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Control of Nanostructures and Interfaces of Metal Oxide Semiconductors for Quantum-Dots-Sensitized Solar Cells

Jianjun Tian[†,‡] and Guozhong Cao[*,†,§]

[†]Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100083, P.R. China
[‡]Institute of Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, P.R. China
[§]Department of Materials and Engineering, University of Washington, Seattle, Washington 98195-2120, United States

ABSTRACT: Nanostructured metal oxide semiconductors (MOS), such as TiO_2 and ZnO, have been regarded as an attractive material for the quantum dots sensitized solar cells (QDSCs), owing to their large specific surface area for loading a large amount of quantum dots (QDs) and strong scattering effect for capturing a sufficient fraction of photons. However, the large surface area of such nanostructures also provides easy pathways for charge recombination, and surface defects and connections between adjacent nanoparticles may retard effective charge injection and charge transport, leading to a loss of power conversion efficiency. Introduction of the surface modification for MOS or QDs has been thought an effective approach to improve the performance of QDSC. In this paper, the recent advances in the control of nanostructures and interfaces in QDSCs and prospects for the further development with higher power conversion efficiency (PCE) have been discussed.
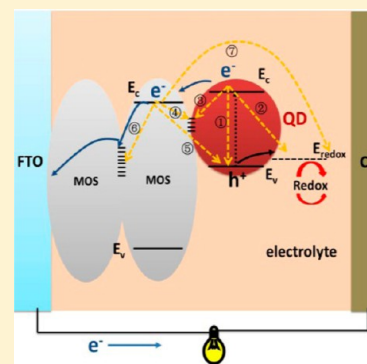
Metal oxide semiconductors (MOS), such as TiO_2 and ZnO, have been regarded as an attractive material for the solar cells, solar fuel, photo catalyst, and energy storage devices due to their excellent photoelectric and electrochemical properties.[1,2] In the past two decades, the development of nanotechnology has created various MOS nanostructures to open up new perspectives for their exploitation, significantly improving the performances of end-user devices.[3,4] For example, MOS TiO_2 with porous nanostructure has been successfully used in dye-sensitized solar cells (DSCs) to get high power conversion efficiency (PCE) of greater than 7% in 1991, which is a significant breakthrough for the next generation solar cells with low cost.[5]

DSC is a category of photovoltaic device based on a photoelectrochemical system in which a porous MOS film with dye molecules adsorbed on the surface serving as the working electrode for light harvesting and the generation of photoexcited electrons.[6] A lot of works have been focusing on improving light absorption of sensitizers.[7−10] In 2014, a recorded PCE of 13% of DSC has been obtained by using a molecularly engineered porphyrin dye coded SM315 and the cobalt (II/III) redox electrolyte.[11] How to obtain an ideal sensitizer for absorbing photons in the full sunlight spectra is still a great challenge. To extend the absorption region, narrow-band gap semiconductor quantum dots (QDs), such as CdS,[12,13] CdSe,[14,15] PbS,[16] InAs,[17] and $(CH_3NH_3)PbI_3$ organic−inorganic hybrid perovskite,[18,19] have been used in DSCs as the photosensitizer instead of organic dyes to form quantum-dot-sensitized solar cells (QDSC) that have been paid particular attention due to (1) adjustable band gap relying on the size of QD, (2) good chemical stability, (3) high light absorption and extinction coefficients, and (4) multiple exciton generation (MEG).[20−22] Efficiencies in the range of 6%

for CdSe[23,24] and CdSeTe[25,26] QDSCs have already been achieved. Recently, the solar cell based on the MOS TiO_2 sensitized with $CH_3NH_3PbX_3$ has achieve PCE of 19%[27] and even more than 20% in the future.[28] So, QDSC will be the next big thing in photovoltaics.[29,30] Figure 1 shows that the
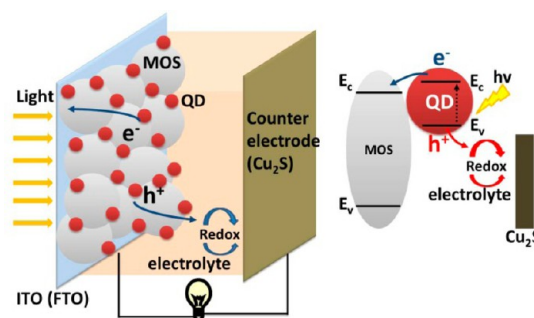

Figure 1. Schematic illustration of the structure of QDSC and photoinduced charge-transfer processes.

QDSC structure consists of a MOS photoanode, QDs (sensitizer), polysulfide electrolyte, and counter electrode. When the photons are harvested by QDs, the electron−hole pairs will be excited and then are rapidly separated into electrons and holes at the interface between the MOS and QDs. The electrons are transferred by MOS, at same time, the holes are released by redox couples in the liquid electrolyte.[22,31]

The principles for choosing QDs and MOS photoanodes to construct QDSs are (1) narrow and direct band gap QDs are preferred due to their high optical absorption and (2) MOS and QDs should have perfect matching in energy levels so that charges transport efficiently in the solar cells.[32] Table 1 shows

Table 1. Energy Band Parameters of Some Most Commonly Used Materials for QDSCs[33,34]

semiconductors	band gap (eV)	conduction band minimum (eV)	valence band maximum (eV)
CdS	2.40	−3.98	−6.38
CdSe	1.74	−4.10	−5.84
PbS	0.37	−4.74	−5.11
PbSe	0.27	−4.93	−5.20
CuInS$_2$	1.50	−4.06	−5.56
TiO$_2$	3.20	−4.21	−7.41
ZnO	3.20	−4.19	−7.39
SnO$_2$	3.50	−4.50	−8.00

the energy band parameters of MOSs and QDs, which are usually chosen to fabricate QDSCs.

