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REVIEW

Luminescence Nanocrystals for Solar Cell Enhancement

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Semiconductor nanocrystals (NCs) prepared by wet-chemical routes have been proposed as an attractive candidate for fabrication of the third-generation thin-film solar cells due to their quantum confinement effects and excellent dispersion ability in polymer films. However, to date, a solar cell incorporating semiconductor NCs in the photoactive layer still has rather low efficiency due to the low carrier mobility of the non-continued NC phase and the possible radiative recombination in NCs. To avoid these disadvantages, NCs have been proposed and applied as a luminescent species in a passive photon converting layer to modify the solar spectrum before the light enters the photovoltaic device. Photon conversion processes, including up-conversion, down-conversion, and down-shifting, have been observed in various colloidal NC samples and have great potential to enhance photovoltaic performance when applied to the existing single-junction solar cells or narrow-band molecular-based devices.

Keywords: Luminescence, Nanocrystal, Solar Cells, Photon Conversion.

CONTENTS

1. INTRODUCTION

Colloidal nanocrystals (NCs) or quantum dots have size-tunable optical properties due to quantum confinement effects and excellent solution processing ability that is compatible with polymer film techniques. Thus NCs have been proposed as a cost-effective candidate for developing third-generation thin-film solar cells.[1] Research on NC solar cells focuses on two configurations: semiconductor NC sensitized porous metal oxide solar cells[2–9] and NC-polymer hybrid solar cells,[10–19] both of which incorporate NCs into the photoactive layer. There have been large amounts of literature and some reviews about NC-based solar cells. The results obtained so far are very impressive. However, despite the great potential of NCs in solar cells, they still have not been demonstrated as an efficient component in the photoactive layer of a solar cell. To date, NC-sensitized solar cells have shown comparatively lower efficiencies than the originally proposed and widely studied organic dye sensitized solar cells (~1%[2] versus 11%[20]), and the NC-polymer hybrid cells show a highest efficiency less than 3%,[11,12] compared to the C_{60}-derivative-polymer hybrid hetero-junction solar cells[21–28] (>5%).

The main problems leading to low efficiency of NC-based cells are lower charge collection and transfer efficiencies, which can hardly be overcome because of the very low carrier mobility in the non-continued NC phase. Meanwhile, semiconductor NCs might act as photoluminescence centers that capture carriers during their transportation and thus lower the device efficiency.

It is known that the solar spectrum contains photons with energies ranging from about 0.5 to 3.5 eV. However, commercial crystalline single p–n junction semiconductor solar cells can convert only a small part of the incident solar energy to current according to the band gap of photovoltaic semiconductor materials, which leads to a theoretical maximum efficiency of 31% under one-Sun irradiation from a Schockley–Queisser analysis.[29] Similarly, new photovoltaic devices based on dye molecules or polymers can

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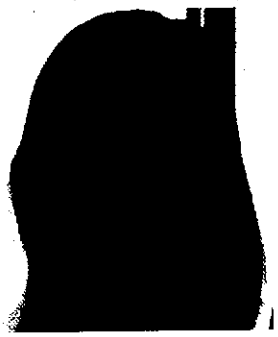
only utilize a small range of the solar spectrum due to their rather narrow absorption bands.

Therefore, many new concepts of solar cell architectures, such as tandem cells, try to adapt materials to the broad spectral range of the incident solar spectrum.[1] However, a high material quality must be fulfilled in tandem architectures in order to achieve improved energy conversion efficiencies, which will not be easy to fulfilled in the near future.

Instead of adapting the photovoltaic cell itself to the broad incident solar spectrum, a passive layer including luminescent species can modify the incident solar light to the spectral response range of the cell before it enters the photovoltaic device. An efficient luminescence converter requires high luminescence efficiency and small absorption/emission band overlap, which are very different from the requirements for an efficient photovoltaic material, thus the material of the converter can be optimized independently of the solar cell material itself. Moreover, a passive luminescence converter can be applied and optically coupled, in principle, to any existing solar cell without any modification of the cell itself. Since a



Dr. Shu-Man Liu graduated from the Wuhan University of Technology, Wuhan, China, in 1994. In 1997, she got her master degree in Science and Technology from the same university. She earned her doctorate (Ph.D.) in Materials Physics and Chemistry from Institute of Semiconductor, Chinese Academy of Sciences in 2000. Since then, she spent her first three years on thin-film electroluminescence devices made from II–VI nanoparticles and polymers at Beijing Jiaotong University. From 2003 to 2005, she conducted research in silicon nanoparticles in University of Hyogo, Japan supported by JSPS fellowship. From 2005 to 2007, she worked on quantum wire lasers in the Institute for Solid State Physics, University of Tokyo, Japan. In 2007, Dr. Liu joined the Institute of Semiconductors, Chinese Academy of Science. Her present research interest is nanocrystal based solar cells.

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Prof. Wang Zhanguo (Z. G. Wang) graduated from the Department of Physics, Nankai University, in 1962. Then he immediately joined the Institute of Semiconductors, Chinese Academy of Sciences (IS, CAS), engaged in studies on semiconductor materials physics and materials characterization till 1980. From 1980 to 1983, he was a visiting scientist at the Department of Solid State Physics, the University of Lund, Sweden, working on photoluminescence and deep levels of semiconductors. By the end of 1983 he became a research professor and a head of Semiconductor Materials Division of IS, CAS in 1986. From 1990, Prof. Wang served as director of Key Lab. of Semiconductor Materials Science and a deputy director of the IS, CAS, vice president of Chinese Materials Research Society and director of Semiconductor and Integration Technology Society, the Chinese Institute of Electronics etc. From 1984 to 1993, he conducted research mainly in the space GaAs crystal growth and characterization, GaAs and InP based superlattice, quantum well structures, MBE growth and its property studies. From 1994 till now, his research work has concentrated to low dimensional semiconductor nanostructures growth and quantum devices fabrication. He has published 3 books and more than 180 refereed papers in many authoritative journals. Prof. Wang was elected as a member of the CAS in 1995.

luminescence converter is only optically coupled to the combined photovoltaic cell—i.e., the converter must be electronically isolated from the cell—there is no carrier transportation between them. Thus it can be seen that the disadvantage of poor carrier mobility in the non-continued NC phase mentioned above can be avoided if luminescent NCs are introduced in the passive luminescence converters.

