directly without any bifunctional linker molecules. Scheme S1† shows a schematic showing the relative band energy levels for charge transfer in the FTO/TiO_2/CIGS/N719 electrolyte. Due to the quantum confinement effect in the $CuIn_{0.7}Ga_{0.3}S_2$ QDs, a higher conduction band edge drives the energetics of $CuIn_{0.7}Ga_{0.3}S_2$ QDs to more favorable levels, for electron injection from photoexcited $CuIn_{0.7}Ga_{0.3}S_2$ QDs into TiO_2.[19,29] More importantly, the TiO_2@CIGS nanocrystals open the path toward high optical density DSSCs that cover a significant part of the solar spectrum.

An one-pot vacuum nanocasting process was proposed and is shown in Scheme S2†. In step A, the as-prepared TiO_2 nanocrystals sample was subjected to a vacuum to remove all of the air in the pores of TiO_2 nanoparticles. In step B/C/D, the vacuum pump was switched off and the solution of $InCl_3$/$GaCl_3$(1:1 molar ratio), $CuCl_2$, Na_2S was allowed into the chamber containing TiO_2 nanoparticles, respectively. The pore channels of the TiO_2 nanoparticles under this transitory vacuum were therefore filled by the solution. Subsequently, the composite were separated and dried under 80℃. Finally, the TiO_2 with quantum dots precusor in the pores were calcined in order to obtain $CuInGaS_2$ quantum dots-loaded TiO_2, with the $CuInGaS_2$ nanoparticles anchored on TiO_2. To accomplish an effient solar device, this synthetic route did not involve any long-chain ligands, which are important for electron injection into TiO_2, thanks to a higher binding affinity for QDs and an improved carrier transport.[32]

The low magnification TEM images of the synthesized TiO_2 nanocrystals (Fig.1a) and TiO_2@CIGS composite nanoparticles

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(Fig.1b and Fig. S1a †) clearly show that the diameter of the prepared TiO_2 particles was about 20-50nm, and some very small particles could be found on the edge of the TiO_2 in the TiO_2 @CIGS samples. A high resolution image in Fig. S1b†, Fig. S1c† and image (Fig.1c) from the highlighted square area in Fig.1b show the quantum dots with homogeneous size (2-5nm) and well-defined lattice structure anchored uniformly on the TiO_2 nanocrystals.

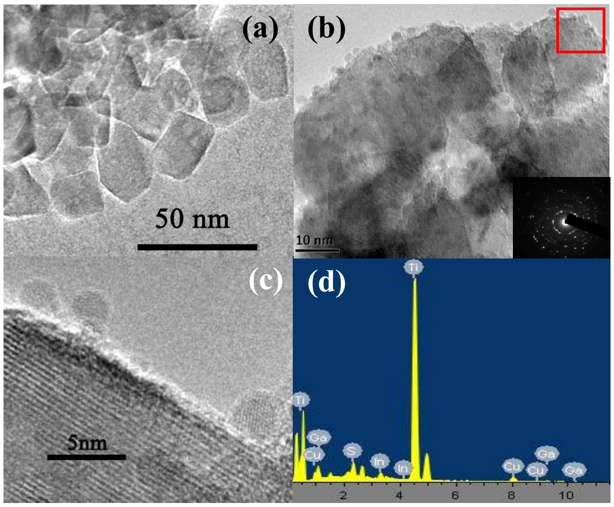

Fig. 1 TEM images of the synthesized TiO_2 nanocrystals (a) and TiO_2@CIGS composite nanoparticles (b); (c) is HR-TEM images taken from the area masked by a red square in (b); (d) Simultaneous energy-dispersive spectroscopy (EDS) of the TiO_2@CIGS sample; selected-area electron diffraction pattern of TiO_2@CIGS inserted in (b).

