

# THREE MISTAKES WE HAVE MADE DURING FABRICATION OF QUANTUM DOTS SOLAR CELL; HOW CAN YOU LEARN FROM THEM

S. K. MUZAKIR<sup>1\*</sup> AND R. UMAR<sup>2</sup>

<sup>1</sup>*Material Technology Program, Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 43600 Gambang, Kuantan, Malaysia*

<sup>2</sup>*East Coast Environmental Research Institute, Universiti Sultan Zainal Abidin, Gong Badak Campus, Gong Badak, Kuala Nerus, 21300 Terengganu, Malaysia*

\*Corresponding Author: saifful@ump.edu.my

## ABSTRACT

Solar cells have been in focus for decades due to their capability to convert solar energy into electrical energy. Quantum dots sensitized solar cell (QDSC) gained much consideration due to their relatively simpler device structure and similarity to dye sensitized solar cell (DSSC). QDs are capable of delivering multiple electron per absorbed photon of sufficient energy, a phenomenon known as multi-exciton generation (MEG). The MEG effect makes QDSCs capable of achieving photovoltaics conversion efficiency (PCE) as high as 60 %. Regardless of the outstanding feature of QDs, QDSCs deliver much inferior practical PCE (~8.6 %) compared to DSSCs (~13 %). Density functional theory (DFT) calculations were engaged to shed some light on the problem in our previous work. Realistic QDs models were empirically developed using DFT and experimental results. Three parameters were concluded to have distinct effects on the photovoltaic (PV) properties of QDSCs. They are (i) the best size of QDs, (ii) ligand usage, and (iii) QDs size distribution; which commonly neglected by researchers. In this work, quantum dots – metal oxide semiconductor (MOS) conjugates were chemically developed; spectroscopically demonstrate various electron injection efficiency from QDs to MOS.

Keywords: quantum dots, density functional theory

## 1. INTRODUCTION

In bare QDs semiconductor, electron excitation from the highest occupied molecular orbital of QD ( $\text{HOMO}_{\text{QD}}$ ) to the lowest unoccupied molecular orbital ( $\text{LUMO}_{\text{QD}}$ ) happens upon absorption of photon with sufficient energy ( $E_{\text{photon}} > E_{\text{QD-bandgap}}$ ). The high energy excited state electron later dissipates its energy via radiative emission and recombines with hole in  $\text{HOMO}_{\text{QD}}$ ; detectable by PL spectroscopy. The photoexcited electron could be harvested before the recombination process by conjugation of the QDs with wide bandgap metal oxide semiconductors (MOS). The excited state electrons preferably injected to the MOS layer with energy level  $\text{LUMO}_{\text{MOS}} < \text{LUMO}_{\text{QD}}$ . The characteristics of electron injection in CdSe QDs conjugated  $\text{TiO}_2$  was studied using UV-Vis absorption and photoluminescence (PL) spectroscopies. A quenched PL intensity of QDs– $\text{TiO}_2$  conjugate as compared to that of bare QDs implies successful electron injection from QDs to  $\text{TiO}_2$  [1].

## 2. EXPERIMENTAL

Five types of conjugation method were utilized viz., (i) ligand assisted (LA), (ii) direct attachment (DA), (iii) successive ionic liquid adsorption and reaction (SILAR), (iv) room temperature organo-metallic heterogeneous nucleation and (v) low temperature chemical bath deposition (CBD). The PL intensity of the conjugates were normalized to the total amount of adsorbed or grown QDs by using the corresponding values of the first excitonic peak of absorption spectra of the QDs aliquots; which were used for QDs adsorption and nucleation process.

### 3. RESULTS AND DISCUSSION

#### 3.1 LA and DA procedures

Pre-synthesized CdSe QDs ( $\varnothing = 7.76$  nm) were adsorbed onto TiO<sub>2</sub> (thickness  $\sim 12$   $\mu\text{m}$ ) using DA and LA procedure. For DA procedure, TiO<sub>2</sub>-FTO glass was immersed in a solution of pre-synthesized QDs (in acetonitrile) for 24 hours. Whereas for LA, the surface of TiO<sub>2</sub>-FTO glass was treated with HCl and functionalized with ligand before the immersion process [2]. The absorbance of QDs-TiO<sub>2</sub> conjugates was relatively lower than that of the bare QDs solution; possibly due to low adsorption of CdSe QDs onto TiO<sub>2</sub> (Fig. 1). The maximum adsorption of QDs was achieved by mercaptopropionic acid (MPA) ligand due to its short chain length ( $\sim 8.71$  Å) that adsorbed QDs cluster stronger ( $E_{ads} = \sim 5.69$  eV) than mercaptosuccinic acid (MSA) ligand with longer chain length ( $\sim 8.73$  Å) with adsorption energy,  $E_{ads} \sim 5.13$  eV. The adsorption energies were calculated and presented elsewhere [3]. The DA procedure recorded the minimum absorbance; which indicates the least adsorbed QDs onto TiO<sub>2</sub> layer [2].