The luminescence conversion approaches involve the use of photon up- and down-conversion for utilizing otherwise lost solar energy, which might increase the photocurrent and/or voltage of solar cells. Figure 1 shows a schematic of a solar cell with up-conversion and down-conversion. A luminescence up-converter[30] transforms sub-band-gap photons transmitted by a solar cell to higher-energy photons, which can subsequently be absorbed by the cell, and thus was suggested to reduce the transmission losses. An up-converter is usually located between a photovoltaic cell and a rear reflector. An ideal down-converter,[31] in which multiple electron–hole (e–h) pairs are generated per incident high-energy photon, is one approach to reduce the thermalization losses efficiently. Another type of down-converter, which transforms a high-energy photon to a low-energy one near the absorption threshold of the solar cell by red-shifted photoluminescence, can also reduce the thermalization losses and is usually called a down-shifter.[32] Significant improvements in efficiency over the efficiencies of conventional single-junction cells have been predicted theoretically for both up-conversion[33–35] and down-conversion[36–39] systems. Meanwhile, it has been reported that NCs can be prepared with near-unity photoluminescence quantum yields[40] by using improved methods for surface treatment. Thereby, such luminescent NCs are expected to act as efficient and tailorable photon converters.

In this article, we will focus our attention on luminescent NC-based solar converters that are up-converters, down-converters, and down-shifters incorporating various NCs as luminescent species. We present the concepts of various converters, operating principles, and state-of-the-art in the development of these types of solar converters.

2. CONCEPT AND THEORETICAL MAXIMUM EFFICIENCY

For a single-junction semiconductor solar cell, the band-gap energy of the semiconductor material establishes a fundamental upper limit for its conversion efficiency. Figure 2[41] illustrates the losses processed in a single-junction solar cell. Process 1 is a lattice thermalization loss, i.e., a photon with high energy creates an e–h pair, and then the photoexcited pair quickly loses the extra energy as heat within the device. Process 2 in Figure 2 denotes the transparency of the semiconductor to sub-band-gap photons. Process 3 means a loss caused by the recombination of photoexcited e–h pairs, which does not contribute greatly to the theoretical efficiency limit. Processes 4 and 5 denote voltage drops across the junction and the contacts in the device. Using the principle of detailed balance between incident and escaping photons and extracted electrons, Shockley and Queisser demonstrated that the one-Sun efficiency limit for a single-material cell is around 31% with an optimal band-gap of 1.3 eV.[29] They assumed in their calculation that there exists only radiative recombination of carriers in the device. For a Si cell with the band-gap of 1.12 eV, the Shockley-Queisser one-Sun efficiency limit is reduced to 30%. Now the best existing lab-scale Si solar cells with a one-Sun efficiency of 24.7%[42] are very close to their theoretical limit. Since Si solar cells dominate the present photovoltaic technologies, studies on luminescence converters have been focused on the application of luminescence up-conversion[43–45] and down-conversion[46] to single-junction Si solar cells in order to achieve ultra-high efficiencies exceeding the Shockley-Queisser limit by overcoming the transparency and thermalization losses described above.

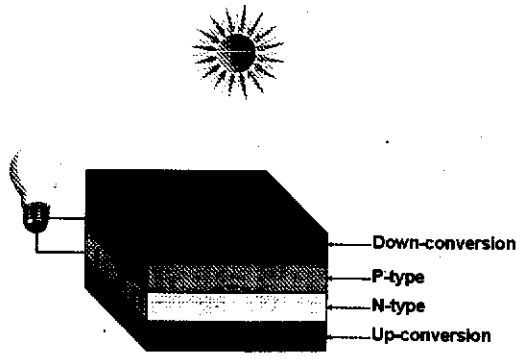

Fig. 1. Schematic of a solar cell using down-conversion nanoparticles to convert UV light to visible light and up-conversion nanoparticles to convert IR light to visible light for solar cell enhancement. Meanwhile, the conversion can reduce the heating effect and prolong solar cell longevity.

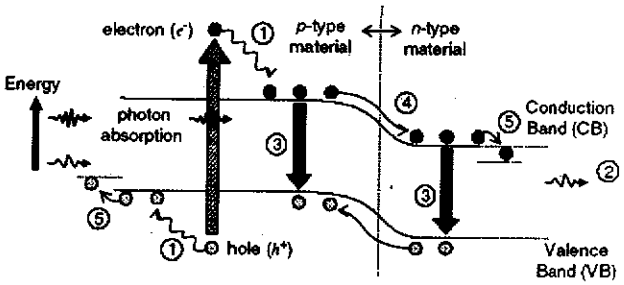

Fig. 2. Loss processes in a single-junction solar cell: (1) lattice thermalization loss; (2) transparency; (3) recombination loss; (4) junction loss, and (5) contact voltage loss. Reprinted with permission from [41]. B. S. Richards, *Sol. Energy Mater. Sol. Cells* 90, 2329 (**2006**). © 2006. Elsevier.

2.1. Up-Conversion and Mechanism

An up-converter ideally consists of a system[30] in which three bands are involved in optical transitions as shown in Figure 3, where each band consists of allowed energy states of a single energy or a range of energies. Several mechanisms have been suggested for up-conversion.[47] One is ground state absorption/excited state absorption (GSA/ESA) as illustrated in Figure 3(a), involving the generation of an excited state by a two-step process through a real, lower-lying, and metastable intermediate state or band. Then, the excited state relaxes via a radiative transition, and an up-converted photon with higher energy is emitted. It is shown that the theoretical maximum solar energy conversion efficiency of an up-conversion system in the radiative limit under this mechanism using a detailed balance model is 63.2% for concentrated sunlight, 47.6% for un-concentrated sunlight using a 6,000 K blackbody spectrum, and 50.7% for an AM 1.5 spectrum for a optimum cell band-gap of ~2.0 eV.[33] These predicted efficiencies are much higher than the Schockley-Queisser limit of 31% for an optimum band gap of 1.3 eV. In their calculation, the main assumptions are perfect photon selectivity within the up-converter, no non-radiative electronic transitions anywhere in the system, and infinite carrier mobilities inside the solar cell.

