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“Mulberry-like” CdSe Nanoclusters Anchored on TiO₂ Nanotube Arrays: A Novel Architecture with Remarkable Photoelectrochemical Performance

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“Mulberry-like” CdSe nanoclusters with well-defined crystallinity have been assembled into vertically aligned TiO₂ nanotubes by photo-assisted electrodeposition method to form new architecture for fabricating semiconductor nanocrystal sensitized photovoltaic cell. The multiple stacked “mulberry-like” CdSe nanoclusters, caused by the synergistic effect of photoetching and electrodeposition, broaden the absorption spectra to entire visible region with a promising behavior of photoinduced charge separation. A photocurrent density of 16 mA cm⁻² was achieved under 100 mW cm⁻² visible light illumination with 0 V bias potential (vs SCE). The remarkable photoresponse should be ascribed to the high-quality of 3-D multijunction structure and the driving force for electron transfer in “mulberry-like” nanoclusters. The experimental demonstration provides a strategy for integrating novel “mulberry-like” nanoclusters to fabricate semiconductor nanocrystal sensitized photovoltaic cells.

Introduction

New initiatives to design highly efficient solar cell would greatly meet the rising demand for clean energy.¹ Recent advances in size- and shape-controllable synthesis of monodisperse short-band-gap semiconductor nanocrystals have enabled a novel inorganic sensitizer in dye-sensitized solar cell with strong potential,^{2,3} owing to unique size- and shape-dependent optic and electronic properties in semiconductor nanocrystals. The performance of inorganic nanocrystals sensitized photovoltaic devices can be easily changed by tailoring the nanocrystals through modification of solution growth methods. The new nanostructured architecture would provide innovative strategies for designing future generation solar energy conversion devices.

With recent advances in nanotube/nanorod architectures, CdSe nanocrystal, which holds a suitable position

of the band edge to form charge separating heterojunctions with several relevant organic and inorganic semiconductors and an ideal bandgap to match solar spectra,⁴ has been linked to different TiO₂ nanostructures by a bifunctional molecule to improve energy conversion efficiency.⁵ The size dependent properties of CdSe nanocrystals have also been successfully investigated to tune the photoresponse and modulate the nanocrystal sensitized solar cell.⁶ It is important to note that monolayer coverage of CdSe nanocrystals on mesoscopic TiO₂ film is analogous to organic sensitized dyes. Nevertheless, the potential of semiconductor nanocrystal has not been fully explored, and the cell efficiency remains at relatively low levels (<3%).⁷ In order to obtain higher light conversion efficiency, it would be extremely useful for both fundamental studies and a wealth of applications in photovoltaic devices to explore new architectures of semiconductor nanocrystals. However, there are few reports of yielding optically active semiconductor nanocrystal assembly that are well-defined.

It is well-known that multilayer cell architecture, equivalent to several photovoltaic cells in series, enables

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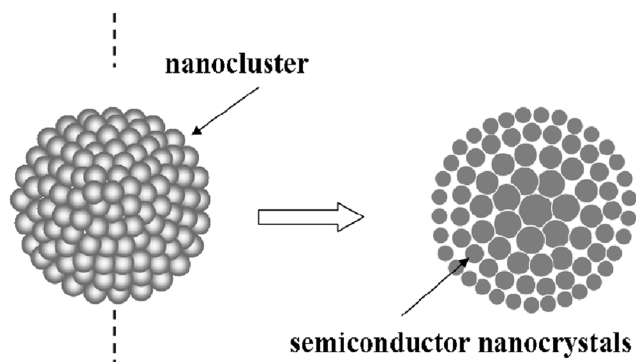


Figure 1. Schematic illustration of the semiconductor nanocrystal cluster with an ordered assembly of the semiconductor nanoparticle with different size. The right section is the profile of the nanoclusters.

absorption over a broad range of photo-energies within the solar emission spectra.⁸ Compared with this multilayer structure, nanoclusters with an ordered gradient assembly of the same type of semiconductor nanoparticle with different sizes from outer to inner exhibit a much higher specific surface area and can be used in various manners, such as powders, films, or being loaded on many substrates. The multilayered structured semiconductor cluster, which we report here the observation of “mulberry-like” semiconductor nanoclusters (as shown in Figure 1), exhibits strong potential in nanostructure devices. The manipulation of “mulberry-like” nanocrystal architecture is charming owing to the combination of shape-/size-dependent properties of individual semiconductor nanocrystals and collective properties of three-dimensional multijunction among the subunits. Because of the size dependent optical properties of semiconductor nanocrystals in hierarchical nanoclusters, a gradient assembly of nanocrystals would form a multilevel absorption in nanoclusters, among which smaller nanoparticles in the outer layer could absorb the shorter wavelengths in solar spectra and the longer wavelengths that transmit through the initial layer could be absorbed by subsequent layers, thus the effective absorption of solar light would be greatly promoted.