From the structure of QDSC, we can know that nanostructured MOS plays a key role in designing QDSCs. The nanostructured MOS not only offers a large surface area to adsorb a large amount of QDs for light harvesting but also collects the electrons from QDs and transfers them to electrodes. So many efforts have been made to look for an ideal structure MOS for QDSC, which could support many more QDs, and to collect and transport the electrons at a short time. MOS nanoparticles film is first used in QDSCs due to its large surface area for loading QDs. However, it is not an ideal structure in regard to the electron transport.[4] The first nonideality results from the lack of a macroscopic electrostatic potential gradient in the film due to the fact that the film is permeated with a concentrated electrolyte.[4] Therefore, the electron transport in the nanoparticle film is dominated by a process of diffusion instead of drift. The drift is a common way in p−n junction solar cells for carrier separation in the presence of an electric field. The second nonideality comes from the fact that the electron transport in a nanoparticle film undergoes a trapping and detrapping process as shown in Figure 2a. Numerous grain boundaries, interface defects, and connections existing in the nanoparticle film also increase the surface charge recombination, and retard effective charge injection and charge transport, which

result in a loss of PCE. In addition, it has been demonstrated[22] that QDs are difficult to penetrate into the inner pores of the nanoparticles film. So, designing a novel structured MOS to replace the nanoparticles has been regarded as an effective approach to increase PCE of QDSCs.

Nanostructured MOS faces a question that there are a large number of interfaces in the nanoscale materials that provide easy pathways for charge recombination. The processes of charge recombination in QDSCs can be simplified as shown in Figure 2b. There are seven pathways of recombination in QDSCs: ① recombination of electrons in the QD conduction band and holes in the QD valence band; ② recombination of electrons with the electron acceptors in the electrolyte; ③ trapping of the exited electrons at the surface states of QDs; ④ trapping of the free electrons at the surface states of QDs; ⑤ back electron injection from MOS to QDs; ⑥ trapping of the free electrons at the interface states of MOS particles; and ⑦ back electron injection from MOS to the electrolyte. The electron quenching (①), recombining with the electrolyte (②), and trapping (③ and ④) strongly depend on the surface quality of QDs. The pathways ⑤, ⑥, and ⑦ relate directly to the interfaces state of MOS. Therefore, a lot of interfaces in the nanostructured MOS provide easy pathways for charge recombination. The state of adjacent surface between QDs and MOS also propels the free electron trapping. The introduction of surface modification for MOS and QDs is believed to be an effective approach for decreasing the charge recombination and improving the transports of the electrons or holes.[35] For example, the surface modification for MOS can increase the interfacial resistance and decrease the surface defects, which results in the recombination reduction through the mechanisms ④, ⑤, ⑥, and ⑦. In addition, the surface modification can also change the surface energy of MOS for loading more QDs.[36]

Recently, significant progress has been made in the QDSC field, and many excellent review and perspective articles have covered the topics such as fundamentals,[31,37,38] QDs,[39,40] surface chemistry of QDs,[30] charge recombination,[35] hole transfer,[24] photoanodes,[41] recent advances, and perspectives.[29,42,43] In this paper, we would focus mainly on the MOS structure and their interface for the optimal light harvesting, electron transport, and charge recombination.

Designing a novel nanostructure of MOS is an effective approach for improving light harvesting and electron transport. *One-Dimensional Nanostructure MOS Offering Direct Pathways for Electron Transport.* One-dimensional (1D) MOS, such as
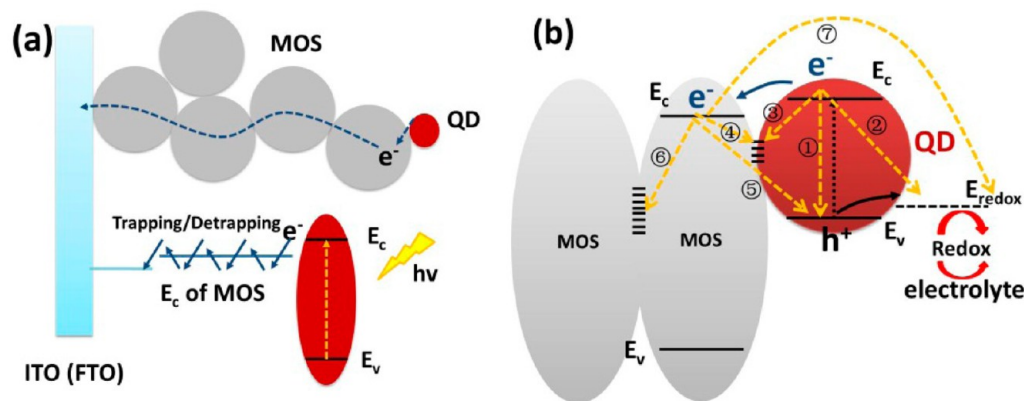

Figure 2. Schematic illustrations of (a) electron transport in a nanoparticle film suffering a trapping/detrapping process and (b) charge recombination processes in QDSSCs.

> Designing a novel nanostructure of MOS is an effective approach for improving light harvesting and electron transport.

single-crystalline nanowire (NW), nanorod (NR), and nanotube (NT) arrays, has a higher electron mobility than that of the nanoparticles, which has been studied as photoanodes for DSCs.[44] For example, ZnO nanowires, the electron diffusion coefficients (D_n) are 0.05−0.5 cm^2 s^{-1}, which are several hundred times larger than those of nanoparticle films. The electron diffusion coefficient determines the electron diffusion length as the following equation:[4]

$$L_n = \sqrt{D_n \tau_n} \qquad (1)$$

where L_n is the electron diffusion length, D_n is the electron diffusion coefficient, and τ_n is the electron lifetime. A longer diffusion length is typically associated with the higher charge collection efficiency. For TiO$_2$, L_n is ~60 μm for NW, only 10−14 μm for nanoparticles film, giving direct evidence of the improved charge transport of 1D nanostructure in the solar cells.[3,4] For QDSCs, such open structures of 1D MOS can also facilitate the permeation of QDs from the surface to the interior of the films. 1D nanostructure offers a straightforward path for the electrons and shorten their transport time inside MOS, and then reduces the charge recombination probability as shown in Figure 3a.[45] So, the 1D nanostructure array is considered the most promising candidate materials for QDSCs owing to its effective electron transport, which helps to collect photogenerated electrons.[46]