The second mechanism of up-conversion is called energy transfer up-conversion, in which sensitizer ions absorb the low energy photons and sequentially transfer to a luminescent center or an activator, already in an excited state, and raise it to a higher energy excited state as seen in Figure 3(b). High-energy up-converted photons are emitted from the luminescent center. The sensitizer ions and luminescent centers are usually rare earth or transition elements or ions. The third mechanism is photon avalanche up-conversion,[48] which involves higher excited state energy levels at very high incident threshold pump powers, and thus is not useful for applications in solar cells.

Up-conversion efficiencies in all the above mechanisms depend on the lifetime of the intermediate metastable energy levels. The longer an electron is in the excited state, the higher the probability of up-conversion. Thus, the energy transfer up-conversion mechanism involving $4f$ electronic structures of rare earth ions typically has higher up-conversion efficiencies compared with GSA/ESA process due to the long lifetime of $4f$ excited states.

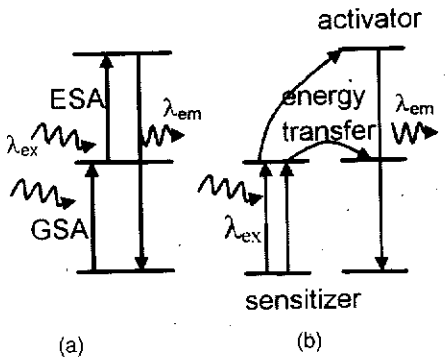

Fig. 3. A schematic illustration of (a) GSA/ESA and (b) energy transfer mechanism of up-conversion processes.

2.2. Down-Conversion with Generation of Multiple e–h Pairs Per Photon

The thermalization of charge carriers, generated by the absorption of high-energy photons, is one of the major loss mechanisms. Thus, solar energy is underutilized in a conventional single-junction solar cell due to thermalization losses. Down-conversion of high-energy photons into near infrared (NIR) or visible photons is a promising route for reducing these energy losses. When a high-energy photon impinges on a down-conversion layer overlying a solar cell, two or more low-energy photons emit. Trupke et al.[36] demonstrated theoretically that a maximum conversion efficiency of 38.6% could be obtained for a 6,000 K blackbody spectrum for an optimum underlying solar cell band gap close to 1.1 eV under detailed balance calculations. The optimum cell band gap energy of 1.1 eV makes this approach very attractive for improving the efficiency of existing silicon solar cells. In a dye-sensitized solar cell or a polymer-based solar cell, the dye molecules or the polymers normally have a narrow absorption band in contrast to inorganic semiconductor materials, such as Si and GaAs, and an even higher efficiency limit of 39.6% is calculated for a down-converter located behind the solar cell. In their calculations, the luminescence converter has one intermediate level, and all involved recombination transitions in the system are radiative.

Recently, Badescu et al.[37,38] proposed a modified model to describe a solar cell with a down-converter at the front or rear of the cell. They considered non-radiative recombination and the refractive indexes of the cell and converter materials and showed that the conversion efficiency is smaller than that estimated by Trupke et al., especially when both the cell and the down-converter have the same low radiative recombination efficiency (less than unity).

3. PHOTON-CONVERTING NANOMATERIALS

3.1. Up-Conversion Observed in NCs

For a practical up-conversion device, a multi-level luminescent material should be used to realize the up-conversion process. Inorganic trivalent rare earth ions have multiple discrete energy levels. In such an ion, an electron can rise up to higher energy levels by absorbing several lower-energy photons. The electron then drops back to the ground state, and a photon is emitted that has a higher energy than the initially absorbed photons. Thus, rare earth ions with characteristic $4f$ energy levels have potential for the up-conversion process.

There exists a large amount of literature on up-conversion of rare earth phosphors. Among the rare earth ions, trivalent erbium (Er^{3+}) is an ideal candidate for single wavelength NIR up-conversion for Si solar cell applications, while as a host material, $NaYF_4$ is most widely investigated, since most rare earth ions can be easily incorporated.

Initial experimental attempts applied the rare earth up-converting phosphors directly to existing Si solar cells to increase photocurrent at IR range. Shalav et al.[43] coupled a layer of polycrystalline Er^{3+}-doped sodium yttrium fluorfide ($NaY_{0.8}F_4:Er^{3+}_{0.2}$) phosphors (~5 μm size) as up-converters to the rear surface of bifacial buried-contact silicon solar cells. They demonstrated that the up-converting layer make the device respond to 1480–1580 nm sub-band-gap light and obtained an external quantum efficiency of $(2.5 \pm 0.2)\%$ at the wavelength of 1523 nm. The energy transfer up-conversion mechanism occurring in this material system is shown in Figure 4, in which (1), (2), and (3) denote one, two, and three step energy transfer up-conversion processes, respectively. The external quantum efficiency of their $NaY_{0.8}F_4:Er^{3+}_{0.2}$ up-converting phosphor was improved to 3.4% very recently,[44] but no cell performance was reported.

A more efficient NIR-visible up-converting phosphor is Er^{3+} and Yb^{3+} co-doped $NaYF_4$. This co-doped up-conversion system works under the energy transfer mechanism with Yb^{3+} as the sensitizer and Er^{3+} as the activator, resulting in visible luminescence. Yb^{3+} is a very good sensitizer for up-conversion because it exhibits a strong and broad absorption band centered at about 960 nm, and the energy transfer from Yb^{3+} to Er^{3+} ions and most other rare earth ions is efficient. However, because both the semiconductor silicon and Yb^{3+} ions absorb the NIR photons