Herein, we report success in synthesizing “mulberry-like” CdSe nanoclusters anchored on a TiO₂ nanotube array substrate by the photo-assisted electrodeposition method for the first time. “Mulberry-like” CdSe nanoclusters with size from about 50 to 100 nm, each of which is composed of close-packed single CdSe nanocrystal, can be specially attached to TiO₂ nanotubes and which, in addition, lead to well-defined morphology of the nanoclusters. A remarkable photoresponse is observed from the new CdSe–TiO₂ architecture. “Mulberry-like” nanoclusters would be a promising style of nano-architecture to promote light absorption and to enhance photoinduced electron–hole separation.

Experimental Section

Preparation of TiO₂ Nanotube Array. The ordered TiO₂ nanotube arrays were synthesized by anodic oxidation in a

0.5 wt % NH₄F and 1 M (NH₄)₂SO₄ aqueous solution.⁹ pH of the electrolyte was adjusted at 3 ± 0.5 by a solution of 2 M H₂SO₄.⁹ First, metal Ti foils were cleaned with ethanol and deionized water. Then the Ti foils were immersed in electrolyte solution and subjected to a constant 20 V anodic potential for 2 h at room temperature in a two-electrode electrochemical cell connected to a DC power supply. After anodic oxidation, the samples were rinsed with deionized water and dried in a N₂ stream. The resulting amorphous titania nanotube arrays were annealed at 450 °C for 2 h with heating and cooling rates of 2 °C min^{−1} in an O₂ atmosphere to crystallize the tube walls and improve their stoichiometry.

Photo-Assisted Electrodeposition of “Mulberry-like” CdSe Nanoclusters. A conventional three-electrode setup in an undivided cell was used for photo-assisted cathodic deposition of CdSe nanocrystals from a solution containing 0.1 M Cd(NO₃)₂, 0.1 mM NaSeO₃, and 10 g L^{−1} sodium citrate, the pH of which was adjusted to 1 by adding nitric acid. (*Warning! Cd(NO₃)₂ is highly toxic and should be used with extreme caution.*) Deposition was carried out potentiostatically at −0.65 V versus the reference electrode under a 100 mW cm^{−2} irradiation provided by a 500 W xenon arc lamp. The new deposited electrode was dried under a stream of nitrogen and then followed by annealing in a N₂ atmosphere at 400 °C for 1 h with a ramp of 2 °C min^{−1}.

Characterization. Scanning electron microscopy (SEM) images were obtained on a FEI Quanta 200F Digital Scanning Microscope at beam potentials of 5 kV. Energy dispersive X-ray (EDX) analysis was performed in the SEM at a magnification of 10 000× and a beam potential of 20 kV. Transmission electron microscopy (TEM) images were obtained on a FEI-Tecnai G² F30 S-Twin. The phases of the samples were identified by an X-ray diffractometer (Shimadzu LabX XRD-6000). Shimadzu UV-2450 UV–vis spectrophotometer was used to record absorption spectra. The photogenerated charge carrier separation and transfer ability of the samples were tested using a lock-in-based surface photovoltage (SPV) measurement system, which consisted of a monochromator (model Omni-λ 3005) and a lock-in amplifier (model SR830-DSP) with an optical chopper (model SR540) running at a frequency of 20 Hz.

Photoelectrochemical Measurements. Photoelectrochemical studies were carried out in a three-electrode cell with a Pt-foil counter electrode and SCE as a reference electrode. The electrolyte was 0.6 M Na₂S. pH was adjusted to 12 by addition of NaOH. *I*–*V* characteristics were performed by a Princeton Applied Research model Parstat 2273 advanced electrochemical system. The working electrode was irradiated with filtered light from a 500 W xenon arc lamp. All measurements were carried out under ambient conditions.