However, QDSCs based on 1D structure have not reached a high conversion efficiency as expected due to the limited surface area for QDs adsorption. Introducing a surface profile modification for 1D MOS can be thought as an effective way to increase QD loading. Figure 3b,c shows SEM images of ZnO NRs arrays before and after surface modification.[45] ZnO NR arrays have been fabricated by growing on seeded indium-doped tin oxide (ITO) substrate without using a template or high temperature conditions. After surface modification, the edges of the ZnO NRs become "rough", which helps to harvest QDs as shown in Figure 3d. The optical absorption results reveal that the absorbance of the sample is increased by modifying treatment, indicating that a greater amount of QDs can be acquired (Figure 3e). Figure 3f shows the charge recombination resistance (R_{ct}) of the solar cell is also increased by surface modification, which results in the decrease of the charge recombination. The main cause is that the charge recombination pathway of electrons in the ZnO conduction band to the oxidized ions in the electrolyte is suppressed. As a result, the PCE of CdS/CdSe QDSC-based ZnO NRs array is increased from 1.54% to 3.14%. Compared to NRs, nanotubes (NT) have a larger surface area to load more QDs. Figure 4 shows the square TiO$_2$ NR arrays are in situ etched to square NT arrays as photoanode for QDSC.[47] The square NRs and NTs would be thought to have large surface area or high surface energy for loading more QDs. The TiO$_2$ NRs convert to NTs by selective hydrothermal etching of the core as shown in Figure 4c. The XRD results as shown in Figure 4d confirm that the strongest peak of (002) in the TiO$_2$ NRs almost disappears after converting to TiO$_2$ NTs by hydrothermal etching due to its high surface energy. QDs can be filled both inside and outside of
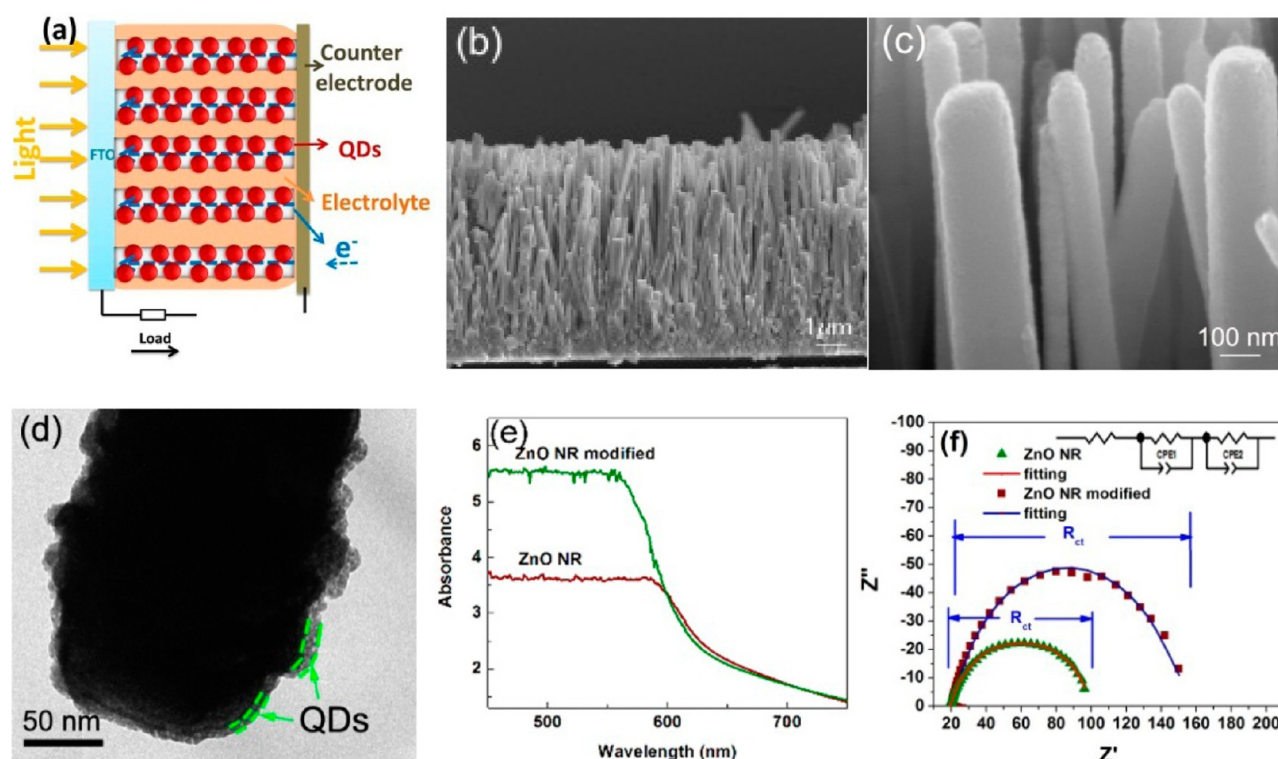