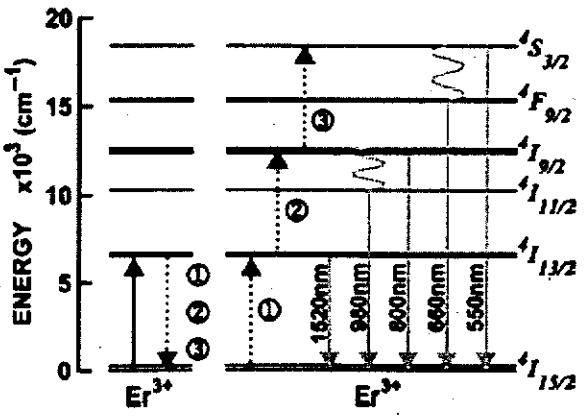

Fig. 4. Three-step up-conversion process between two erbium (Er^{3+}) ions. Energy relaxation from one Er^{3+} ion (the sensitizer) can result in energy transfer to a neighboring Er^{3+} ion (activator) giving rise to higher energy photons. Solid lines represent photon absorption (up) and emission (down), dotted lines represent energy transfer, wavy lines represent phonon emission. Reprinted with permission from [43], A. Shalav et al., *Appl. Phys. Lett.* 86, 013505 (**2005**). © 2005, American Institute of Physics.

of wavelengths between 900 and 1100 nm, and there is an essential competition between them, these NIR-visible up-converting phosphors are not suitable for crystalline Si solar cells but are potentially useful for higher band gap photovoltaic materials such as organic polymers, e.g., a-Si, CdTe, or GaAs.

Gibart et al.[45] demonstrated experimentally the up-conversion of sub-band gap light in photovoltaic devices by attaching a Yb^{3+}, Er^{3+}-doped vitroceramic behind a substrate-free GaAs solar cell. They obtained an NIR conversion efficiency of 2.5% from their up-converter-attached cells under 1 W laser illumination at 890 nm. The efficiency of the system is too low for practical solar cell applications.

Recently, the size of the rare earth-doped up-converting phosphors has been reduced to the nanoscale, and lots of wet-chemical routes to prepare up-converting colloidal materials have been developed.[49–79] The latest work on these up-converting nanomaterials is listed in Table I.

Boyer et al.[49] prepared monodisperse up-converting lanthanide-doped $NaYF_4$ NCs via a thermal decomposition reaction of trifluoroacetate precursors in a mixture of technical grade chemicals, octadecene, and the coordinating ligand oleic acid. Figure 5 shows the transmission electron microscopy images of a $NaYF_4:Er^{3+}$, Yb^{3+} NC sample. One can see that the synthesized particles appear to be hexagonal in shape and are nearly monodisperse. The average particle size was 27.6 ± 1.6 nm. The colloidal samples of the Er^{3+}, Yb^{3+}-doped and Tm^{3+}, Yb^{3+}-doped NCs exhibit green/red and blue up-conversion luminescence, respectively, under 980 nm laser diode excitation with low power densities. These $NaYF_4$ NCs can be dispersed in non-polar organic solvents. A dense thin film formed from such non-polar organic colloid can be easily applied on the bottom of a solar cell as an up-converting layer.

Schafer et al.[50] prepared $NaYF_4:Yb^{3+}$, Er^{3+} nanocrystals showing high colloidal solubility in water by treating the nanocrystals with 1-hydroxyethane-1,1-diphosphonic acid. Such aqueous colloid solutions of up-converting NCs are suitable especially for bio-applications and thus have attracted a great deal of attention. By their surface treating method, the authors observed enhancement of the up-conversion efficiency. Coating the luminescent rare earth-doped NCs with an undoped inorganic shell is also a popular route for efficiency enhancements. Yi et al. reported[51] the preparation of hexagonal phase nanoparticles of $NaYF_4:Yb^{3+}$, Er^{3+} (Tm^{3+}) core and $NaYF_4:Yb^{3+}$, Er^{3+} (Tm^{3+})/$NaYF_4$ core/shell. The schematic structure and up-converting emission images of $NaYF_4$:Yb, Er(Tm) core, core/shell, and poly(acrylic acid) (PAA)-coated core/shell NCs are shown in Figures 6(a) and (b). After coating with an un-doped $NaYF_4$ shell. they observed up-conversion fluorescence enhancements for $NaYF_4:Yb^{3+}$, Er^{3+} and $NaYF_4:Yb^{3+}$, Tm^{3+} colloids.

Table I. Selection of up-converting nanomaterials reported recently.

Material	Size (nm)	Excitation (nm)	Excitation power	Emission (nm)	Reference
$NaYF_4$:Yb, Er	28	980	100 Wcm^{-2}	525, 541, 655, 800	[49]
$NaYF_4$:Yb, Tm	28	980		450, 646, 800	
$NaYF_4$:Yb, Er	26	975	150 Wcm^{-2}	550, 670	[50]
$NaYF_4$:Yb, Er	8.5	980	15 Wcm^{-2}	540, 655	[51]
$NaYF_4$:Yb, Tm	8.5	980		470, 800	
$NaYF_4$:Yb, Er	200	980	45 mW	525, 550	[52]
$NaYbF_4$:Er	20	980		520, 540, 655	[53]
$NaYbF_4$:Tm	20	980		476, 800	
$NaYbF_4$:Ho	20	980		540, 750	
$NaYF_4$:Yb, Er	20	980	1–1000 $mWcm^{-2}$	4410, 455, 480, 525, 540, 665, 800	[54]
$NaYF_4$:Yb, Er	21	980	50 $mWcm^{-2}$	407, 521, 539, 651	[55]
$NaYF_4$:Yb, Tm	21	980		450, 479	
$NaYF_4$:Yb, Er	8–14	980	0–800 mW	524, 540, 654	[73]
$NaYF_4$:Yb, Er	28	980	1.9–12.2 Wcm^{-2}	524, 541, 655	[74]
$NaYF_4$:Yb, Er	50–80	980	126–500 mW	520, 550, 660	[75]
$KMnF_3$:Yb, Er	20	980	<100 mW	525, 553, 653	[76]
$LaPO_4$:Yb, Er	40	970	300 mW	525, 550, 675	[77]
Y_2O_3:Yb, Er, Li	40–54	970	40 Wcm^{-2}	560, 650	[78]
YF_3:Yb, Tm	2 × 700	980	220 Wcm^{-2}	291, 347, 363, 454, 477	[79]
CdS	4	660	2–60 mW	437	[57]
$CdZn_{0.13}S$	4	660		430	
$CdZn_{0.66}S$	4	660		414	
CdS	4.1	800	760 GW/cm^{-2}	470	[59]
CdTe	2.5	830	2–60 mW	537	[60]
	3.5			600	
CdSe	2.5	767	2–60 mW	542	[64]
	3.5			605	
	6.0			642, 688	

The PAA coating renders the NCs water soluble due to the hydrophilic carboxyl group of PAA extending outward. However, PAA-coated core/shell nanoparticles showed a decreased fluorescence, in contrast to the results of acid-treatments reported by Schafer et al.[50] In addition, Zhuang et al.[52] prepared hexagonal $NaYF_4$ microtubes co-doped with Yb^{3+}/Er^{3+} ions, and observed more intense green up-conversion emission than from cubic $NaYF_4$ or hexagonal $NaYF_4$ nanoparticles.