Results and Discussions

“Mulberry-like” CdSe Nanoclusters Anchored TiO₂ Nanotubes. The SEM image of TiO₂ nanotube arrays is shown in Figure S1 (in the Supporting Information). The image displays the presence of well-aligned nanotubes vertically oriented from the Ti foil substrate, which provides not only an accessible access for depositing high concentration of sensitizer nanocrystals but also promotes unidirectional charge transport due to the one-dimensional features of the tubes.

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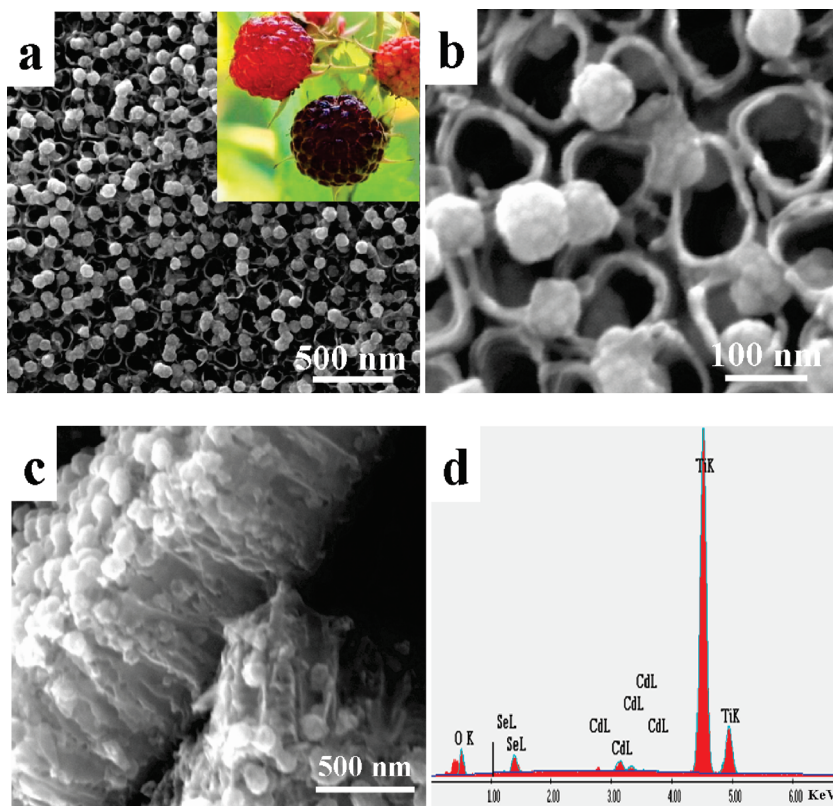


Figure 2. SEM images of “mulberry-like” CdSe nanocluster anchored TiO₂: (a) and (b) are top views obtained at two different magnifications; inset of (a) is the actual mulberry; (c) is the cross-section view; and (d) is the EDX spectrum.

Photo-assisted electrodeposition was employed to load CdSe nanocrystals into the TiO₂ nanotube array to fabricate a functional composite structure. Figure 2 shows the SEM images of the surface of “mulberry-like” CdSe nanoclusters anchored TiO₂ nanotubes. The top view (Figure 2a) displays that deposited CdSe is in an ordered assembly with a uniform distribution. As shown in Figure 2b, CdSe nanoclusters are successfully embedded into the TiO₂ nanotubes. For the “mulberry-like” CdSe nanoclusters, secondary monodisperse 3-D spheres form from numerous primary nanocrystals. The cross-sectional SEM images further confirm that CdSe nanocrystals are deposited into the TiO₂ nanotubes (Figure 2c). The “mulberry-like” CdSe nanoclusters inside the nanotubes are smaller, which may due to the space constraint of the nanotubes. EDX analysis of the CdSe/TiO₂ surface shows ~0.98 atom % CdSe and the results are presented in Figure 2d.

