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Design criteria of transition metal dopants in TiO_2/CdS photoelectrode for enhanced photovoltaic response

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ABSTRACT

We investigated transition metals (nickel (Ni), manganese (Mn) and iron (Fe)) doping in TiO_2/CdS photoelectrodes for understanding their impact on photovoltaic performance. The work function of the transition metal is considered as the parameter of choice in evaluating and comparing their photovoltaic response. We observed that the photocurrent is enhanced up to 34% with Mn doping and reduced up to 20% and 87% with Ni and Fe doping, respectively. Further, the electron lifetime measurements revealed that average electron lifetime for Mn doped system is similar to that of the pure TiO_2/CdS system and is reduced significantly for Fe doped system, causing poor photovoltaic response for Fe doped TiO_2/CdS photoelectrode based devices.

1. Introduction

Solar photovoltaic systems showed potential in solving global energy demand, providing an attractive option for large-scale power production and distributed energy applications. For example, silicon photovoltaic systems are used widely in generating several gigawatt (GW) electrical energy across the globe in conjunction with small-scale distributed applications [1]. However, there are continuous efforts to reduce the cost of photovoltaic systems to providing energy at lower cost. This compels for alternative photovoltaic technologies such as dye and quantum dot sensitized solar cells. In the recent past, nanostructured sensitized solar cell are investigated intensively after Graetzel's landmark work on dye-sensitized solar cell [2]. Quantum dot sensitized solar cell (QDSSCs) is another similar class of such sensitized solar cell that use inorganic quantum dots as absorber instead of organic dyes, used in dye-sensitized solar cells (DSSCs) [3]. Quantum dots are small size systems with dimensions of the order of excitonic Bohr radius, whose physical properties can be tailored by varying their size. Quantum dots based sensitized solar cell provide a platform to explore the possibilities such as band gap tunability [4] to realize the wide spectral absorption, large absorption coefficient [5] and multiple exciton generation possibilities towards realizing more than 100% internal quantum efficiency [6]. Quantum dots are not only limited to photovoltaic applications but also proven their potential for numerous applications including display [7], sensors [8], field effect transistors [8] and source of entangled photons useful in quantum communication and teleportation [9]. Quantum dots are used in several configurations for the photovoltaic applications like (i) Schottky quantum dot solar cell, (ii) heterojunction colloidal quantum dot solar cell and (iii) bulk quantum dot sensitized solar cell [10,11]. These configurations are schematically presented in Fig. 1. Schottky quantum dot solar cell works at the cost of band bending at metal and semiconductor junction. This band bending creates built-in field/potential for photo-generated charge extraction and carriers are collected at selective contacts. In the heterojunction colloidal quantum dot solar cell, QD layer is deposited between electron transport material (ETM) and hole transport material (HTM), where electrons are accepted by ETM and holes by HTM. In bulk heterojunction solar cells, QDs absorbers are intermixed to electron transport material like sensitized solar cells, where the interface between QDs absorber and electron transport material is distributed and carriers are injected to electron transport material.

Thus, a quantum dot sensitized solar cell normally comprises of a nanostructured wide band gap semiconductor porous network that works as electron transport media (ETM). Quantum dots are used as absorber material and electrolyte as a hole transport media (HTM). The photo-generated electrons and holes are collected at selective contacts [3].

There are efforts improving the performance of quantum dot sensitized solar cell [12]. These efforts include the manipulation of quantum dots e.g. (i) core-shell design of QDs, (ii) alloying of quantum dots, (iii) surface passivation of QDs to reduce recombination, and (iv) ligand exchange for better conduction and sensitization. These schemes are shown schematically in Fig. 2. Among these, core-shell structures, especially exciplex quantum dots, showed relatively better performance

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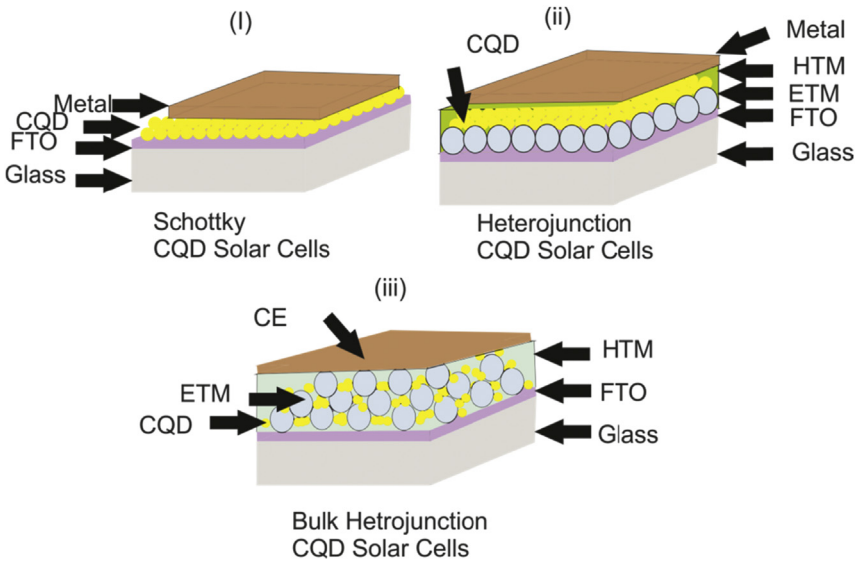