Figure 3. (a) Schematic illustration of the structure QDSC-based ZnO NR array photoanode, (b) SEM images of ZnO NR array, (c) SEM image of modified ZnO NR array, (d) TEM image of ZnO NR coated by QDs, (e) UV−visible spectra of ZnO NR arrays photoelectrodes loaded with QDs, and (f) Nyquist plots curves of QDSCs under forward bias (−0.6 V) and dark condition. (Reprinted with permission from ref 45. Copyright 2013, The Royal Society of Chemistry.).
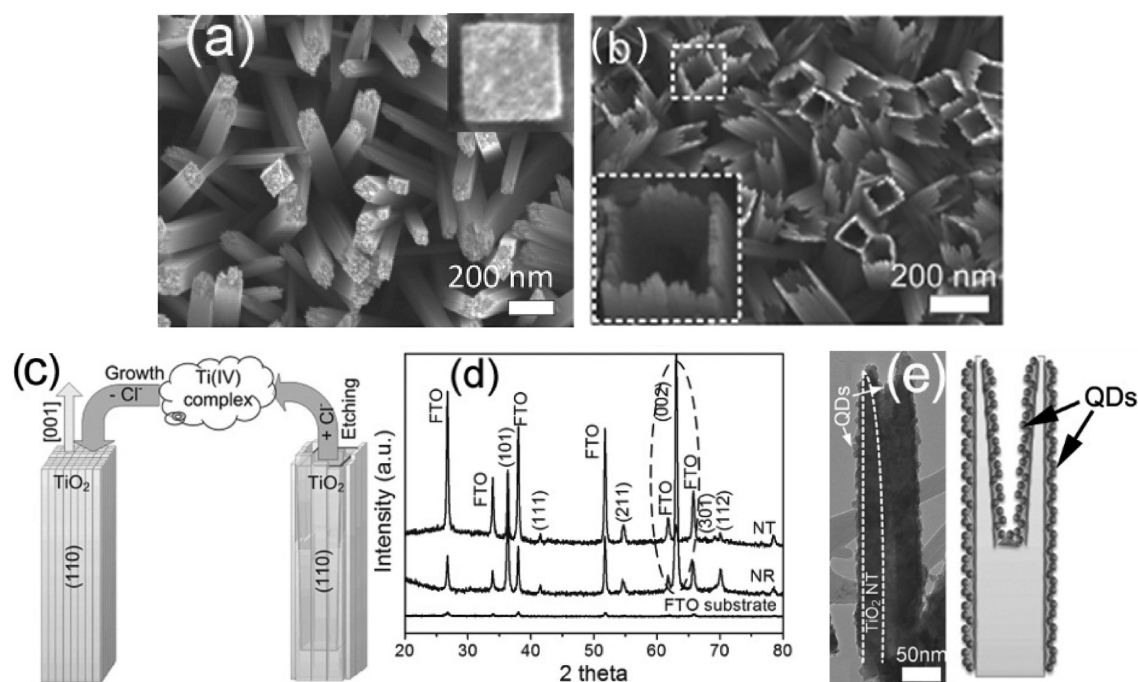
Figure 4. (a) SEM image of square TiO$_2$ NRs, (b) SEM image of TiO$_2$ NTs from NRs, (c) schemes of growth and etching mechanism of the TiO$_2$ NR array, (d) XRD patterns of TiO$_2$ NRs and NTs, and (e) TEM image and schematic illustration of the CdSe QDs deposited on the TiO$_2$ NT. (Reprinted with permission from ref 47. Copyright 2013, Wiley.)
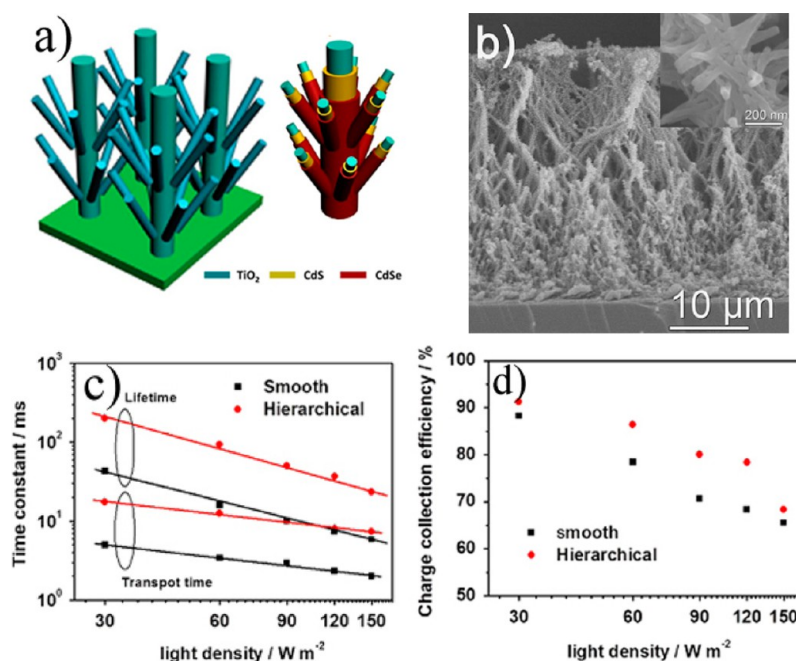

Figure 5. (a) Schematic structure of CdS/CdSe cosensitized branched TiO$_2$ nanowire, (b) SEM images of the hierarchical branched TiO$_2$ NW arrays, (c) electron transport time and electron lifetime, and (d) charge collection efficiency of QDSSCs based on different TiO$_2$ photoanodes as a function of various light intensities. (Reprinted with permission from ref 49. Copyright 2014, Elsevier.)

NTs (Figure 4e), which results in almost double enhancement of PCE for QDSC.

Hierarchical Branched 1D Nanostructure Enlarging the Surface Area to Increase the QDs Loading. It is well known that the surface area of photoanodes is a key factor for the loading of QDs. For 1D nanostructured MOS, a fundamental drawback is the insufficient internal surface area owing to a low roughness factor or the considerable free space between adjacent 1D nano-structures.[48] Hierarchical branched nanostructures are derived

from 1D nanostructures, but with a consideration to enlarge the surface area through using extended "'branches'",[4] which mainly include branched and dendritic nanowires or nanorods. Recently, Rao et al.[49] prepared a nanostructure of TiO$_2$ NW arrays with branched architectures via a simple surfactant-free hydrothermal route for QDSCs as shown in Figure 5a,b. The branched architectures not only increase the surface area and light-scattering ability to enhance the photogenerated current density but also help the electron injection for improving the
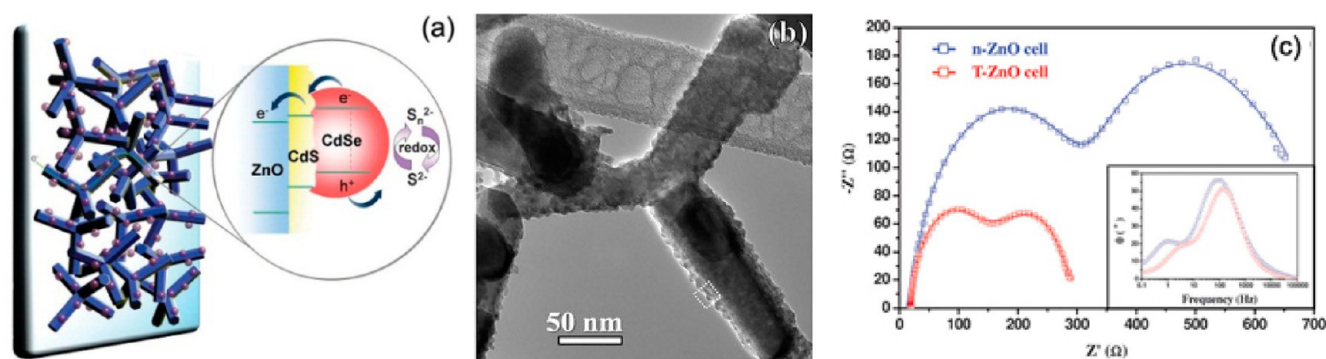
Figure 6. (a) Schematic representation of the charge transfer of the CdS/CdSe-sensitized ZnO photoelectrode and possible electron transport pathway across the tetrapod-like ZnO nanoparticles, (b) TEM images of the tetrapod-like ZnO nanoparticles, and (c) Nyquist plots of CdS/CdSe-sensitized QDSCs composed of 14 μm thick photoelectrodes with commercial ZnO (denoted as n-ZnO) and tetrapod-like ZnO nanoparticles (denoted as T-ZnO), respectively. (Reprinted with permission from ref 51. Copyright 2012, The Royal Society of Chemistry.)