The electrodeposition method, which gives a close binding between semiconductors, has been used to the fabricate heterojunction electrode.¹⁰ Compared with direct electrodeposition method (Figure S2, Supporting Information), which forms a CdSe layer (~0.42 atom %) that coated the pore of TiO₂ nanotube, the new strategy forms a high quality “mulberry-like” CdSe nanoclusters that are embedded in TiO₂ nanotube. Because of the overlapped patterns of {111} planes of zinc blende

CdSe and {101} planes of anatase TiO₂, X-ray diffraction (XRD) patterns of “mulberry-like” CdSe nanoclusters anchored TiO₂ nanotube shows only a broader peak at 25.35° (CdSe, zinc blende, JCPDS 19-0191) compared with that of TiO₂ nanotube (Figure S3, Supporting Information). Nevertheless, a broaden XRD peak reflects the dispersion of very small CdSe nanocrystallites in “mulberry-like” CdSe nanoclusters. This indicates a well crystalline nature of the “mulberry-like” CdSe nanoclusters, while few CdSe peaks are observed at CdSe layer coated TiO₂ nanotube electrode. It is worth noting that a well-crystalline material is beneficial for photovoltaic research due to its high charge transport properties and low recombination losses.

The evolution of UV-vis spectra with the photo-assisted electrodeposition time provides proof of size quantization effects of CdSe nanocrystallites in “mulberry-like” CdSe nanoclusters (Figure 3). The absorption edge successively shifts to red with prolonged deposition time. This concludes that the quantized properties of CdSe nanocrystallites are kept in “mulberry-like” CdSe nanoclusters, just similar to the reported quantum dot system.¹¹ The broad XRD peak further confirms that the size of CdSe nanocrystallites might be still within the scale of quantized confinement, though it cannot be directly calculated by Scherrer equation because of the overlapped patterns. Interestingly, multiple excitonic peaks

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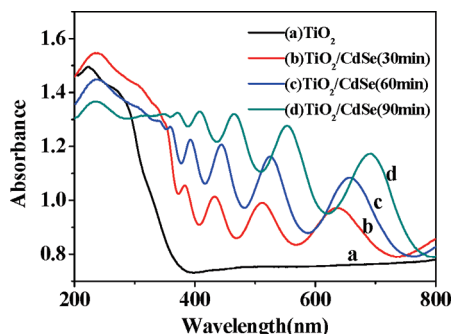


Figure 3. UV-vis absorption spectra of TiO₂ nanotube (a) and “mulberry-like” CdSe nanoclusters anchored TiO₂ nanotube with different deposition times.

are observed from the absorption spectra of “mulberry-like” CdSe nanoclusters. Such a phenomenon may be ascribed to multilevel absorption caused by the multisized nanocrystallites in “mulberry-like” CdSe nanoclusters, which matches well with the anisotropy of CdSe nanocrystallites as observed from the TEM images from Figure S4 (Supporting Information). However, the size of small CdSe nanocrystallites cannot be measured from the TEM images because of the close-packed structure of nanocrystallites in “mulberry-like” CdSe nanoclusters.

The surface photovoltage (SPV) spectra, defined as the light-induced variation of the surface potential due to the drift, accumulation, and recombination of photogenerated carriers,¹² is a good technique for characterizing nanostructured materials. Figure 4 shows the SPV spectra of TiO₂ nanotube, CdSe layer coated TiO₂ nanotube, and “mulberry-like” CdSe nanocluster anchored TiO₂ nanotube. By contrast, the novel “mulberry-like” CdSe nanocluster anchored TiO₂ nanotube exhibits distinguished SPV response. Moreover, its photovoltage response greatly expands to the visible region. The higher absorption strength for new multijunction structures ascribes to the optical absorption increase of CdSe nanocrystals in nanoclusters and the effectiveness of the “mulberry-like” CdSe nanoclusters architecture system. The higher SPV signal also reveals that the separation rate of photogenerated electron–hole pairs is remarkably promoted in the new CdSe/TiO₂ junction.

Furthermore, a stepwise absorption edge corresponding to the band edge absorption of the CdSe barrier is observed in the SPV spectrum of the “mulberry-like” CdSe nanocluster anchored TiO₂ nanotube, while the sharp SPV spectra features of the uniformly sized nanocrystals are lost. Four CdSe nanocrystal related features are clearly exhibited, reflecting the anisotropy of the “mulberry-like” CdSe nanoclusters. Because the energy distribution of nanocrystal follows a Gaussian-like distribution, to determine the values of CdSe nanocrystal related transitions, the SPV data was fitted with five Gaussian line shapes (inset of Figure 4). The left peak should be ascribed to the transitions of TiO₂, while the