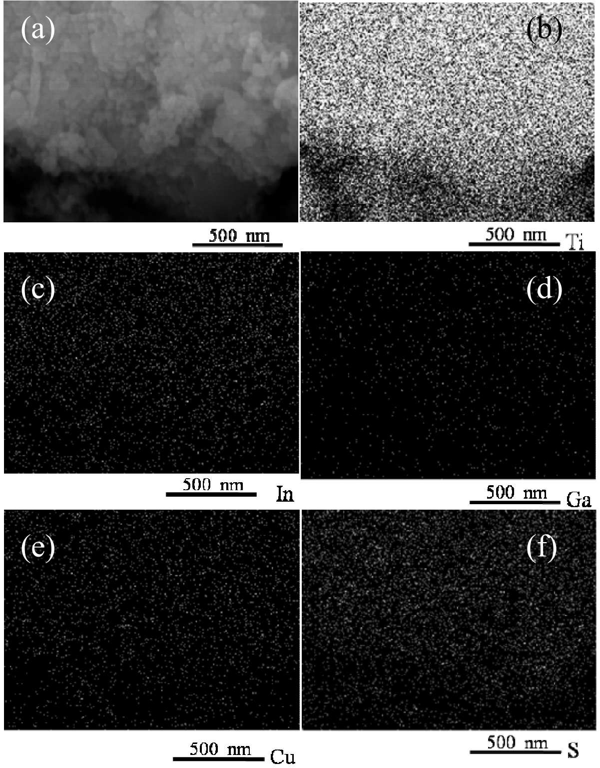

Fig. 2 SEM image (a) of TiO_2@CIGS nanocrystals. SEM-EDS elemental mapping (b) of Ti, (c) of In, (d) of Ga, (e) of Cu and (f) of S.

Fig.1d is the energy-dispersive spectroscopy (EDS) image of sample TiO_2@CuInGaS nanocrystals. It proves the existence of Cu, In, Ga, S elements in the quantum dots, and the ratio of Cu/In/Ga/S is 1.07(±0.2) : 0.73(±0.1) : 0.27(±0.1): 2.0. To further prove it, SEM-EDS elemental mapping was conducted in Fig. 2, we can conclude that the quantum dots are off-stoichiometry $CuIn_{0.7}Ga_{0.3}S_2$.

Fig. 3 shows the XRD pattern of the TiO_2@CIGS matched well with that of anatase TiO_2 ($I4_1$/amd, JCPDS 73-1764) and $CuIn_{0.7}Ga_{0.3}S_2$.[23] However, the presence of a minor portion of the chalcopyrite $CuIn_{0.7}Ga_{0.3}S_2$ (tetragonal, $I\bar{4}2d$)[23, 27] cannot be ruled out, corresponding to the (101) lattice plane of $CuIn_{0.7}Ga_{0.3}S_2$ confirmed by HRTEM analyses (Fig. S1c†). Note that, as no pattern was reported in the JCPDS database for this exact composition, a pattern was calculated for this phase by Liberato Manna.[23] The XRD diffraction features of TiO_2@$CuIn_{0.7}Ga_{0.3}S_2$ sample indicated a composite materials of anatase TiO_2 and chalcopyrite $CuIn_{0.7}Ga_{0.3}S_2$.

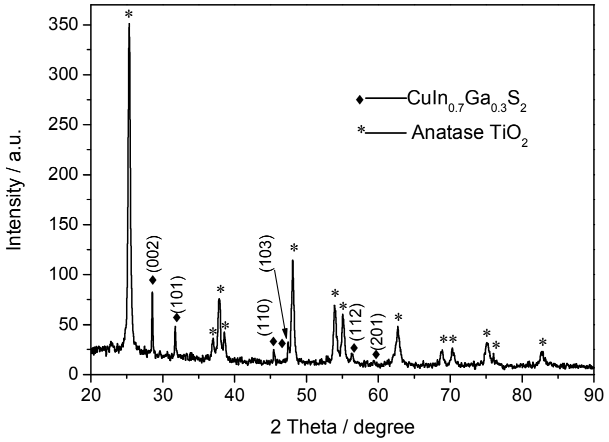

Fig. 3 XRD pattern of sample TiO_2@CIGS

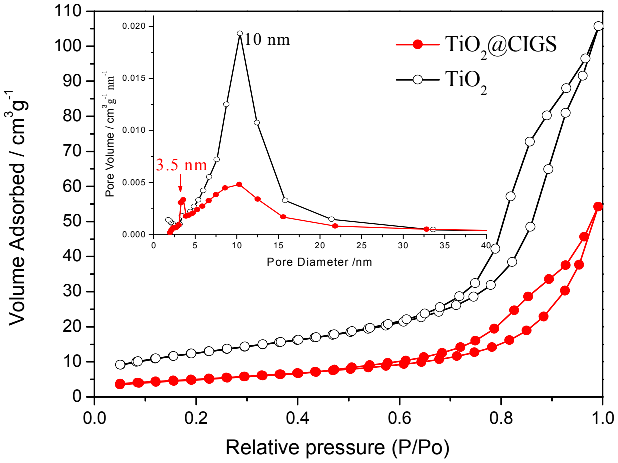

Fig. 4 N_2 adsorption–desorption isotherms and the corresponding pore diameter distribution curves of different samples (inset).