charge collection efficiency as shown in Figure 5c,d. A PCE of 4.2% of QDSC based on the hierarchical TiO$_2$ NW is attained, which is 30% higher than that of smooth nanowires devices due to improved short-circuit current density (J_{sc}) and fill factor (FF). Zhu et al.[50] also found that the branched films had a longer electron lifetime than the nonbranched films. They designed a double-layer architecture photoanode for QDSC, which consisted of a ZnO NR underlayer and a ZnO nano-tetrapodtop (TP) layer. Such double-layer and branching strategies had significantly increased PCE to as high as 5.24%. In addition to branched NW and NR, a branched tetrapod-like structure of nanoparticles for QDSC has been reported as shown in Figure 6.[51] From electrochemical impedance spectroscopy (Figure 6c), the anisotropic tetrapod-like ZnO nanoparticles, with a high electron diffusion coefficient, can afford a better carrier transport than traditional ZnO nanoparticles. The resultant solar cell yielded an excellent performance with a PCE of 4.24%. Compared to 1D structure, the hierarchical branched structure becomes compact and the gaps between MOS and substrate become narrow.[52] For yielding electron−hole pairs from QDs, they are rapidly separated into electrons and holes at the interface between the MOS and QDs. The electrons are injected into the MOS and holes are released by redox couples (S^{2-}/Sn^{2-}) in the electrolyte. Electrons in the compact hierarchical structure are easily transported to the counter electrode rather than back into the electrolyte. However, the branched 1D structure still faces a drawback of its lower surface area than that of nanoparticles. The future works should focus on designing a high surface area and more compact structure branched 1D nanostructured MOS for QDSCs.

Hierarchical Aggregates Structure Enhancing Light Scattering and Extending Light Pathway. The hierarchical aggregates have been employed for DSCs due to their larger surface areas for dye adsorption and stronger light scattering for efficient photon harvesting.[53−56] Cao's research group[4,6,32,55,57−59] have designed an aggregate structure of ZnO consisting of primary nanocrystallites that can provide both large specific surface area and light scattering effect for enhancing the performance of DSCs. The hierarchical structure of aggregates is thought to have similar function as photoanode for QDSCs. Figure 7a shows TiO$_2$ nanocrystallite aggregates with the size of ∼500 nm consisted of ∼10 nm nanocrystallites, which is synthesized by microwave assisted method at 150 °C for a short time (∼10 min).[60] The TiO$_2$ aggregates film shows a better light scattering property than P25 nanoparticles film (Figure 6b,c),

which can extend the light pathway to enhance light harvesting. Different from dye, QD is difficult to enter into the interior of the aggregates film due to their large size, which results in the low loading of QDs. Zhou et al.[61] proposed a two-step fabrication method of TiO$_2$ aggregates to increase the porosity of the aggregates. Figure 7d shows SEM image of the mesoporous TiO$_2$ beads aggregates. The aggregates were first synthesized using precipitation and solvothermal process. Then, an optimal amount of ammonia was adopted to etch TiO$_2$ spheres and achieve the desired porosity of the beads for QDs adsorption. The ammonia etches the precursor aggregate beads to open the pore size of the aggregates. From Figure 7e, the absorbance of the films increases with increase of the addition ammonia, which followed the trend of increased pore size and pore volume but a decreased specific surface area. The properties of QDSCs are almost in accordance with the light absorbance of the aggregates (Figure 7f). As a result, a PCE of the solar cell up to 4.05% has been achieved for a CdS/CdSe QDSC. Owing to the strong light scattering, the aggregates can be used as a scattering layer for enhanced photogeneration current density of QDSC. Figure 8 shows a bilayer structure constructed by ZnO NP film and ZnO NS aggregates scattering layer.[62] In comparison with ZnO NPs film, the short circuit current density (J_{sc}) of QDSC assembled by ZnO bilayer structure is increased from 10.3 mA/cm^2 to 16.0 mA/cm^2, which is an enhancement of 55%. Such structured QDSC exhibits a high PCE of 5.08%.

