

PHOTOCURRENT SWITCHING ON ELECTROPHORETIC CdSe QD ELECTRODES WITH DIFFERENT LIGANDS

YAUHEN ANISKEVICH

*Faculty of Chemistry and Research Institute for Physical Chemical Problems, Belarusian State University, Minsk,
220030. Belarus
aniskevich.y.m@gmail.com*

MIKALAI MALASHCHONAK

*Faculty of Chemistry, Belarusian State University, Minsk, 220030. Belarus
e-mail malasche@bsu.by*

ARTSIOM ANTANOVICH

*Research Institute for Physical Chemical Problems, Belarusian State University, Minsk, 220006. Belarus
e-mail Artsiom.antanovich@gmail.com*

ANATOL PRUDNIKAU

*Physical Chemistry, TU Dresden, Bergstrasse 66b, Dresden 01062, Germany
e-mail anatol.prudnikau@chemie.tu-dresden.de*

GENADY RAGOISHA

*Research Institute for Physical Chemical Problems, Belarusian State University, Minsk, 220006. Belarus
e-mail ragoisha@yahoo.com*

EUGENE STRELTSOV

*Faculty of Chemistry, Belarusian State University, Minsk, 220030. Belarus,
e-mail streltea@bsu.by*

Received Day Month Year

Revised Day Month Year

Photoelectrochemical behavior of oleate- and sulfide-capped CdSe QD films obtained via electrophoretic deposition has been investigated in Na₂SO₃ aqueous electrolyte. The oleate substitution for sulfide led to considerable increase in photocurrent efficiency. Films of the both types show photocurrent switching under 465 nm light irradiation. The photocurrent direction switching potential strongly depends on particle size demonstrating negative shift of the potential with size: from 0.0 V for 2.4 nm to -0.2 V for 6.3 nm.

Keywords: CdSe, quantum dots, photoelectrochemistry, photocurrent switching, ligand exchange

1. Introduction

Variability of quantum dots (QDs) properties controlled by particle size, dimension and surface chemistry made them attractive for use as materials for solar cells, photodetectors and photocatalysts. A deep insight into processes occurring at an interface between QD ensembles and electrolyte under illumination is required for further optimization of such devices.

QD photoelectrochemistry differs from photoelectrochemistry of bulk semiconductors by several distinct features. QD ensembles typically miss surface space-charge layer which causes charge separation in bulk semiconductor. The charge separation in nanostructured material is strongly controlled by kinetics of the surface reactions dependent on electron or hole acceptors. Further, the charge separation efficiency depends on interparticle contact. The latter is strongly influenced by surface ligand (e.g. bulky organic vs. small inorganic) and film preparation (chemical bath deposition, electrophoretic deposition etc).

Here we performed a comparative study of photoelectrochemical behavior of oleate- and sulfide-capped CdSe QD films in Na_2SO_3 electrolyte solution. Films of the both types present photocurrent-switching with pronounced size effect, whereas sulfide-treated films reveal considerably higher cathodic and anodic photocurrent.

2. Experimental

CdSe QD films were prepared via electrophoretic deposition (EPD) from oleate-capped CdSe QD colloidal solution in nitrobenzene using transparent conducting FTO-glass substrates. Oleate substitution for sulfide was performed by film immersion in 0.2 mg/ml Na_2S methanol solution for 1 hour [1].

Photoelectrochemical measurements were performed with Elins P-8 (Russia) potentiostat. A three-electrode cell made of a transparent cuvette with Pt-counter and $\text{Ag}|\text{AgCl}|\text{KCl}(\text{sat.})$ reference electrode was used. The CdSe QD films on FTO were investigated as working electrode which was illuminated from solution side. Photocurrent spectra were obtained using a high-intensity grating monochromator with a 250 W halogen lamp, and a light chopper. Incident photon-to-current conversion efficiency (IPCE) was calculated from the

photocurrent spectra and light intensity distribution at the monochromator output.

Absorbance spectra were obtained using Ocean Optics DH-2000 white light source.