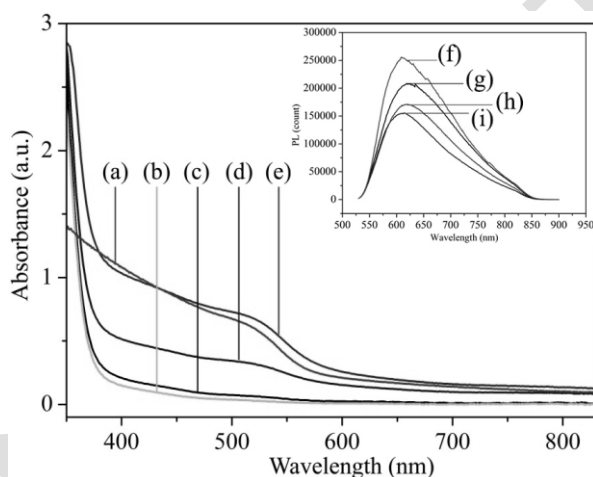


Fig. 1. Absorption spectra of (a) as synthesized CdSe QDs, (b) bare TiO<sub>2</sub> film, (c) CdSe-TiO<sub>2</sub> (DA), (d) CdSe-MSA-MOS and (e) CdSe-MPA-MOS. Insets show PL of (f) as prepared CdSe QDs solution, (g) CdSe-MPA-MOS, (h) CdSe-MSA-MOS and (i) CdSe-MOS conjugates

Fig. 1 (inset) shows PL spectra comparison of bare CdSe QDs solution with that of CdSe-TiO<sub>2</sub> (DA), CdSe-MSA-TiO<sub>2</sub> and CdSe-MPA-TiO<sub>2</sub> conjugates. The PL intensity was quenched in the conjugate structures; indicates occurrence of electron injection from CdSe QDs to the TiO<sub>2</sub>. However, the quenching percentage was low, i.e., (i) 18.83 % in MPA assisted, (ii) 33.24 % in MSA assisted and (iii) 39.23 % in DA conjugates. This observation supports the DFT calculations in our previous work; that show energy level misalignment of MSA and MPA ligands with that of CdSe ( $\text{LUMO}_{\text{ligand}} > \text{LUMO}_{\text{CdSe}}$ ); that hinders efficient electron injections [3]. Slight PL quenching percentage improvement was observed in DA-based conjugate even with the least amount of adsorbed QD.

#### 3.2 SILAR procedure

Small CdSe clusters were grown onto anatase TiO<sub>2</sub> nanowires (TNWs) by SILAR procedure, and their absorption and PL spectra were recorded. Fig. 2.b shows the TiO<sub>2</sub>/CdSe

core/shell structures, which shows deposition of CdSe clusters onto TiO<sub>2</sub>. Fig. 3 shows the XRD pattern of bare TiO<sub>2</sub> matched very well with the standard anatase TiO<sub>2</sub> peaks (JCPDS 84-1286). Additional broad peaks were observed coincide with the sharp TiO<sub>2</sub> peaks in the XRD pattern of the conjugate; possibly originated from the grown CdSe QDs on the TiO<sub>2</sub> nanowires. Fig. 4 shows the absorption spectra of the bare CdSe and the shell structures are similar. From the absorption spectra, the estimated size of the cluster is ~1.96 nm which could be assigned to (CdSe)<sub>13</sub>.