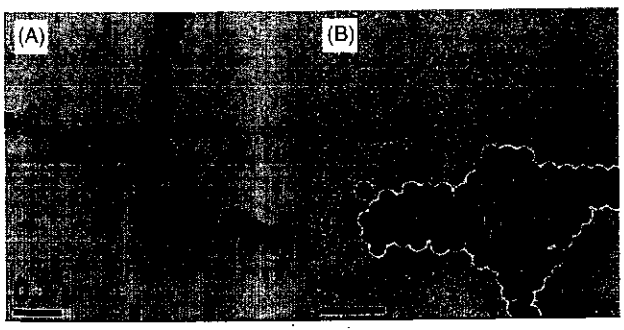

Fig. 5. Low-resolution transmission electron micrographs of $NaYF_4$: 2% Er^{3+}, 20% Yb^{3+} sample. Reprinted with permission from [49], J. C. Boyer et al., *Nano Lett.* 7, 847 (**2007**). © 2007, American Chemical Society.

At present, experimental studies mainly aim at demonstrating the up-conversion concept, i.e., achieving higher energy luminescence at sub-band-gap excitation by up-conversion from these nanomaterials, and the color of up-conversed emission can be controlled by doptants and doping concentration. Ehlert et al.[53] prepared IR-to-visible up-converting nanoparticles about 20 nm in size of $NaYbF_4:Tm^{3+}$, $NaYbF_4:Ho^{3+}$, $NaYbF_4:Tm^{3+}$, $NaYbF_4:Er^{3+}$, and $NaYF_4:Yb^{3+}$ and thus observed four different spectrally resolvable up-conversion emissions with a single excitation source of 980 nm. Wang et al.[54] reported that the up-conversion emission colors were tuned from visible to NIR under single-wavelength excitation in $NaYF_4$ nanoparticles doped with Yb^{3+}, Tm^{3+}, and Er^{3+} by precise control of different combinations and concentrations of lanthanide dopants as shown in Figure 7. These studies suggest a potential route for the development of novel luminescent converters that are particularly useful in conversion of IR sunlight to the whole visible range according to the requirement of photovoltaic materials of

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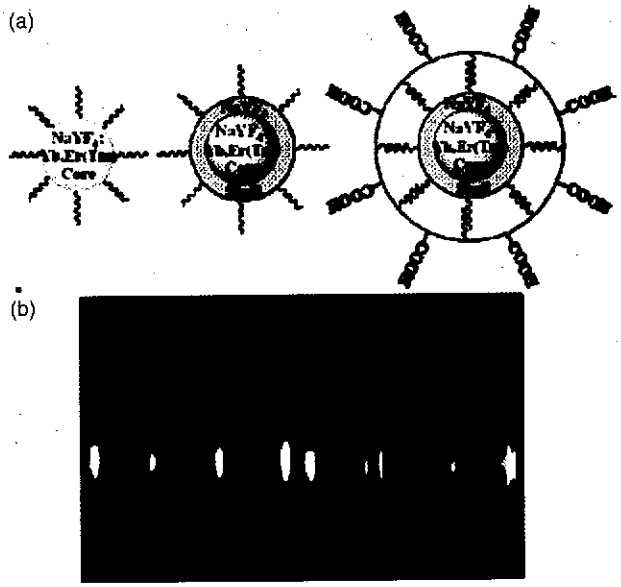

Fig. 6. (a) Structure scheme, and (b) up-conversion fluorescence image (green from $NaYF_4$:Yb, Er and blue from $NaYF_4$:Yb, Tm). Reprinted with permission from [51], G. S. Yi and G. M. Chow, *Chem. Mater.* 19, 341 (**2007**). © 2007, American Chemical Society.

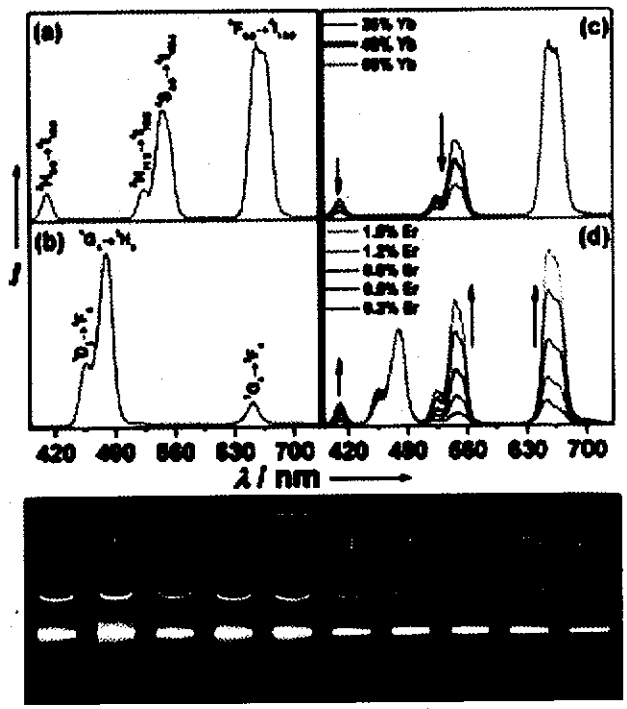

Fig. 7. Up-conversion emission spectra of (a) $NaYF_4$:Yb/Er (18/2 mol%), (b) $NaYF_4$:Yb/Tm (20/0.2 mol%), (c) $NaYF_4$:Yb/Er (25–60/2 mol%), and (d) $NaYF_4$:Yb/Tm/Er (20/0.2/0.2–1.5 mol%) particles. Compiled luminescent photos showing corresponding colloidal solutions of (e) $NaYF_4$:Yb/Tm (20/0.2 mol%), (f)–(j) $NaYF_4$:Yb/Tm/Er (20/0.2/0.2–1.5 mol%), and (k)–(n) $NaYF_4$:Yb/Er (18–60/2 mol%). Reprinted with permission from [54], F. Wang and X. Liu, *J. Am. Chem. Soc.* 130, 5642 (**2008**). © 2008, American Chemical Society.

a cell. Very recently, $NaYF_4$:Yb^{3+}, Er^{3+}(Tm^{3+}) hexagonal plate-like nanoplates (~30 nm × 45 nm side surface) were reported to exhibit significant up-conversion emission under 50 $mWcm^{-2}$ illumination at 980 nm.[55] Such low excitation power is comparative to the AM1.5 sunlight radiation.

