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Review

Quantum dot based molecular solar cells

Josep Albero [a], John N. Clifford [a], Emilio Palomares [a,b,*]

[a] Institute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans, 16, Tarragona E-43007, Spain
[b] ICREA, Passeig Lluis Companys, 23, Barcelona E-08010, Spain

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ABSTRACT

In this article, the various methods used to prepare semiconductor nanocrystals with quantum confined properties including colloidal quantum dot synthesis, successive ionic-layer adsorption and reaction (SILAR), chemical bath deposition (CBD) and electrophoretic deposition (EPD) are reviewed. Device working principles and the state-of-the-art of the main solar cell architectures employing semiconductor nanocrystals are discussed. Finally, we present several of our own studies from the last number of years that concern investigations of charge recombination reactions in solar cells employing semiconductor nanocrystals.

1. Properties of semiconductor nanocrystals

The use of semiconductor nanocrystals with quantum properties in photovoltaic applications has attracted great interest in the last 25 years. Such nanocrystal-based photovoltaic devices have been included in the so-called "third-generation" or "next-generation" of photovoltaics. The recent advances in synthetic methods, and the improved knowledge of quantum dot (QD) photophysics has opened up new possibilities for these inexpensive materials to be incorporated into device structures with potential efficiencies higher than other third-generation photovoltaic devices (dye sensitised solar cells or organics solar cells).

Abbreviations: QD, quantum dot; SILAR, successive ionic-layer adsorption and reaction; CBD, chemical bath deposition; EPD, electrophoretic deposition; ITO, indium doped tin oxide; FTO, fluorine doped tin oxide; TCO, transparent conducting oxide; EQE, external quantum efficiency; QDSSC, quantum dot sensitised solar cell; CB, conduction band; MEH-PPV, poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene]; P3HT, poly(3-hexylthiophene); MDMO-PPV, poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene-vinylene]; PCPDTBT, poly[2,6-(4,4-*bis*-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]; L-TAS, laser-transient absorption spectroscopy; TPV, transient photovoltage; CE, charge extraction.

* Corresponding author. Tel.: +34 977920241.
E-mail address: epalomares@iciq.es (E. Palomares).

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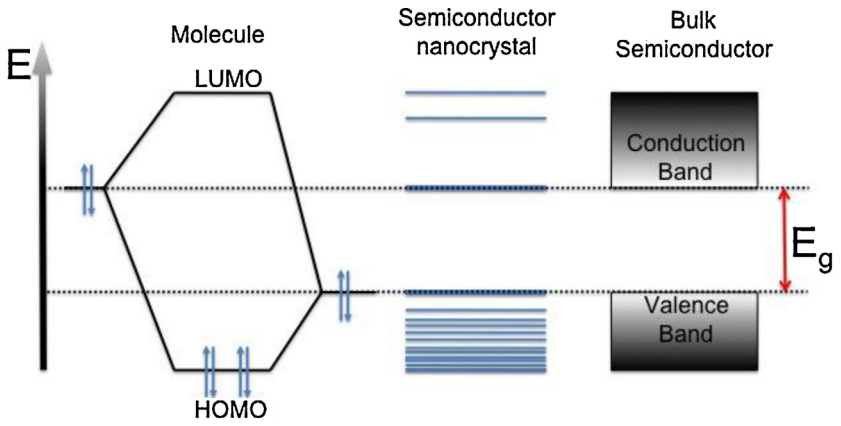

Fig. 1. Scheme showing the electronic energy states for discrete molecules, nanocrystals and bulk semiconductor materials.

Nevertheless, the still incomplete knowledge of the free-carriers (electrons and holes) recombination processes that take place between nanocrystals and other materials present in the device has limited the efficiency of these devices up until now.

QDs are defined as a class of quasi-zero-dimensional nanoparticles in which carrier motion is restricted in all three spatial dimensions. Bulk crystalline structure is preserved in the semiconductor nanocrystals, however, due to the three-dimensional quantum confinement of this material, quantum dots have atomic-like discrete energy spectra that are strongly size dependent [1].

In QDs, it is established that the frontiers between molecular and bulk are not well defined and are material dependent. A representative scheme of the different electronic energy states of a nanocrystal in the transition from discrete molecules to bulk material is shown in Fig. 1. The size regime of the semiconductor nanocrystals takes place in a range from Angstroms to a few tens of nanometers. The smaller size of the QD is determined by the stability of the crystalline structure while the bigger nanocrystals start collapsing when the charges are mobile inside the structure [2,3].

From classical semiconductor theory, the length of electronic excitations in bulk semiconductors is given by the Bohr exciton radius (r_{Bohr}), which is determined by the strength of the electron–hole (e–h) Coulomb interaction, which is also called as exciton. However, in quantum dots with size ranges comparable to or smaller than r_{Bohr}, the dimensions of the nanoparticles themselves define the spatial extent of the e–h pair state (but not the strength of e–h Coulomb coupling), and hence the size of the spatial confinement of electronic wave-functions This is also known as "quantum confinement". As the quantum dot size is reduced, the electronic excitations shift to higher energy, and the oscillator strength is concentrated in just a few transitions [4,5].

Scientists soon realised that by using this effect, it was possible to fine tuning the quantum dot energy gap (E_g), and so the optical properties, by simply varying the nanocrystal dimensions [6]. The change in optical properties as a function of size is one of the most extraordinary properties of semiconductor nanocrystals [7]. For example, the band gap in CdSe QDs may be varied from deep red (700 nm) to green (500 nm) by reducing the nanoparticle diameter from 80 to 20 Å. An example of this effect is presented in Fig. 2. One of the most critical steps on the size control is the initial nucleation step and the reaction time for the nucleation. Usually, excessive nucleation times will lead to an undesired broad range of quantum dot sizes. A quick method to evaluate the quality of the quantum dots synthesis is the fluorescence emission spectrum. For a narrow size distribution of quantum dots a sharp and intense emission band should be expected with the amplitude shorter than 30 nm measured at HWHM (Half Width at Half Maximum). Moreover, a clear correlation between the electrochemical properties (electrochemical gap) of the quantum dot and the nanocrystal size has also been observed. The maximum electrochemical potentials, corresponding to the quantum dot oxidation (removing an electron from the Valence band/HOMO) and the introduction of an electron into the nanocrystal Conduction band/LUMO, quantum dot reduction, varies with the quantum dot size in good agreement with the optical changes mentioned above [8–11]. Thus, a straightforward technique as cyclic voltammetry also provides fair experimental details of the electrochemical gap and its relation with the quantum dot size.

2. Synthesis of nanocrystals with different shapes

In semiconductor nanocrystals different crystalline facets can be identified. Due to the small size of these facets a change of only a few atoms can change its morphology completely. The shape of a crystal depends on the relative rates at which the individual facets grow. The faster a crystal grows on one facet the more likely this facet is to disappear [12].

Controlling the morphological evolution of nanocrystals has been a challenge even for the most conventional theoretical approaches [13]. Classic theories about crystal formation argue that the structure is determined by the specific shell energy of each wall of the crystal. Moreover, the surface energy of QDs depends strongly

Fig. 2. Digital picture of CdSe colloidal QDs of different sizes prepared at ICIQ illuminated with UV light.