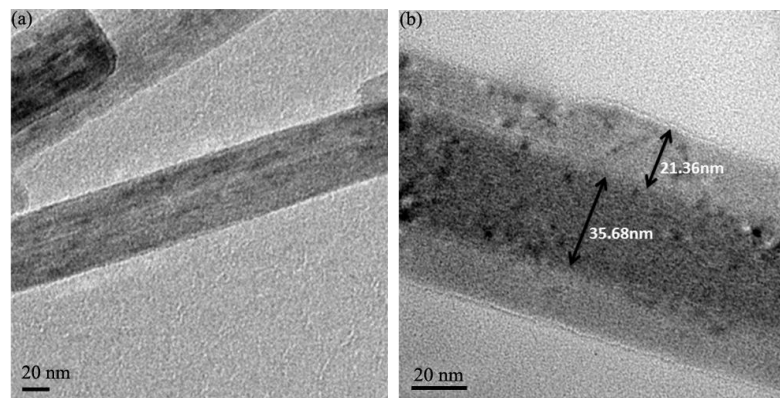


Fig. 2. (a) Bare TiO<sub>2</sub> nanowires before CdSe QDs attachment and (b) successful CdSe QDs attachment onto TiO<sub>2</sub> in a form of core-shell nanowire by the SILAR technique as observed using transmission electron microscopy

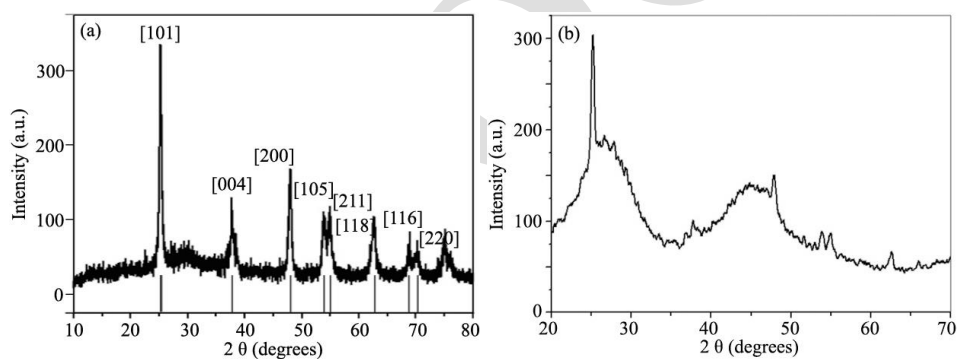


Fig. 3. XRD pattern of (a) bare anatase TiO<sub>2</sub> nanowire film on FTO, and (b) CdSe QDs-TiO<sub>2</sub> nanowire on FTO

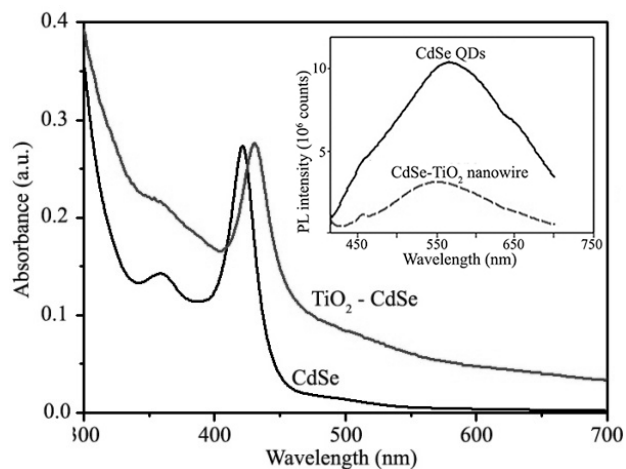


Fig. 4. Similar absorption curve of bare CdSe and CdSe-TiO<sub>2</sub> showed a successful sensitization. Inset shows quenched PL intensity in the core-shell nanowire curve (dashed curve); a successful electron injection from CdSe to TiO<sub>2</sub>

Fig. 4 (insets) depicts the PL spectra of bare CdSe QDs (solid curve) with a broad emission spectrum which imply the existence of inter-band gap-lying energy states [4]. The PL was quenched in the TiO<sub>2</sub>-CdSe core/shell, hence implying efficient electron injection into the TiO<sub>2</sub>. The percentage of PL quenching increased significantly (72.73 %) in comparison with that of the DA (39.23 %); most probably due to (i) easiness of excited state electron at surface atoms in (CdSe)<sub>13</sub> cluster to be injected to TiO<sub>2</sub> and (ii) strong cohesion between CdSe QDs and TiO<sub>2</sub>.