In addition to rare earth-doped nanocrystals, up-conversion luminescence has also been readily observed in several semiconductor NCs, also shown in the lower part of Table I, such as ZnS:Mn^{2+},[56] CdS,[57–59] ZnCdS,[57] CdTe,[60–63] and CdSe[64–66] NCs; CdSe/ZnS and CdSe/ZnSe core/shell nanostructures;[67–70] and III–V quantum dots.[71,72] Unlike the energy transfer up-conversion mechanism in the above-mentioned rare earth-doped nanomaterials, the mechanisms for up-conversion luminescence in semiconductor NCs are still under debate. Auger recombination, two-photon absorption, and thermally assisted surface-state processes have been proposed to explain the up-conversion found in semiconductor NCs. Chen and co-workers prepared a series of II–VI semiconductor NCs including CdSe,[64] CdTe,[60] ZnS:Mn^{2+},[56] CdS, and ZnCdS,[57] and observed efficient up-conversion emission from these NCs of several nanomerters in size. The up-conversion mechanism was investigated based on the measurements of the power dependence and decay dynamics. They observed a near-quadratic laser power dependence, which indicates a two-photon absorption mechanism of the up-conversion process in their samples.

In Jakubek's report,[65] up-converted luminescence was also observed in a CdSe NCs colloidal sample when the sample was excited in the onset of the absorption tail. However, this up-conversion emission was attributed to a single-photon excitation. The authors claimed that the up-conversion process in their CdSe NC sample was thermally assisted. Although explanations of the up-conversion process in semiconductor NCs samples are still not consistent at present, the strong up-conversion luminescence and the quantum-confined luminescence, i.e., the energy of an emitted photon can be adjusted by NC size, make them even more attractive for practical applications.

The nanomaterials mentioned above show up-conversion luminescence usually at rather high intensity illumination from an IR laser source and, thus, can hardly be utilized as solar up-converters at present. One of the key issues of up-conversion nanomaterials is, thus, whether the photon up-conversion can be excited by a low power light source, or rather, sunlight. If light up-conversion in NCs can be activated under sunlight irradiation, the NCs can be readily incorporated into the existing wide-gap solar cells.

Recently, Castellano et al. have observed low power up-conversion luminescence in molecular systems using metal-to-ligand charge transfer (MLCT) sensitizers.[80,81] In their work, Ru(II) complex was used as the MLCT sensitizer, and green-to-blue up-converted fluorescence was easily visualized in a mixture of Ru(II) complex and 9,10-diphenylanthracene (DPA) under low power excitation.

They claimed that the light up-conversion of the system resulted from selective excitation of the sensitizer under low power and subsequent MLCT to DPA through triplet–triplet annihilation. The image in Figure 8 demonstrates the efficient photon up-conversion, in which a commercial (pulsed) green laser pointer ($\lambda_{ex} = 532$ nm, peak power < 5 mW) was used as excitation source. The green laser beam traverses the sample from bottom to top where up-converted blue light is visualized by the naked eye. Recently, Chen and Castellano have been collaborating on up-conversion NCs for biological imaging. The up-conversion emission can be seen under sunshine excitation, which is very attractive for application in solar cells. Therefore, we believe that the up-conversion efficiency of both rare earth-doped and semiconductor NCs colloidal systems can be further improved in the near future with increasing demand for up-conversion luminescence materials. Since these up-converting nanomaterials can be easily applied on the bottom of a solar cell as a dense passive thin film, they are very good candidates for enhancing the performance of solar cells having the best spectral response in the visible range of sunlight, such as organic solar cells and wide band-gap inorganic cells. Coupling the above-mentioned up-conversion luminescent nanocrystals to solar cells with wide band-gap active materials can efficiently utilize the otherwise transparent NIR solar light which constitutes ~25% of the full solar spectrum; thus, it is possible to achieve apparent efficiency improvements at low cost, compared to other new-concept third generation approaches.

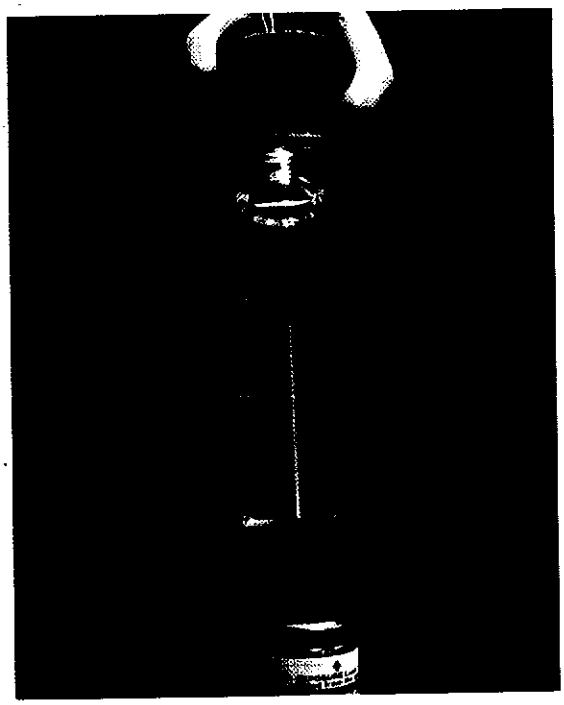

Fig. 8. Digital photograph of up-converted emission produced in a mixture of Ru(II) complex and DPA. Excitation by a green laser pointer ($\lambda_{ex} = 532$ nm, <5 mW peak power). Reprinted with permission from [81], R. R. Islangulov et al., *Chem. Comm.* 3776 (**2005**). © 2005, The Royal Society of Chemistry.