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Introduction an Interface Modification for QDSCs Can Reduce the Charge Recombination. As for nanostructured MOS, the large
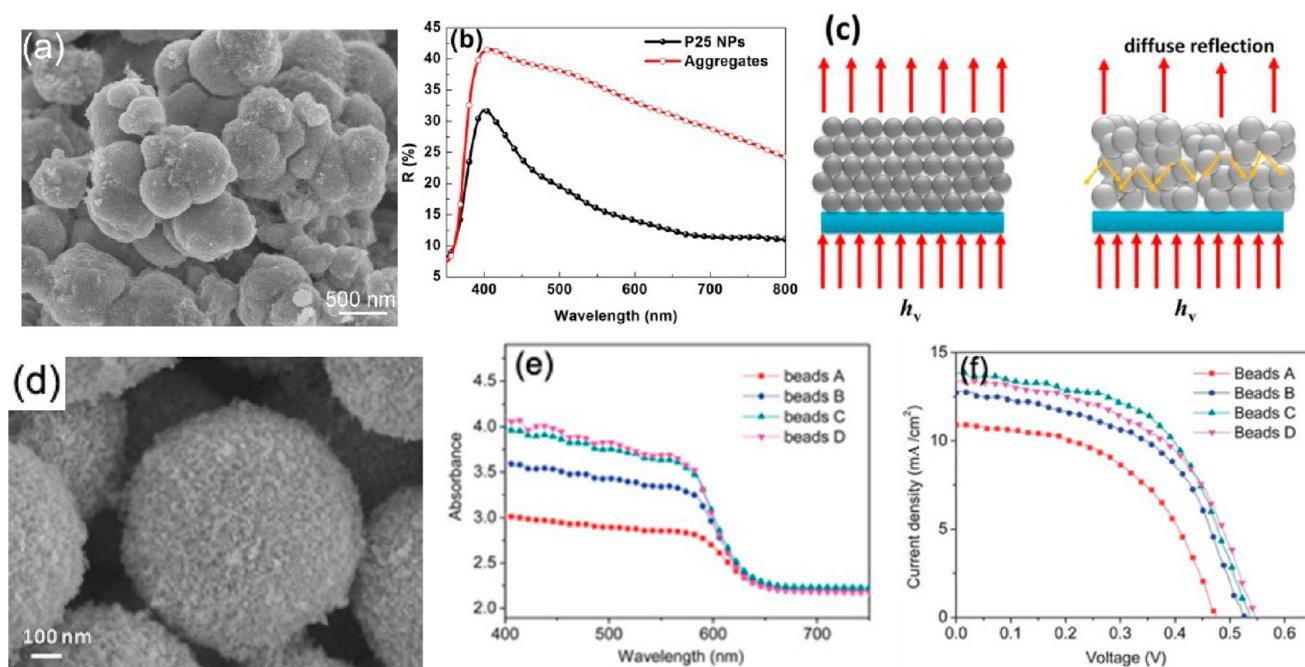
Figure 7. (a) SEM images of mesoporous TiO_2 aggregates prepared by microwave synthesis, (b) diffuse reflection of P25 nanoparticles TiO_2 film and TiO_2 aggregates film, and (c) schematic illustration of the effect of the aggregates for the light scattering. (Reprinted with permission from ref 60. Copyright 2014, The Royal Society of Chemistry.) (d) SEM image of TiO_2 beads aggregates, (e) UV−vis spectra of CdS/CdSe QDs cosensitized TiO_2 beads aggregates films, and (f) J− V curves for CdS/CdSe QDs cosensitized solar cells using the photoanodes prepared by TiO_2 beads aggregates. The beads prepared with the addition of 0, 0.5, 1, and 2 mL of ammonia to a mixture of 12 mL of ethanol and 6 mL of deionized water during the solvothermal treatment are denoted as beads A, B, C, and D, respectively. (Reprinted with permission from ref 61. Copyright 2014, The Royal Society of Chemistry.)
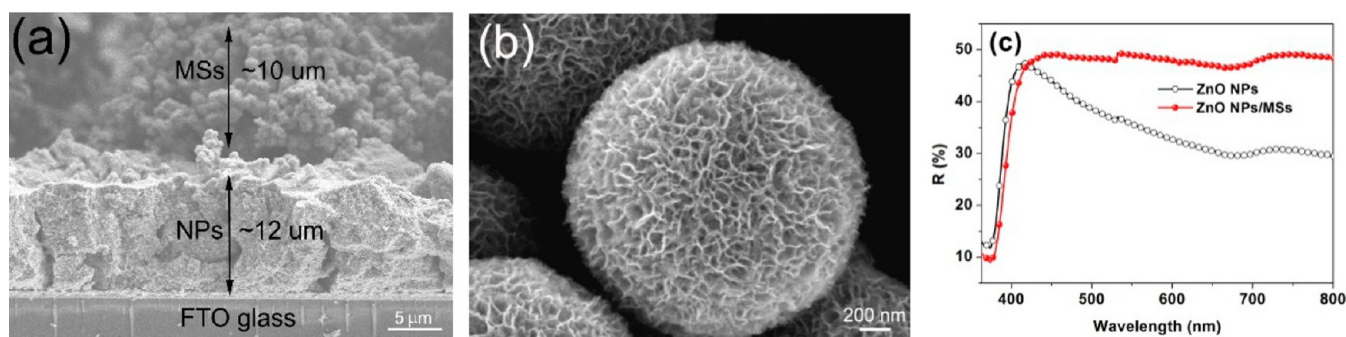

Figure 8. (a) SEM image of the bilayer structure composed of ZnO NPs film and NSs aggregates layer, (b) SEM image of the ZnO NSs aggregate, and (c) diffuse reflection spectra curves of ZnO films. (Reprinted with permission from ref 62 . Copyright 2014, American Chemical Society.)

surface area also provides an easy pathway for charge recombination, and surface defects and connections between adjacent nanoparticles may retard effective charge injection and charge transport, which leads to a loss of power conversion efficiency. For nanometer-sized QDs, there is a very high proportion of surface to interior atoms.[40] Such surface atoms have a low coordination number and high defect concentration so that the electrons or holes are easy to be trapped at the surface. In addition to the surface defects, the surface facets and chemistry of photoanodes and QDs may also affect the conformal coating and adhesion of QDs. To further enhance the performance of QDSCs, scientists should pay much more attention to the surface modification of photoanodes to reduce the charge recombination during the electron transport. On the other hand, many efforts also should be made to control the surface state of QDs to improve the performance of QDSCs.

Surface Modification of MOS Photoanodes for QDSCs. For the DSCs, many research results have showed that the charge recombination could be reduced by applying a passivation layer to form core−shell configuration.[63,64] Such a core−shell configuration is expected to suppress the charge recombination by forming an energy barrier to prevent the electrons in the conduction band of the semiconductor from transferring to the oxidized dyes and ions in the electrolyte, which leads to the increase of open circuit voltage and short current density.[63−65] Many novel core/shell structures, for example, ZnO/TiO$_2$, ZnO/Al$_2$O$_3$, TiO$_2$/Al$_2$O$_3$, TiO$_2$/ZrO$_2$, ZnO/ZrO$_2$, and ZnO/MgO photoelectrodes, have been used in DSCs for this purpose.[63−69] Although the charge recombination of QDSCs was thought to be a little different than that of DSCs,[35] we believe that the introduction of a shell structure as an energy barrier can also prevent the electrons from transferring to the electrolyte and therefore improve the performance of QDSCs.
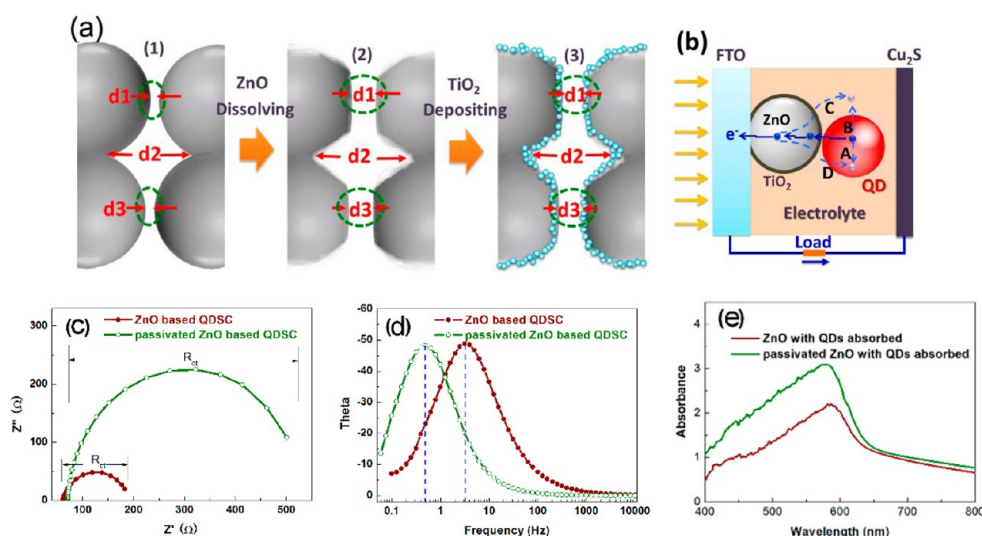
Figure 9. (a) Passivation process of the ZnO mesoporous film, (b) surface charge recombination pathways of the QDSC, (c) Nyquist plots curves, and (d) bode plot curves of the QDSCs under forward bias (−0.6 V) and dark condition, and (e) UV−vis spectra curves of the ZnO films loaded with QDs. (Reprinted with permission from ref 70. Copyright 2013, The Royal Society of Chemistry.).