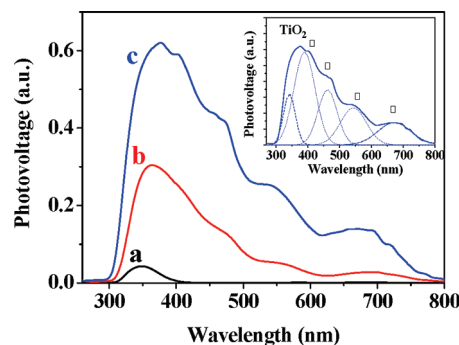


Figure 4. Surface photovoltage (SPV) spectra of (a) TiO₂ nanotube, (b) CdSe layer coated TiO₂ nanotube, and (c) “mulberry-like” CdSe nanoclusters anchored TiO₂ nanotube. Inset shows the deconvolution of SPV spectra of (c) into five Gaussian features.

other four peaks may be caused by the different-sized CdSe nanocrystals. A satisfactory fit obtained indicates the broadening is inhomogeneous probably because of the fluctuations in the nanocrystal size of “mulberry-like” nanoclusters.¹³ This further confirms the multi-sized CdSe nanocrystallites in “mulberry-like” nanoclusters, as well as the quantum confinement effects of nanocrystallites, which is consistent with the observed absorption spectra as shown in Figure 3. The increase of the size of CdSe nanocrystals leads to a redshift due to the decrement of band gap energy during the nanocrystal growth process. Of special interest is the onset of photovoltage spectra showing a red shift to about 755 nm, which is beyond the absorption edge of bulk CdSe (< 712 nm). Though similar results have been reported, to get the origin of such a red shift is still a difficulty.^{11b,14} In the present system, it is proposed that the close-packed nanocrystallites whose sizes are retained in the quantum scale in the “mulberry-like” nanocluster cause a strong interacting strain field in the nanoclusters and result in intense electronic coupling between nanocrystallites. Such coupled interfaces promote an energetic red shift absorption of low energy photons, at last generating the observed extended photopotential. The combination of size and shape of CdSe nanocrystals in the close-packed assemblies contributes to the inhomogeneity, which broaden the spectra features.

The basic structure of the “mulberry-like” CdSe nanocluster anchored TiO₂ nanotube–array electrode is depicted in Figure 5. The formation of “mulberry-like” nanoclusters structure may be ascribed to the synergistic effect between electrodeposition and photoactivation. In the reduced state, the pore bottom can be selectively switched to a higher conductivity by the electrochemical self-doping ($\text{Ti}^{4+} + \text{e}^- \rightarrow \text{Ti}^{3+}$).¹⁵ This is of significance in

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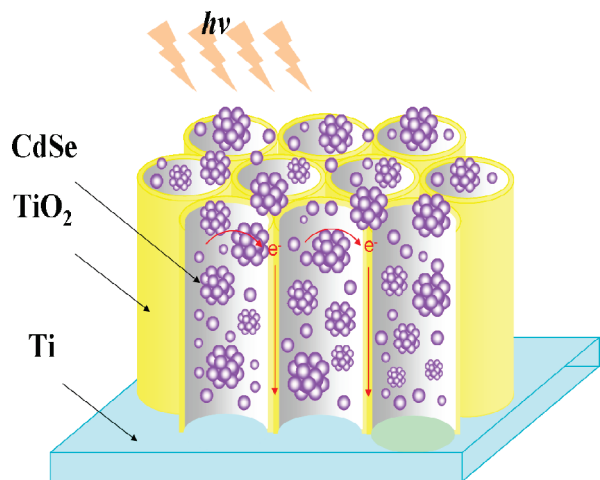


Figure 5. Schematic illustration showing the structure of the "mulberry-like" CdSe nanocluster anchored TiO₂ nanotube electrode.

filling TiO₂ with various semiconductor materials with variable band gap properties to design a multijunction photovoltage material. To minimize the surface defects (such as surface nonstoichiometry and unsaturated bonds) of CdSe nanocrystals, illumination using a xenon lamp was provided throughout the deposition. Photo-etching and surface recombination processes occurred concurrently during irradiation. The tubular morphology of TiO₂ also afforded spatially selective illumination. SEM images (Figure S5, Supporting Information) and UV-vis absorption spectra were monitored at different growth stages to probe the growth process of "mulberry-like" CdSe nanoclusters anchored on the TiO₂ nanotube. In the initial stage of growth, CdSe was first nucleated on TiO₂ surfaces. With a prolonged electrodeposition time under the xenon lamp illumination, the nanocrystal growth encounters two states: the growth of nanocrystals to large size and the new nanocrystals seeded around the large nanocrystals, which happened simultaneously throughout the deposition process. Such evolution resulted in a gradient distribution of multisized CdSe nanoparticles in nanoclusters, which had larger nanoparticles located in the inner layer and smaller nanoparticles in the outer layer as shown in Figure 1. The quantized CdSe nanoparticles in "mulberry-like" nanoclusters were evidenced from the absorption spectra shown above (Figure 3). Photo-irradiation reduced the excess selenium and surface defects of the CdSe nanocrystals and thus improved the crystallinity of nanoclusters. "Mulberry-like" CdSe nanoclusters, assemblies of CdSe nanocrystals with an ordered gradient, were fabricated, and thus constructed a high-quality multijunction coupled with the TiO₂ nanotube. The new architecture may provide a versatile platform for an ordered assembly of "mulberry-like" nanoclusters, which has strong potential for fabricating a multijunction photovoltaic device.