3.2. Down-Converting Materials

Experimentally, down-conversion luminescence has also been investigated extensively in rare earth-doped materials. In the early 1970s, down-conversion emission in the visible range of the spectrum was observed in various Pr^{3+}-doped materials under excitation of Pr^{3+} ions between 125 and 215 nm.[82,83] In addition, down-conversion emission with quantum yield greater than unity was observed on many other rare earth pairs under the energy transfer mechanism, such as Gd^{3+}–Eu^{3+},[84–89] Tm^{3+}–Yb^{3+},[90,91] Eu^{3+}–Tb^{3+},[92] Ce^{3+}–Yb^{3+},[93] Tb^{3+}–Yb^{3+},[94–98] and Er^{3+}–Ce^{3+}.[99] However, the down-conversion emissions in these rare earth-doped materials can only be excited at very short wavelengths of ultraviolet (UV) or vacuum UV (VUV); thus, they have not been used for solar light down-conversion to date.

Another type of down-conversion, different from that in rare earth-doped nano-materials, is called carrier multiplication, or multiple exciton generation in semiconductor NCs,[100–110] in which absorption of a high-energy photon at least twice the band gap of semiconductors or the difference of the energies of highest occupied molecular orbital and lowest occupied molecular orbital of organic systems produces two or more electron–hole pairs. However, the photo-generated multi-excitons are observed to undergo non-radiative Auger recombination in a sub-picosecond timescale and, thus, can hardly be used as a down-converter optically coupled to a solar cell.

3.3. Down-Shifters Incorporating NCs

Although a down-converter is expected to convert an incident high-energy photon into two or more lower-energy photons that better match the spectral response of the photovoltaic material in a solar cell, all down-conversion process have been observed at rather high energy and high intensity excitation. Thus, the present studied down-converting materials cannot be used for terrestrial solar cells. Down-shifting is similar to down-conversion as a spectral converter, but an important difference is that the down-shifting process converts high-energy photons into low-energy ones with the quantum efficiency lower than unity. In spite of the less-than-unity quantum efficiency, a down-shifter applied on top of a solar cell can covert high-energy solar photons into low-energy ones that match the spectral response of the photovoltaic material, and consequently, the thermalization losses caused by otherwise direct absorption of the high-energy photons in the cell material will be significantly reduced. van Sark et al.[111,112] modeled a down-shifter of 4.3-nm CdSe NCs emitting at 603 nm on top of multi-crystalline silicon solar cells. The multi-crystalline silicon has low spectral response at

short wavelengths (blue) and high spectral response at long wavelengths (red). Their calculation showed that the short-circuit current was increased by nearly 10%, and the efficiency can be 30–40% as the low-response blue solar light has been converted to the high-response red one.

Svrcek et al.[113] embedded Si NCs into a spin-on-glass antireflecting SiO_2-based solution and spun the solution onto standard silicon solar cells. High-energy solar photons are absorbed by Si NCs and transformed via photoluminescence to red ones at ~700 nm, which should be converted into electricity more efficiently by silicon solar cells. Their experiments have shown that the Si/SiO_2 down-shifting layer enhanced the internal quantum efficiency of a standard Si solar cell in the region where the Si NCs absorb light. However, the cell efficiency shows only a slight increase of 0.4%, which should be increased further by enhancement of the photoluminescence quantum yield of Si NCs and/or optimization of the refractive index of the down-shifting layers.

Recently, Nayfeh et al.[114] investigated the effect of monodispersed luminescent Si nanoparticle coatings on polycrystalline Si solar cells by monitoring the current–voltage characteristics. They found that films of ~3-nm red luminescent Si nanoparticles improved the cell power performance by ~60–70% in the UV and by 10% in the blue, where polycrystalline Si has very low spectral response. However, the cell performance was mainly improved by large voltage enhancements instead of current increase, which is in contrast to that expected by the wavelength down-shifting mechanism. They explained the improvement in cell performance by charge resonant transport across the nanofilm and Schottky-like rectification at nanoparticle-metal interface.

A luminescent solar concentrator (LSC) composed of a plastic coating incorporating organic fluorescent molecules was originally proposed in the 1970s.[115] Figure 9 shows a sketch of the LSC, which consists of a stack of transparent sheets doped with appropriate organic dyes. In each sheet, the sunlight is absorbed by the dye and then re-emits and is trapped in the sheet by internal reflection. The trapped light propagates to the edge of the sheet through total internal reflection and is absorbed by a solar cell with the band gap matching the luminescence energy. The excess photon energy is dissipated in the collector by the Stokes' shift. Thus, the heat in the cell is largely reduced, which is of benefit to efficiency improvement. Furthermore, the area of a solar cell attached at the edge of the LSC is greatly reduced, which is of benefit to cost reduction of solar cells. Alternative to organic dyes, semiconductor NCs have been proposed recently for use in the LSC, since their absorption spectrum is broad compared to that of organic dye molecules, and their emission wavelength can be tailored easily due to the effects of quantum confinement.[116] Some experiments have been conducted recently on NC solar concentrators. Schuler et al.[117] incorporated CdS NCs into silicon oxide films that were deposited on glass substrates by a sol–gel dip-coating process. CdS NCs with different size have been prepared by changing the temperature of thermal annealing. A photograph of the samples formed at 250, 350, and 450 °C is shown in Figure 10. The samples are illuminated by UVA radiation, and emission from the edges of the samples can be visualized. If a solar cell with a band gap matched to the emission wavelength of CdS NCs is attached to edge of the glass sheet, solar light concentration can be realized. Sholin et al.[118] fabricated LSCs with polymers and commercially available CdSe/ZnS core–shell NCs, but they concluded that the NCs were not viable because of their large absorption/emission band overlaps and relatively low quantum yields compared to the polymer LSCs. Gallagher et al.[119] fabricated concentrator systems with CdSe/CdS quantum dots and achieved a rather high fill factor of 0.7. However, they also claimed that higher quantum yields are necessary for the quantum dot concentrators to improve the performance. Bose et al.[120] reported that

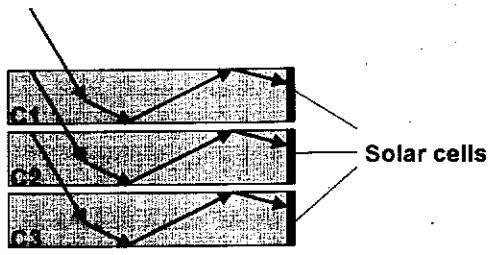

Fig. 9. Schematic of a stack of three luminescent solar concentrators.