### 3.3 Organometallic procedure

Conjugation of CdSe QDs on TiO<sub>2</sub> nanorods was carried out using organometallic heterogeneous nucleation procedure at room temperature (~23 °C). TiO<sub>2</sub> nanorods (TNRs) were grown on conducting glass substrate using hydrothermal method. The TiO<sub>2</sub> coated FTO glasses were immersed in trioctylphosphine-Se (TOP-Se) and TOP-Cd bath for 4, 24 and 168 hours in Argon environment. The QDs covered area was examined using XRD; matched the rutile TiO<sub>2</sub> standard peaks (JCPDS 88-1175) with additional of four sharp peaks at 33.98, 38.02, 51.82 and 61.9 ° as indicated in Fig. 5 (inset). Diffraction peak of CdSe was undetected due to lower diffraction intensity than that of TNRs; originated from small size (~1.90 nm) and low amount of grown CdSe on the TNRs. The conjugation also undetectable by FESEM as shown in Fig. 5 due to the same reason.

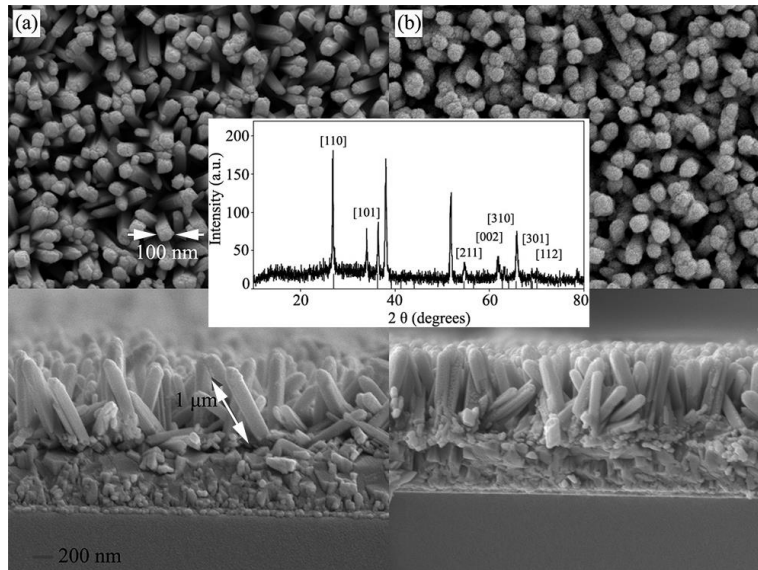


Fig. 5. FESEM micrographs shows (a) bare TNRs grown on FTO and (b) CdSe QDs-TNRs at 30 000 magnifications from top view (top) and cross-section view (bottom). Inset shows XRD pattern of CdSe QDs-TNRs on FTO

The CdSe QDs of size  $\sim 1.90$  nm could be assigned to  $(\text{CdSe})_{13}$  cluster; determined using similar procedure as our previous work [5]. The QD conjugation was confirmed by the increment of absorbance of TNRs – FTO film immersed in the CdSe QDs aliquots. The size distribution of the QDs was determined from full width half maximum (FWHM) of the first excitonic peak of UV-Vis absorption spectra; correspond to size distribution of  $\sim 4.5$  %. The PL intensity quenching was recorded (61.73 %) lower than that of the fresh conjugate prepared within 4 hrs immersion time (80.03 %) as showed in Fig. 6 (insets).

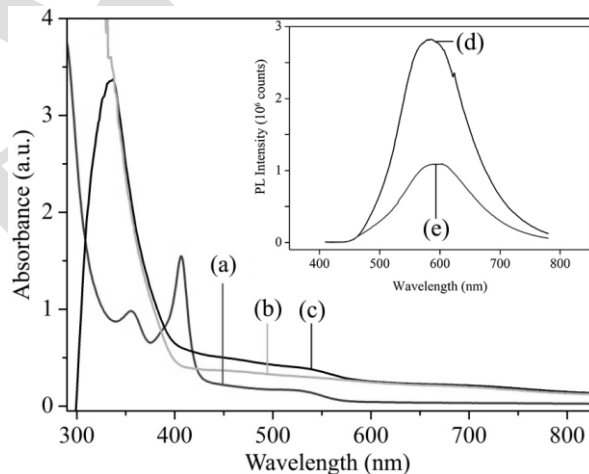


Fig. 6. Absorption spectra of (a) CdSe QDs aliquots at 24 hours of reaction time, (b) bare TNRs – FTO and (c) TNRs – FTO immersed in TOP CdSe QDs aliquots. Insets are PL of (d) CdSe QDs aliquots, and (e) CdSe QDs-TNRs