However, the shell layer will reduce the porosity of the MOS film, which could result in the decrease of the loading of QDs. Our recent work reported[70] a facile chemical passivation strategy for ZnO mesoporous photoelectrode, which not only enlarged the apertures in the ZnO mesoporous photoelectrode to harvest more QDs but also introduced a thin TiO_2 nanoparticle layer on the surface of ZnO to decrease the surface charge recombination. Figure 9a shows the variation of pore size, porosity and surface area of the film during the passivation process. ZnO is dissolved by reacting with H_3O^+ so as to open the apertures and pores, at same time, TiO_2 particles are deposited on the fresh surface and combine with the newly broken chemical bonds to form a passivation layer. Figure 9b illustrates the recombination pathways of QDSCs. The passivation layer can increase the interfacial resistance and lead to recombination reduction through decreasing the back electron injection from photoanode to electrolyte. According to the results of EIS and light absorbance as shown in Figure 9c−e, both QDs loading and electron lifetime have been improved by the surface modification. The PCE of QDSC is also increased from 2.38% to 4.68%.

Surface Modification of QDs for QDSCs. The important characteristic of the nanometer-sized QDs is a high ratio of surface atoms to the core. So, the nature of QDs is largely determined by the state of the surface atoms. The surface atoms are chemically different from the core atoms due to the termination of the semiconductor lattice at the QD surface.[30] Controlling and modifying the surface of QDs for improving the performance of QDSCs has become an emerging field in QDs related research.[24,30,35,71,72] A major step toward the fabrication of stable QDs has been made by introducing passivation surface layer using the inorganic wide band gap semiconductor.[35,72] For early research, CdSe QDs were modified by coating ZnS for improving the quantum yield of QDs[73] and performance of QDSCs.[35,72] For QDSCs, ZnS coating layer can overcome the recombination losses leading to higher photocurrents.[35] Recently, Pan et al.[74] achieved effective surface passivation of the ternary $CuInS_2$ (CIS) QDs using ZnS to form core/shell CIS/ZnS (CIS-Z) QDs. The ZnS shell increases the charge collection efficiency by suppressing the charge recombination as shown in Figure 10. The QDSCs-based CIS/ZnS QDs show a very high

PCE of 7.04% and a certified efficiency of 6.66%. Recently, Kamat's research group[75] provided a novel idea for surface modification of QDs by the introduction of a interfacial Cu_xS layer, which mediates hole transfer to polysulfide electrolyte by collection of photogenerated holes from QDs. In addition, Cu_xS was also found to interact directly with defect states on the QD surface and quench emission characteristic of electron traps resulting from selenide vacancies. Together these effects were found to work in a tandem cell to deliver 6.6% PCE using Mn-doped CdS and CdSe cosensitized QDSC.[75]

PCE of QDSC-based inorganic semiconductor QD has already reached 7% and further breakthroughs (PCE > 10%) are certainly expected via emerging strategies of nanotechnology and surface modification.

> PCE of QDSC-based inorganic semiconductor QD has already reached 7% and further break-throughs (PCE > 10%) are certainly expected via emerging strategies of nanotechnology and surface modification.

Future Issues and Challenges. To make a big breakthrough in QDSCs, it is necessary to develop novel architecture by combining the advantages of the different MOS nano-architectures. Rational design and engineering the surface and interface chemistry would favor charge transfer and at the same time prevent or minimize the charge recombination. There is a large space for the improvement in surface and interface; consequently, both fill factor and open circuit voltage would be quite enhanced. Of course, the further work is needed to ensure the full conformal coverage of monolayer of QDs, which would ensure the high load of QDs for light absorption and minimal charge recombination. The number of QDs loaded to the photoanode so far has not been as well studied as what has been done in dye-sensitized solar cells. In addition, the control and tailor of morphology of QDs with desired size and certain
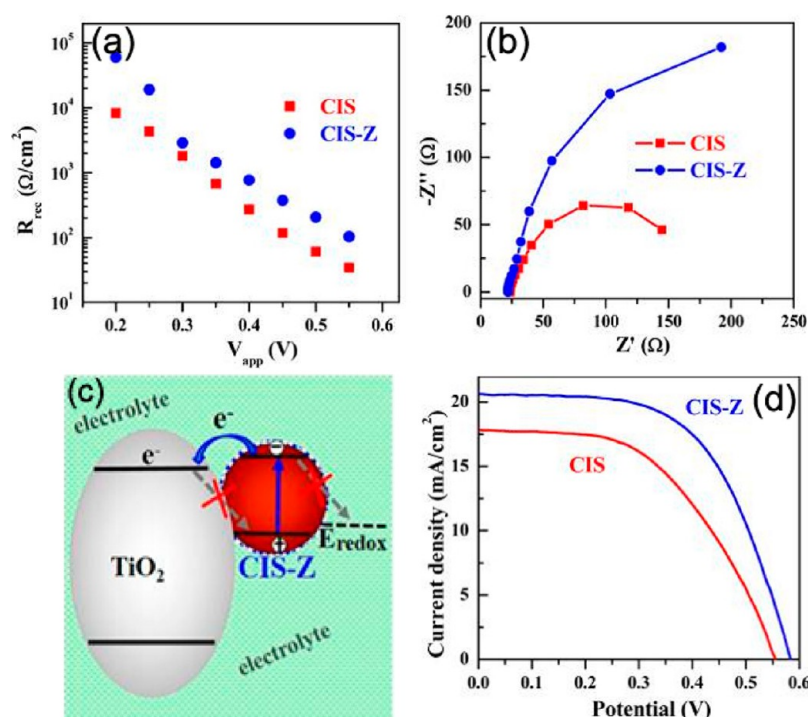
Figure 10. (a) Recombination resistance R_{rec} on applied voltage (V_{app}), (b) Nyquist plots of both cells at −0.55 V forward bias, (c) schematic illustration of the effect of ZnS modification layer on electron transport and charge recombination, and (d) $J−V$ curves of CIS-Z- and CIS-based champion cells. (Reprinted with permission from ref 74 . Copyright 2014, American Chemical Society.)
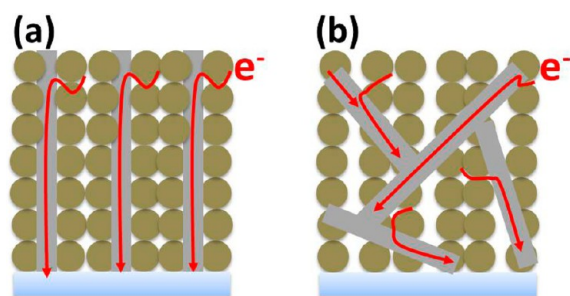