3. Results and Discussion

Fig. 1 shows IPCE spectra on the CdSe electrodes in 0.1 M Na_2SO_3 . The sulfite oxidation by photoholes generated in CdSe nanoparticles is likely to give the anodic photocurrent while photoelectrons are transferred from CdSe to external circuit.

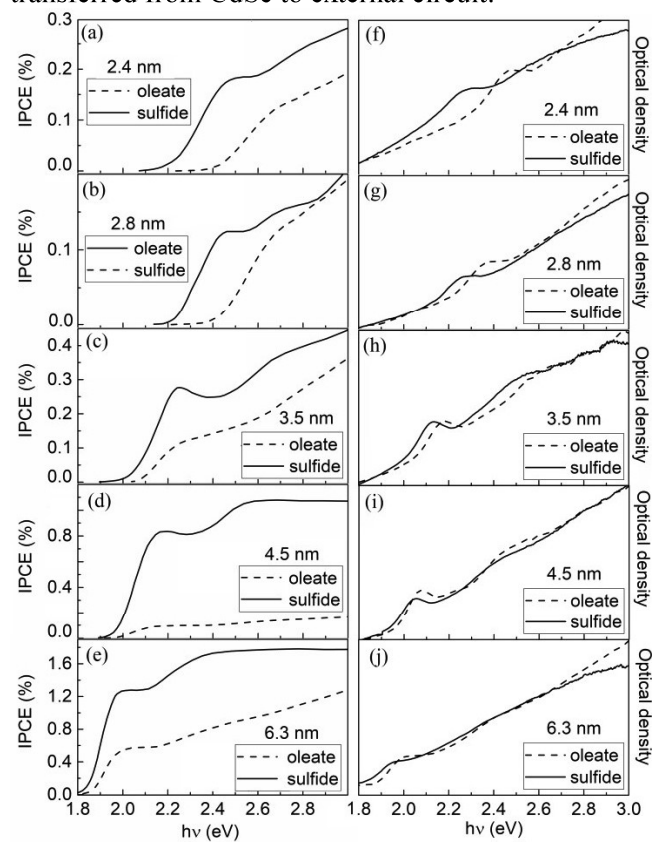


Fig. 1. Spectral distribution of IPCE at $E = 0.2$ V (a-e) and optical absorption spectra (f-j) for oleate- and sulfide-capped CdSe electrodes at different CdSe particle size

IPCE increases in the whole spectral range with CdSe particle size and with oleate substitution by sulfide. The latter effect is due to a more efficient electric contact between sulfide-capped particles and reduced recombination losses in the film. The oleate substitution results in formation of Cd-S surface layer on CdSe QDs [1], which can formally be considered as a particle size increase manifested by the red shift in photocurrent spectra (Table 1). The red shift is also observed in optical absorption spectra (Fig. 1 (f-j)).

Table 1. CdSe QD bandgap determined from photocurrent spectra $E_g(\text{ph})$ and optical spectra $E_g(\text{op})$

d , nm	oleate		sulfide	
	$E_g(\text{ph}), \text{eV}$	$E_g(\text{op}), \text{eV}$	$E_g(\text{ph}), \text{eV}$	$E_g(\text{op}), \text{eV}$
2.4	2.51	2.47	2.30	2.30
2.8	2.31	2.38	2.19	2.27
3.5	2.13	2.18	2.11	2.13
4.5	2.02	2.08	2.02	2.05
6.3	1.89	1.99	1.88	1.97

Figure 2 shows photopolarization curves for CdSe films at variable CdSe particle size.