Photoelectrochemistry of "Mulberry-like" CdSe Nanoclusters Anchored TiO₂ Nanotube Electrode. The photoresponse characteristics of CdSe/TiO₂ electrodes were evaluated by inserting them in a photoelectrochem-

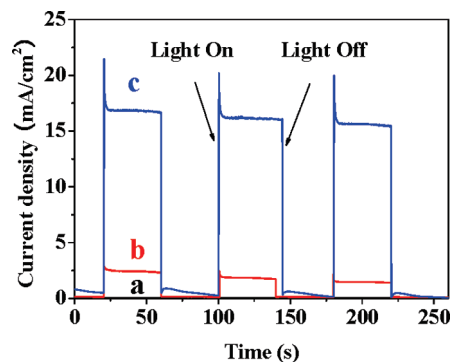


Figure 6. Photocurrent response of the electrodes to On-Off cycles of illumination: (a) TiO₂ nanotube, (b) CdSe layer coated TiO₂ nanotube, and (c) "mulberry-like" CdSe nanoclusters anchored TiO₂ nanotube under 0 V bias potential (vs SCE). Light intensity was 100 mW/cm² (excitation > 420 nm).

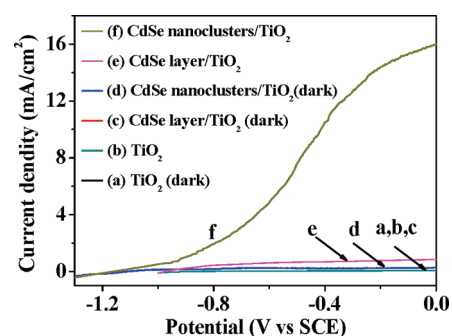


Figure 7. Current density vs voltage (I - V) curves of prepared electrodes. Light intensity was 100 mW/cm² (excitation > 420 nm).

ical cell under intermittent illumination with 0 V bias potential (vs SCE). Figure 6 shows the reproducibilities and stabilities of the photocurrent generation on CdSe layer coated TiO₂ electrode and "mulberry-like" CdSe nanoclusters anchored TiO₂ electrode, respectively. Both electrodes are prompt in generating photocurrent with a reproducible response to On-Off cycles compared with TiO₂ electrode in the visible region. It is interesting to note that "mulberry-like" CdSe nanoclusters anchored TiO₂ electrode exhibited a remarkable photocurrent. The combination of a short hole retrieval and fast electron transport may account for the excellent charge separation of the "mulberry-like" CdSe nanoclusters, thus enhance the photoresponse. The big change of the photocurrent of the mulberry-like CdSe-TiO₂ system before stabilization may be ascribed to the saturation effect of electron transportation at heterointerface.^{5a}

Representative current density versus voltage (I - V) characteristics of photovoltage electrodes are presented in Figure 7. The applied anodic bias provides the transport of photogenerated electrons from CdSe nanocrystals to TiO₂ surfaces. The "mulberry-like" CdSe nanocluster anchored TiO₂ nanotube electrode exhibits 10-fold higher photocurrent than that of the CdSe layer coated TiO₂ nanotube electrode, further confirming the role of "mulberry-like" architecture in improving the photoelectrochemical performance. The higher potential of CdSe