Figure 11. Two kinds of composited architectures: (a) perpendicular nanowires array and nanoparticles and (b) unordered nanowires and nanoparticles.

facets would lead a better fundamental understanding and the control of charge transfer through the interface, would open ways for further tuning of the physical properties of QDs, and thus would pave the way for higher power conversion efficiency.

Combining the Advantages of Nanoparticles and 1D Architectures. More and more efforts are made in fabricating elegant hierarchical 1D architectures for photovoltaics due to their high light absorption, rapid electron transport, long electron diffusion length, and lifetime. However, the PCE of QDSCs based on these nanostructures is still much lower than that of the nanoparticle films. The main cause is the insufficient internal surface area of 1D architectures for QDs loading. Designing a novel architecture with combining the advantages of both nanoparticles and 1D nanostructures would be a promising way to prepare high efficiency QDSCs. Single-crystalline 1D nanostructures, such as nanowires and nanorods, serves as the backbone for direct electron transport. Meanwhile, the nanoparticles can load much more QDs due to their large surface area. So, the composite architectures of 1D nanostructures and nanoparticles
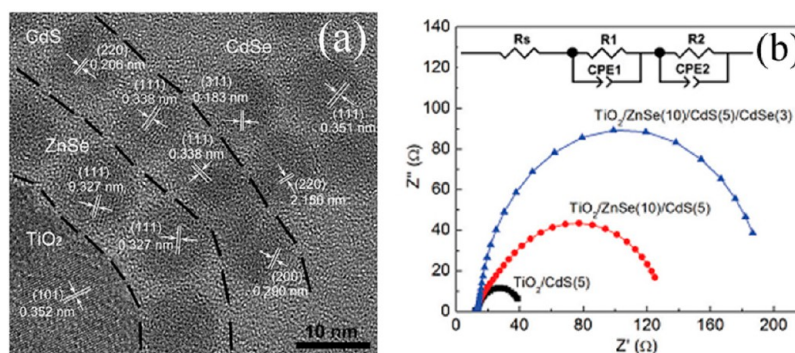

Figure 12. (a) High-resolution TEM image showing the arrangement of ZnSe/CdS/CdSe QDs around a TiO$_2$ crystallite and (b) Nyquist curves of the different layered QD-sensitized solar cell measured in the dark at −0.6 V bias. (Reprinted with permission from ref 76. Copyright 2014, The Royal Society of Chemistry.).

should be paid much attention for QDSCs. Figure 11 shows two kinds of composited architectures consist of nanowires and nanoparticles. How to optimize 1D nanostructure parameters, such as areal distribution and density, arrangement angle, space between two nanowires or nanods, length, and diameter, is also an important topic for us to explore.

Multilayered QDs on the Surface of Photoanodes. Inserting a layer of nonsensitized QDs on the surface of MOS photoanodes not only helps to grow the subsequent sensitized QDs but also suppresses the back charge recombination between the electrons in oxide and the holes in electrolyte. Recently, Yang et al.[76] prepared a multilayered semiconductor (ZnSe/CdS/CdSe) QDs on the surface of TiO$_2$ mesoporous films as shown in Figure 12. The multilayered QDs-sensitized solar cells showed a larger short circuit currents and higher efficiency than those of single-layered QDs-sensitized solar cells due to a complementary effect in light harvesting. Figure 12b shows the recombination resistance is also increased by a seeding layer of ZnSe, which leads the reduction of the charge recombination and the prolonging of the electron lifetime. The possible reason is that the cascade structure of multilayered semiconductor is advantageous to the electron injection and hole recovery of QDs. Therefore, researchers may concentrate on designing more multilayered QDs for QDSCs.

High Hole Transfer Layer on the Surface of QDs. To suppress charge recombination, the use of ZnS as a capping layer on the surface of QDs is nearly ubiquitous in QDSCs, though the mechanism of improved performance in this case has remained elusive.[24] However, surface modification of QD by the capping layer has an important influence on the hole transfer process from QD to electrolyte. ZnS is an n-type semiconductor that is not a good transfer layer for holes. Introducing a layer of hole transfer on the surface of QDs is thought to be a new approach to improve the performance of QDSCs. Recently, Kamat's research group provided a p-type semiconductor Cu$_x$S layer on the surface of CdSe QD to promote holes transfer from CdSe to electrolyte.[75] Besides p-type semiconductors, some organic hole transport materials may have similar functions for improving the performance of QDSCs, which may attract more attention to the study of the effect of hole transfer layer on the properties of QDSCs.

AUTHOR INFORMATION

Corresponding Author
*E-mail: gzcao@u.washington.edu.

Notes
The authors declare no competing financial interest.

Biographies

Jianjun Tian is an associate professor in the Institute of Advanced Materials and Technology at University of Science and Technology Beijing, China. He earned a Ph.D. degree in material science from this university in 2007. His current research focuses on quantum dots and their application for the photovoltaic conversion devices.

Guozhong Cao is the Boeing−Steiner Professor of Materials Science and Engineering, Professor of Chemical Engineering, and Adjunct Professor of Mechanical Engineering at University of Washington. His current research is focused on chemical processing of nanomaterials for energy-related applications including solar cells, lithium-ion batteries, supercapacitors, and hydrogen storage. See http://depts.washington.edu/solgel/ for further details.

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