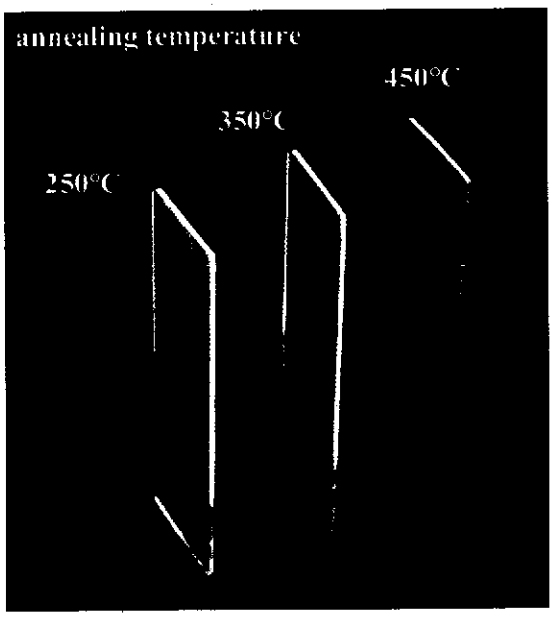

Fig. 10. Photograph of the CdS NCs dispersed in SiO_2 films deposited on glass substrates. Reprinted with permission from [117], A. Schuler et al., *Solar Energ.* 81, 1159 (2007). © 2007, Elsevier.

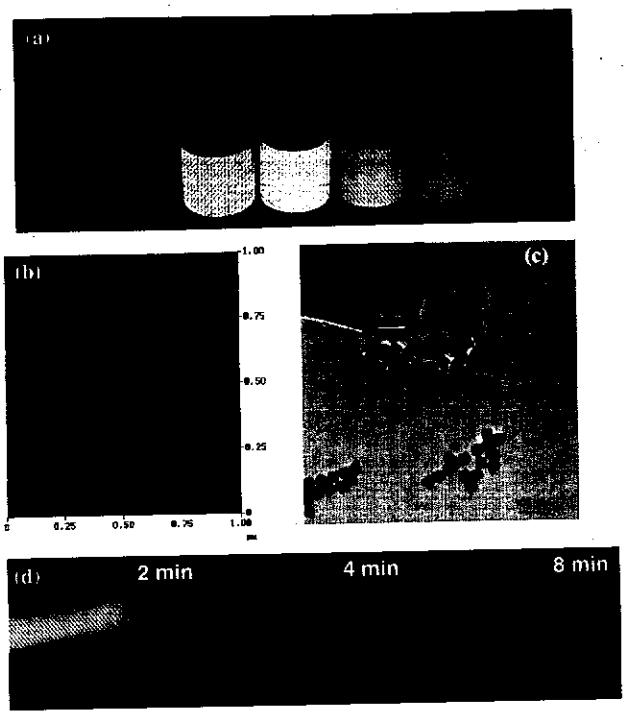

Fig. 11. (a) A photograph of luminescent NCs with high quantum efficiency of 80%, (b) atomic force microscope image of CdTe quantum dots and (c) transmission electron microscope image of PbS nanoparticles. (d) Afterglow emission of CaF_2:Mn, Eu nanoparticles at 2, 4, and 8 minutes after the X-ray excitation (250 KeV for 2 min) was turned off.

LSCs containing CdSe/ZnS core/shell NCs as luminescent species also show much lower concentration ratios compared to dye-incorporated LSC. More experimental results and theoretical models of LSCs can be found in a recent review.[121]

Down-shifting emission from NCs can usually be seen under low excitation since rather high quantum efficiency can be attained in several material systems. Another issue worthy of note is that if the passive luminescence component absorbs solar energy during the daytime, and re-emits light at night, the efficiency of a solar cell will of course be improved significantly. Recently, Chen and co-workers prepared high quality NCs that emit brightly under X-ray irradation.[122] Furthermore, they conjugated the NCs with organic molecules and observed energy transfer following X-ray irradiation.[123] They also found that after the X-ray excitation (50 KeV for 2 min) was turned off, the afterglow emission lasted for a long period. A photograph of their NC samples with high quantum efficiency of 80%, a typical atomic force microscopy image, and a transmission electron microcscopy image are shown in Figures 11(a), (b), and (c), respectively. Figure 11(d) shows the images of afterglow emission of the NCs at 2, 4, and 8 min. More interestingly, the luminescence of these nanoparticles can be activated by solar light and can last up to 8 h and, thus, can make solar cells work in the night time.[124]

4. SUMMARY

We presented the concepts of photon up-conversion, down-conversion, and down-shifting for application in solar cells. The photon converters are expected to enhance photovoltaic performance by modifying the wavelength of incoming solar light before it enters phtovoltaic devices. We focused on luminescent nanocrystals among a large range of photon-converting materials since the emission wavelength of nanocrystals can be easily adjusted by size and shape. Moreover, nanocrystals can be produced as aqueous colloids or non-polar organic dispersions according to the requirements of their applications. Up-converting nanocrystals including rare earth-doped systems and semiconductor nanocrystals are well suited for application to solar cells if the up-conversion emission can be activated under sunlight, which has been achieved very recently. Down-converting systems investigated to date seem hardly to be used for terrestrial solar cells since the excitation wavelengths are too short in the UV or VUV region. Down-shifting layers containing luminescent nanocrystals have been applied to existing Si and organic solar cells, but no enhanced performance has been achieved, probably due to rather low photoluminescence quantum yields of the incorporated NCs. However, it is believed that enhanced cell performance will be attained with luminescent NCs with high quantum efficiency very soon.

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