Fig. 1. The schematic representation of different configurations for QDs based solar cells: (i) Schottky colloidal quantum dot (CQD) solar cell, (ii) Heterojunction CQD solar cell, and (iii) Bulk heterojunction CQD solar cell. FTO = Fluorine doped tin oxide, CQD = colloidal quantum dot, ETM = electron transfer medium, HTM = hole transfer medium. (Color online only). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

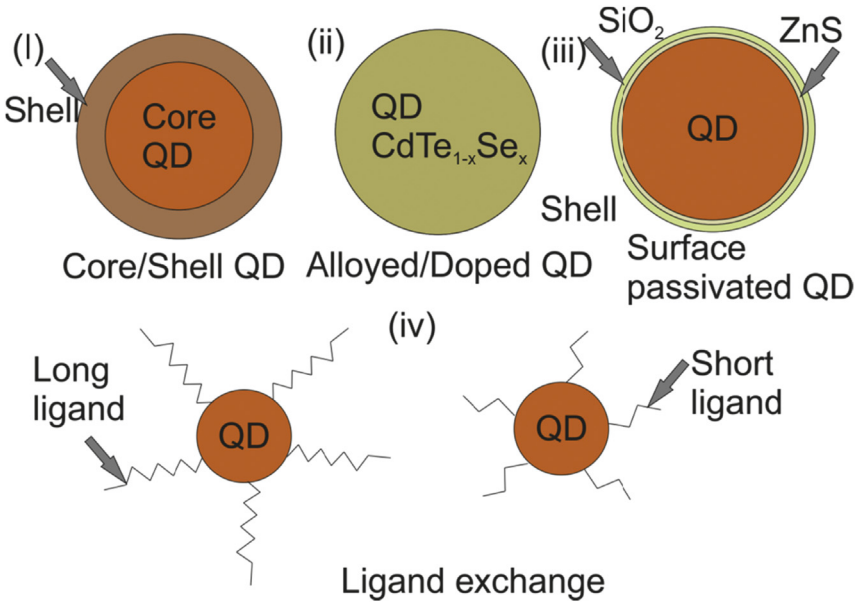

Fig. 2. The schematic representation of adopted strategies for improvement of QDSSCs performance with (i) core-shell QDs, (ii) alloy/doped QDs, (iii) surface passivated QDs and (iv) ligand-exchanged QDs. (Color online only). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

in quantum dot sensitized solar cell [13].

The transition metal, especially manganese (Mn) doped QD systems, showed very good improvement in photovoltaic efficiency [14]. The transition metal doped QD studies are summarized in Table 1, showing significant enhancement in their photovoltaic response. Kamat et al. attributed the reported improvement in photocurrent to the introduction of Mn intraband electronic transition ($^4T_1$-$^6A_1$), having a longer lifetime in between conduction and valance levels of cadmium sulfide (CdS) quantum dot band transitions as represented schematically in Fig. 3 [14]. Jianheng Luo et al. used Mn-CdS with copper indium sulfide ($CuInS_2$) and reported the improved photocurrent [16]. G. Halder et al. used pre-synthesized Mn-doped CdS QDs and identified Mn emission using temperature-dependent photoluminescence (PL) and confirmed Mn substitutional doping in CdS using X-ray photoelectron spectroscopy (XPS) studies [19]. Further, a possibility of exchange coupled Mn cluster is also suggested for higher Mn doping concentrations in

Table 1
The summarized different transition metal doped QDs based solar cells with respective short-circuit current density (J_{sc}), open circuit voltage (V_{oc}) and efficiency with relative improvement without transition metal doped QDs solar cells.

QDs system	J_{sc} (mA/cm^2)	V_{oc} (Volt)	Efficiency (%)	Relative enhancement in short-circuit current density (J_{sc})	Reference
Mn-d-CdS/CdSe	20.7	0.558	5.42	20%	[14]
Cu-d-PbS/CdS	21	0.34	2.01	57%	[15]
$CuInS_2$/Mn-d-CdS	19.29	0.58	5.38	10%	[16]
Mn-d-CdSe	19.15	0.58	6.33	30%	[17]
Co-d-CdS/CdSe	16.62	0.45	3.16	26%	[18]
Mn-d-CdS	8.39	0.5	2.08	60%	[19]
CdS/CdSe/Mn-d-ZnSe	17.59	0.584	5.67	39%	[20]