

# Adsorption and photoreactivity of CdSe nanoparticles at liquid|liquid interfaces

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## Abstract

The voltage induced assembly and photoreactivity of cadmium selenide (CdSe) nanoparticles protected by mercaptosuccinic acid are studied at the polarisable interface between water and 1,2-dichloroethane electrolyte solutions. Cyclic voltammograms and admittance measurements show an increase of the interface excess charge associated with the adsorption of CdSe nanoparticles as the Galvani potential difference is tuned to negative values with respect to the potential in the organic phase. Within the potential range where the nanoparticles are adsorbed, band-gap illumination leads to heterogeneous electron transfer from CdSe nanoparticles to electron acceptors located in the organic phase. The interfacial Galvani potential difference plays an important role in these phenomena, as it affects the interfacial density of the nanoparticles, as well as the driving force for the electron transfer. The photocurrent efficiency also strongly depends on the formal redox potential of the electron acceptor, indicating that the heterogeneous photoreaction is kinetically controlled. The interfacial electron transfer occurs via depopulation of the deep trap states in the band gap. Analysis of the photocurrent transient responses reveals that the magnitude of the instantaneous photocurrent upon illumination is determined by the kinetics of heterogeneous electron transfer, while photogenerated holes are swiftly captured by species present in the aqueous phase. The photocurrent decay upon constant illumination is associated with the diffusion of the acceptor to the interfacial region. From the phenomenological point of view, the photoelectrochemical behaviour of CdSe nanoparticles can be compared to a self-assembled ultrathin p-type semiconductor photoelectrode.

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## 1. Introduction

Photoinduced heterogeneous electron transfer reaction at the polarisable liquid|liquid interface has proved to be a valuable approach to artificial photosynthetic and photocatalytic processes at two phase boundaries [1–3]. At this molecular junction, photocurrent responses originating from the heterogeneous quenching of photoexcited water-soluble dyes by hydrophobic re-

dox species have been studied in detail [4–11]. It has been observed that the Galvani potential difference across the liquid|liquid interface can affect the surface coverage of the photoactive species as well as the dynamics of photoinduced electron transfer and back electron transfer. Water-soluble porphyrins, chlorines and phthalocyanines have been employed as photoactive dyes at the interface between water and 1,2-dichloroethane (DCE) [4,6–10,12].

Recently, it has been demonstrated that titanium dioxide (TiO<sub>2</sub>) nanoparticles can be assembled at the polarised interface between water and DCE electrolyte solutions upon applying a potential bias [13,14]. Band-gap illumination of the interface led to the interfacial

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transfer of holes or electrons to redox species located in the organic phase. The charge transfer reactions can be monitored by photocurrent measurements phenomenologically similar to those observed on solid photoelectrodes [15–17]. In this paper, we shall extend the study to semiconductor quantum dots sensitised liquid|liquid interfaces. Semiconductor quantum dots have all three dimensions in the nanometer range and possess unique electronic and optical properties that are strongly size dependent [18–20]. They are not only interesting from a theoretical viewpoint, but also a variety of applications have been considered. For example, luminescent semiconductor quantum dots are a promising alternative to organic dyes for fluorescence applications since they are more stable against photobleaching and have narrow and size-tunable multicolour emission as well as the functional advantages [21,22]. Some of the most exciting applications involve new generation of optoelectronic [23–26] and photovoltaic devices [27] and exploratory biotechnology research as ultra-sensitive biological fluorescent tags [22,28–31].

In this work, we shall describe the reversible adsorption of cadmium selenide (CdSe) quantum dots at the water|DCE interface by tuning the Galvani potential difference. In the presence of electron acceptors in the organic phase, heterogeneous photocurrent responses arising from the adsorbed CdSe nanoparticles can be recorded upon illumination of the interfacial region. Analysis of the photocurrent responses as a function of the applied potential difference and the formal redox potential of the organic phase quencher suggests that the heterogeneous electron transfer takes place from occupied trap states in the CdSe nanoparticles.

## 2. Experimental

### 2.1. Synthesis of CdSe nanoparticles

Water dispersible mercaptosuccinic acids (MSA) protected CdSe nanoparticles were prepared using a published protocol [32], in which Na<sub>2</sub>Se was used instead of NaHSe. In a typical synthesis, 513.3 mg (2.35 mmol) of CdCl<sub>2</sub> · 2H<sub>2</sub>O is dissolved in 125 mL of water, and 866.4 mg (5.77 mmol) MSA is added under stirring, followed by adjusting the pH to 11.2 by dropwise addition of 1 M solution of NaOH. After bubbling the solution with N<sub>2</sub> for 40 min, newly prepared solution of 1.1 mmol Na<sub>2</sub>Se in 22 mL water was introduced under stirring. The resulting mixture was then subjected to a reflux at 100 °C under open air condition. During the reflux, aliquots were taken out of the flask at different times to measure the absorption spectra to monitor the growth of the nanoparticles.

The transparent solution with bright-orange colour was first concentrated on a rotary evaporator, then ace-

tone was added dropwise to precipitate the nanoparticles inside the solution. The resulted mixture was stirred for 30 min, and the precipitate and supernatant were separated through centrifugation. The precipitate was washed five times with water/acetone mixture, then dried and used in photoelectrochemical measurements.

### 2.2. Spectroscopic and microscopic instrumentation

The absorption and luminescence spectra were obtained from an Ocean Optics CHEM2000-UV-Vis spectrometer and a Perkin-Elmer LS50B Luminescence Spectrometer, respectively. High resolution transmission electron microscopy (HRTEM) images were collected from a Philips CM 300 transmission electron microscope operating with an accelerating voltage of 300 kV.

### 2.3. Photoelectrochemical measurements

The electrochemical experiments were performed using a homemade four-electrode system connected to a Stanford Research System DS335 function generator. The interfacial capacitance was calculated from admittance measurements using a Stanford Research System SR830 lock-in amplifier at a frequency of 6 Hz and amplitude of 10 mV rms. A three-compartment cell featuring a cross-section of 1.53 cm<sup>2</sup> was employed in all the measurements. The reference electrodes were placed in two separate compartments featuring Luggin capillaries. The electrolyte solutions were prepared from ultrapure water from a Milli-Q system (Millipore Milli-Q.185) and 1,2-dichloroethane (DCE) (Fluka 98% for HPLC). The composition of the electrolyte solutions is indicated in Fig. 1. The organic supporting electrolyte, bis(triphenylphosphoranylidene) ammonium tetrakis-(pentafluorophenyl)borate (BTPPATPFB), was prepared as previously reported [33]. The Galvani potential difference ( $\Delta\phi^w$ ) was referred to as that of the minimum of the differential capacitance curves obtained in the absence of the nanoparticles.

All photocurrent measurements were carried out with the 454-nm line of an Omnicrome S43 tunable Ar-ion laser under transmission mode. Photocurrent transients were measured employing an optical shutter with an aperture time in the range of microsecond. The incident photon flux was quantitatively determined by measuring the incident light intensity with a photomultiplier (Model 70316, Thermo Oriel Instruments).

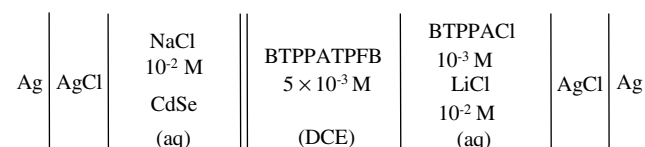


Fig. 1. The composition of the electrochemical cell.

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