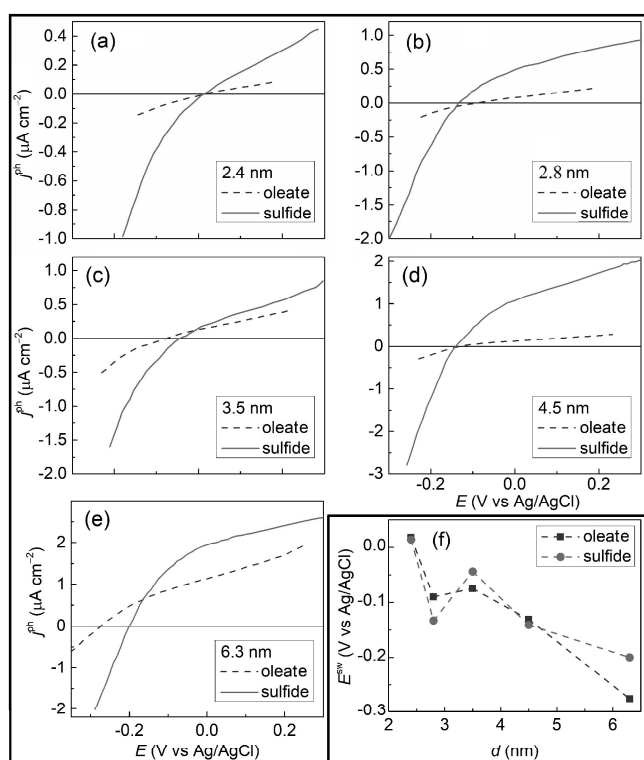


Fig. 2. Photopolarization curves (a-e) for oleate- and sulfide-capped CdSe nanoparticles of different size; (f) photocurrent switching potential (E^{sw}) dependence on particle size. Illumination conditions: monochromatic light; $\lambda = 465 \text{ nm}$; $J = 400 \mu\text{W cm}^{-2}$

The anodic photocurrent density decreases gradually with the potential decrease and the photocurrent direction switching is observed at the photocurrent switching potential E^{sw} (Fig. 2 a-e). The cathodic photocurrent may result from photoelectron transfer to adsorbed water or surface states of CdSe. E^{sw} shifts to lower potential with CdSe particle size increase from 2.4 nm to 6.3 nm (Fig.2). The capping ligand exchange has insignificant effect on E^{sw} for relatively small (2.4 – 4.5 nm) particles but the photocurrent switching potential shifts from -0.27 V to -0.20 V for the particles of 6.3 nm when oleate is replaced by sulfide.

The photocurrent is generated by different mechanisms in bulk and nanostructured CdSe electrodes. The separation of charges in bulk semiconductor is controlled by the potential gradient in the space charge region which is dependent on doping level and conductivity type (n - or p -type). On the contrary, no space charge layer is formed in semiconductor nanoparticles and charge separation is controlled by kinetics of photocharge interaction with acceptors in the electrolyte. The trapping of photoelectrons gives cathodic photocurrent and photohole trapping results in the anodic photocurrent. The observed dependence of the photocurrent switching potential on CdSe particle size can be explained by different effect of size on LUMO and HOMO energies. LUMO energy increase for small particles is stronger than the corresponding variation in HOMO energy which favors photoelectron transfer more efficiently than photohole transfer, thus resulting in the cathodic photocurrent on small particles. We observed earlier [2,3,4] similar effects on chemically deposited CdSe nanoparticles [2], nanostructured BiOI [3] and BiOBr [4] electrodes.

4. Conclusions

CdSe QD films obtained via EPD show photocurrent switching in sulfite solutions both when oleate or sulfide is used as capping ligand. The photocurrent switching potential strongly depends on particle size which is likely a result of LUMO shift. The substitution of oleate for sulfide enhances IPCE. The results can be of interest for understanding of QD/electrolyte interface properties under illumination and for design of CdSe QD solar cells.

Acknowledgments

This research was supported by BRFFI grant X17M-003 and EU Horizon 2020 MSCA RISE-2017 project 778357.

References

1. Y.M. Aniskevich *et al.*, J. Phys. Chem. C. (Just Accepted, doi: 10.1021/acs.jpcc.8b10318)
2. M.V. Malashchonak *et al.*, J. Solid State Electrochem. **3**, 905 (2017).
3. M.E. Kazyrevich *et al.*, Electrochim. Acta. **190**, 612 (2016).
4. M.E. Kazyrevich *et al.*, Electrochim. Acta. **290**, 63 (2018).