### 3.4 CBD procedure

CdSe QDs of size  $\sim 3.02$  nm were deposited onto TNRs using low temperature chemical bath deposition [6]. Even and wide QD adsorption area was developed by immersion of TNRs in 0.0053 M  $\text{Cd}(\text{NO}_3)_2$  and  $\sim 0.25$  M sodium selenosulfite ( $\text{Na}_2\text{SeSO}_3$ ) precursors at  $\sim 2$  °C for 24 hours (Fig. 7). QDs aggregation was controlled by slow reaction rate; achieved by slow generation of Se anions of  $\text{Na}_2\text{SeSO}_3$  [7]. The size of deposited QDs were estimated ca. 3.02 from the first excitonic peak position at  $\sim 549$  nm [8]. The absorbance of the conjugate was found higher than that of the organometallic-fabricated conjugates; indicate that more amount of QDs were grown onto the TNRs. However, in spite of the large number of QDs adsorption, the PL intensity was quenched lesser (53.34 %) than that of the organometallic-fabricated conjugates depicted in Fig. 7 (inset).

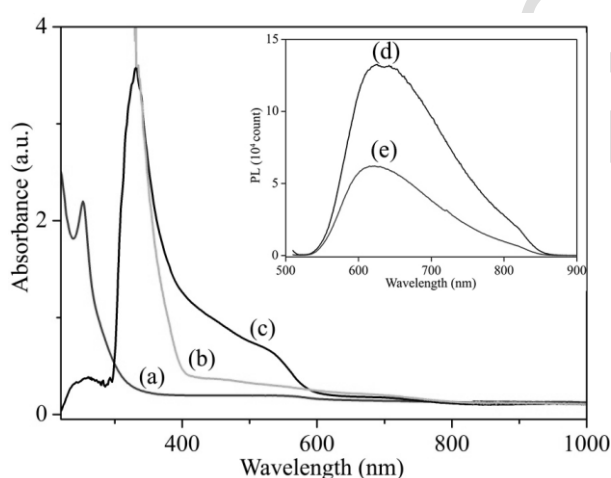


Fig. 7. Absorption spectra of (a) CdSe QDs aliquots at 24 hours of reaction time, (b) bare TNRs – FTO and (c) TNRs – FTO immersed in CBD aliquots. Insets are PL of (d) CdSe QDs aliquots, and (e) CdSe QDs-TNRs

## 4. CONCLUSIONS

Efficiency of electron injection from QDs to MOS is correlated with the percentage of PL intensity quenching; which depends on (i) size of QDs, (ii) QDs attachment method, and (iii) QDs size distribution. Organo-metallic and SILAR procedure showed the highest PL quenching of  $\sim 73$  % which both presented the narrowest size distributions of 4.5 %. Furthermore, both procedures yielded similar size of QDs which correspond to  $(\text{CdSe})_{13}$  which theoretically hypothesized could inject electron efficiently to the MOS in our previous work. The DA and LA adsorption of pre-synthesized QDs on MOS procedure yielded low percentage of quenching  $\sim 39$  and 19 % respectively; presence of ligand further suppressed the electron injection efficiency.

## ACKNOWLEDGEMENTS

This work is funded by the Research & Innovation Department of Universiti Malaysia Pahang (RDU150321 grant).

## REFERENCES

1. I. Robel, V. Subramanian, M. Kuno and P. V. Kamat, *Journal of the American Chemical Society* 128 (7), (2006) 2385-2393.
2. D. R. Pernik, K. Tvrdy, J. G. Radich and P. V. Kamat, *The Journal of Physical Chemistry C* 115 (27), (2011) 13511-13519.
3. S. K. Muzakir, N. Alias, M. M. Yusoff and R. Jose, *Physical Chemistry Chemical Physics* 15 (38), (2013) 16275-16285.
4. C. F. Landes, M. Braun and M. A. El-Sayed, *Journal of Physical Chemistry B* 105, (2001) 10554-10558.
5. S. K. Muzakir, *Universiti Malaysia Pahang*, 2014.
6. C. Chen, M. Ye, M. Lv, C. Gong, W. Guo and C. Lin, *Electrochimica Acta* 121, (2014) 175-182.
7. H. Choi, J. G. Radich and P. V. Kamat, *The Journal of Physical Chemistry C* 118 (1), (2014) 206-213.
8. W. W. Yu, L. Qu, W. Guo and X. Peng, *Chemistry of Materials* 15 (14), (2003) 2854-2860.