The N_2 adsorption-desorption isotherms of TiO_2 nanoparticles and TiO_2@CIGS are shown in Fig. 4 for comparison. Both the

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isotherms of TiO_2 nanoparticles and TiO_2@CIGS exhibit a type-H1 hysteresis loop, characteristic of mesoporous materials, with clear adsorption and desorption jumps at 0.6 and 0.9. The pore size distribution of TiO_2@CIGS derived from the desorption branch using the Barrett-Joyner-Halenda (BJH) method indicates an unaffected large mesopore size of 10nm and small mesopore size of 3.5nm aggregated by quantum dots, but the specific BET surface area and the mesopore volume reduced by 59.8% and 48.8%, respectively, (see Fig.4 and Table S1†) after loading of CIGS quantum dots, due to the small particle size (2-5nm) and large molecular weight of quantum dots. The BET surface area and the mesopore volume of TiO_2@CIGS are 18.2m^2/g and 0.084cm^3/g, which are enough for the high capacity enrichment of N719 dye.

Fig. 5 shows the absorption spectra of the naked TiO_2 film, and the TiO_2@CIGS film. The TiO_2 film absorbs only UV light (wavelengths of <400nm). After QDs sensitization, the absorption spectra of the TiO_2 films extend to the visible light region. The absorption onset for TiO_2@CIGS at approximately 550nm. The optical absorption spectra of the TiO_2@CIGS showed a corresponding red shift of the band edge as the QDs capped TiO_2 NPs. Fig. S2† reports a plot of $(Ah\nu)^2$ versus $h\nu$ (A = absorbance, h = Planck's constant, and ν = frequency), from which it is possible to extrapolate the slope near the absorption edge and extract the band gap energy. The fits yielded 2.06 eV for TiO_2@CIGS. The band gap value is close to those reported for wurtzite C(IG)S nanocrystals,[27, 23] due to the density of state (DOS) of TiO_2/QDs contributed by the surface states of QDs.[28] A Bohr excitonic radius of 5.6 nm for $CuIn_{0.7}Ga_{0.3}S_2$ QDs was calculated by the Bohr excitonic radius formula and Brus formula.[34] Due to quantum con-finement, reducing the dimensions of QDs smaller than its exciton Bohr radius effectively widens its energy gap.[35]

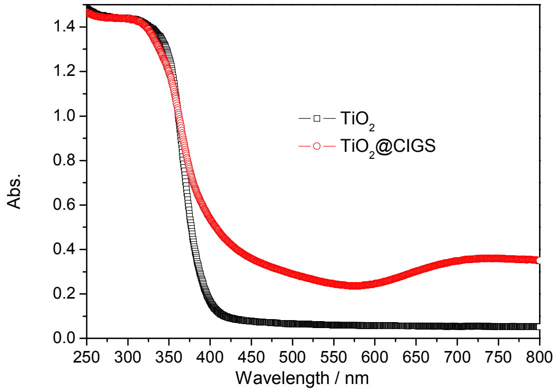

Fig. 5 UV-vis absorption spectra of different samples.

Co-sensitization with QDs or dyes has also been shown as an effective strategy for improvement.[11, 25, 26, 29] The contribution of the two absorbers to the overall cell performance is also evident in the I-V curves presented in Figure 6. Comparing the bisensitizer nanoporous configuration (TiO_2@CIGS/N719) with a monosensitizer cell (TiO_2/N719 and TiO_2@CIGS), we obtained a significant increase in all cell parameters. The short-circuit current density, Jsc, increased from 12.28 to 18.44 mA/cm^2 (+50.2%), the open-circuit voltage, Voc, increased from 730 to 767 mV (+37mV), however, the fill factor (FF) reduced from 0.62 to 0.53, due to electron recombination and larger Rsh which can be validated from the slope of Jsc point in the J-V curve. Consequently, under operating conditions (1 sun illumination), the bisensitizer configuration improved the conversion efficiency from 5.51% to 7.51% (+36.3%), 215.5% higher than 2.38% of the QDs sensitized solar cell (TiO_2@CIGS).