nanocluster anchored TiO₂ electrode corresponding to zero current might be attributed to a well-crystalline nature of CdSe in nanoclusters and a better CdSe/TiO₂ interface. Compared with the reported CdSe nanocrystals anchored on the TiO₂ electrode,⁵ the remarkable photoactivity in the present system is probably due to the multilevel absorption of “mulberry-like” nanoclusters toward solar light and decreased recombination kinetics at the junction interface, which can be ascribed to the 3-D multijunction between “mulberry-like” CdSe nanoclusters and TiO₂ nanotube generated during photoetching, avoiding the textured junction generated in the electrodeposition process. The photoresponse of the new electrode reflects the synergy arising from the excited interaction between “mulberry-like” CdSe nanoclusters and TiO₂ nanotube arrays. In addition, the 3-D architecture of “mulberry-like” nanoclusters would enhance the light scattering in the nanotube structure and thus promote the light absorption from the solar, resulting in an increase in the generation of electron–hole pairs. These results indicate the necessity of optimizing nanostructure assemblies in an orderly manner.

Proposed Mechanism for “Mulberry-like” Nanocluster Coupled CdSe–TiO₂ Photoelectrode. On the basis of the principle of sensitizing large-band-gap semiconductors with inorganic nanocrystals, the photoresponse characteristic highly depends on the positions of their conduction and valence bands as well as their geometrical arrangement. The higher-lying conduction band of CdSe compared to TiO₂ favors the electron injections after being activated by light.¹⁶ In light of the evidence in the preceding section, a multijunction mechanism, which refers to an ordered assembly of “mulberry-like” CdSe nanoclusters, is proposed for the achieved high performance. The new architecture of the “mulberry-like” CdSe nanoclusters, as well as those close-anchored on TiO₂ nanotube wall, drives the intensive vector to favorable levels to charge transportation from excited CdSe to TiO₂ nanotube. The SPV spectra provide the indirect evidence to estimate multisized CdSe nanocrystals in “mulberry-like” nanoclusters. The tunable band edge of CdSe nanocrystals indicates the promising ability to capture incident light in the entire solar region. As the cell was under illumination, an orderly gradient of CdSe nanocrystals in “mulberry-like” nanoclusters would continuously absorb the light ranging from short wavelength (blue light) to long wavelength (red light), resulting in more photo-absorption and electron–hole generation.

To understand the charge transfer and recombination kinetics of such a cell, Marcus theory,¹⁷ which has been proven a valuable tool (eqs 1 and 2) to investigate the electron transfer (ET) between the semiconductors,^{6,18} is used to estimate the driving forces for the

ET in “mulberry-like” nanoclusters anchored TiO₂ electrode.

$$k_{\text{ET}} = \frac{1}{\sqrt{4\pi\lambda kT}} \exp(-\Delta G/T) \quad (1)$$

$$\Delta G = E_{\text{CB}}(\text{CdSe}) - E_{\text{CB}}(\text{TiO}_2) \quad (2)$$

where k_{ET} is the ET rate, λ is the reorganization of energy for ET process, $-\Delta G$ is the driving force, and E_{CB} is the conduction band energy. As the driving force increases, the rate of ET increases. The energy level splitting in quantized particles increases the band gap of CdSe nanocrystals and thus increases the driving force for the electron transfer from CdSe nanocrystal to TiO₂. The small energy difference obtained by decreasing particle diameter of assembled CdSe nanocrystals is sufficient to increase the electron transfer rate by several orders of magnitude.⁶ The inhomogeneous “mulberry-like” CdSe nanoclusters make the arrangement of the absorption spectrum unambiguously different. The “mulberry-like” nanocluster structure provides a new type of architecture to grow a multitude of correlated nanocrystals and consequently contributes to an improvement in photovoltaic performances. Furthermore, the new high-quality multijunction architecture allows a fast and efficient electron transfer to cross the junction barriers.

Conclusions

In summary, “mulberry-like” CdSe nanoclusters anchored on TiO₂ nanotube arrays are successfully fabricated by the photo-assisted electrodeposition method. The architecture of “mulberry-like” nanoclusters, which is formed by the synergistic effect of electrodeposition and photoactivation/photoetching, leads to a remarkable response to the entire visible region of sunlight. A significant increase of the photoresponse represents the beneficial role of unique architecture to facilitate photo-generated electron propagation and kinetic separation. Furthermore, the photo-assisted electrodeposition process opens up a promising technique for a low-cost nanocrystal sensitized solar cell. Efforts are underway to build such architecture of photovoltaic materials for the multijunction solar cell.

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Supporting Information Available: SEM images, TEM images, XRD, and UV–vis spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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