The higher efficiency of TiO_2@CIGS/N719 co-sensitized solar cell is mainly attributed to its broader light absorption. To further investigate the role of $CuIn_{0.7}Ga_{0.3}S_2$, Fig. S3† show the incident photon to current conversion efficiency (IPCE) spectra. In general, the trends of the IPCE spectras (Fig. S3†) of TiO_2@CIGS/N719 co-sensitized solar cell and TiO_2 /N719 dye-sensitized solar cell are consistent with that of UV-vis absorption spectra (Fig. 5).

It was shown that by the utilization of two sensitizing layers were able to increase the optical density of our photoanodes. the energy of photons absorbed by the QDs can be transferred to a dye using Forester resonance energy transfer (FRET).[30] In this manner, one can separate the actions of light harvesting and charge separation. The $CuIn_{0.7}Ga_{0.3}S_2$ QDs on the TiO_2 NPs could not only contribute to absorb more photons to generate more photoexcited electrons, but also form uniform shell to reduce direct contact areas between the naked TiO_2 surface and eletrolyte, consequently decreasing electrons recombination in the TiO_2 to the hole-transport material of electrolyte[24]. As a consequence, improved solar cell performance can be achieved using a combination of a high-extinction-coefficient light-absorbing QD donor with an efficient electron-injecting acceptor dye molecule.[31]

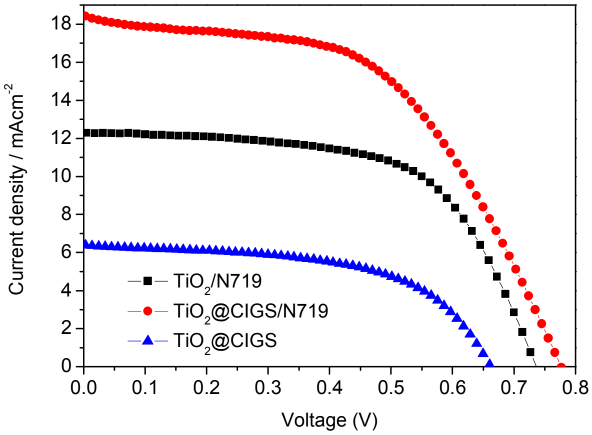

Fig. 6 Photocurrent-voltage characteristic curves of different samples.

In conclusion, the TiO_2@CIGS nanoparticles have been successfully synthesized with the method of vacuum one-pot-nanocasting process for the first time, which the $CuIn_{0.7}Ga_{0.3}S_2$ QDs (2-5nm) homogeneously anchor on TiO_2 nanoparticles (<50nm) directly. The TiO_2@CIGS nanoparticles are composite of anatase TiO_2 and chalcopyrite $CuIn_{0.7}Ga_{0.3}S_2$. The absorption onset for TiO_2@CIGS at approximately 550nm and the band gap value is 2.06 eV. The best device, fabricated with the TiO_2@CIGS photoanode, shows a power conversion efficiency η of 7.51%. The proposed TiO_2@CIGS synthesis method is more facile and costs less compared to other existed methods, and this strategy might be suitable for large-scale synthesis of nanomaterials for low-cost perovskite solar cell and layer-built solar cell.

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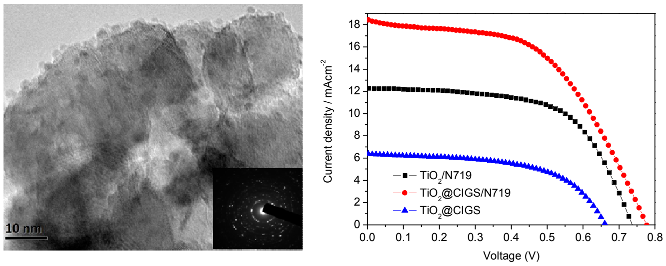

TiO_2 @ $CuIn_{0.7}Ga_{0.3}S_2$ QDs (2-5 nm) were firstly synthesised by a vacuum one-pot-nanocasting process without long-chain ligands.

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