Homogeneous Photosensitization of Complex TiO$_2$ Nanostructures for Efficient Solar Energy Conversion

Jingshan Luo$^{*}$, Siva Krishna Karuturi$^2$, Lijun Liu$^3$, Liap Tat Su$^2$, Alfred Iing Yoong Tok$^2$ & Hong Jin Fan$^1$

$^1$Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore, $^2$School of Materials Science and Engineering, Nanyang Technological University, 639798 Singapore.

TI$O_2$ nanostructures-based photoelectrochemical (PEC) cells are under worldwide attentions as the method to generate clean energy. For these devices, narrow-bandgap semiconductor photosensitizers such as CdS and CdSe are commonly used to couple with TiO$_2$ in order to harvest the visible sunlight and to enhance the conversion efficiency. Conventional methods for depositing the photosensitizers on TiO$_2$ such as dip coating, electrochemical deposition and chemical/vapor-deposition suffer from poor control in thickness and uniformity, and correspond to low photocurrent levels. Here we demonstrate a new method based on atomic layer deposition and ion exchange reaction (ALDIER) to achieve a highly controllable and homogeneous layering of sensitizer particles on arbitrary TiO$_2$ substrates. PEC tests made to CdSe-sensitized TiO$_2$ inverse opal photoanodes result in a drastically improved photocurrent level, up to $\sim$15.7 mA/cm$^2$ at zero bias (vs Ag/AgCl), more than double that by conventional techniques such as successive ionic layer adsorption and reaction.

Ever since the seminal paper of photoelectrolysis of water by Fujishima and Honda$^1$, TiO$_2$ has received wide attentions in photocatalysts, water splitting and solar cells due to its high photoactivity, low cost and excellent chemical stability$^{2-5}$. The limiting factor for TiO$_2$ is the large band gap ($\sim$3.2 eV), which defines its light absorption only in the UV range. During the past three decades, tremendous efforts have been put to enhance the visible light harvesting ability of TiO$_2$. Heterogeneous structures have been proposed to couple TiO$_2$ with materials exhibiting visible light harvesting ability, and the first trial was done by Serpone et al. to couple TiO$_2$ with CdS which showed a significant improvement$^6$. Later on Graetzel made a significant breakthrough in sensitizing TiO$_2$ with dye molecules, viz., the dye-sensitized TiO$_2$ photoanode$^7$. Following the invention of Graetzel cell, quantum dot sensitized solar cells (QDSSC) quickly catch up following the mature quantum dot synthesis protocol developed by Peng and Alivisatos$^8$-$^9$. The key development of QDSSC was made by Kamat in 2005, with the pre-synthesized CdSe nanocrystals linked to TiO$_2$ thin films by organic molecules$^{10}$. Since then various methods of sensitization have been developed, and they can be summarized into two main categories: assembly of pre-synthesized QDs and direct growth$^{11-12}$. Pre-synthesis provides the feasibility of facile control in the size, size distribution and morphology. However, the charge transfer would be retarded by the surface functional molecules. Also the loading of the sensitizer prepared by this method is usually low. Direct growth allows both a compact contact of the sensitizer with TiO$_2$, and the ease of increasing the loading of the sensitizer. A diverse range of methods are reported for the direct coating of the sensitizing materials, such as chemical bath deposition$^{13-14}$, successive ionic layer adsorption and reaction (SILAR)$^{15-17}$, electrochemical deposition$^{18}$, chemical vapour deposition$^{19}$ and electrophoretic deposition$^{20}$.

Despite the development of various sensitization methods, the sensitizers still suffer from poor thickness and uniformity control especially for deposition on high aspect-ratio TiO$_2$ nanostructures. As the size of QDs is much larger than dye molecules, penetration of QDs into TiO$_2$ nanoarchitectures with a depth $\geq$10 $\mu$m is more difficult than the case in dye-sensitized solar cells$^{11}$. Due to the quantum confinement effect and the limited charge diffusion length, the size of the QDs plays an important role in charge transfer process. The poor control in conventional deposition techniques usually leads to aggregation of QDs into large particles, thus causing high internal recombination loss.

Atomic layer deposition (ALD) is a thin film deposition technique that is based on self-limiting surface reactions by sequential exposure of the substrate to different gas phase precursors$^{21}$. ALD provides precise thickness control at the angstrom or monolayer level and deposition on high aspect ratio nanostructures with...
excellent step coverage. By employing ALD for QD sensitization, excellent infiltration and conformity could be achieved, and the size of QDs could be varied simply by tuning the number of ALD cycles. Recently Stacey et al showed the ALD CdS for solid state QDSSC22. However, there is a serious safety issue for such ALD CdS process, as the precursors of dimethyl cadmium (DMCd) and hydrogen sulfide (H2S) are highly toxic.

Liquid-phase reaction via ion exchange has been developed as a method to fabricate semiconductor heteronanostructures23–25. The principle of ion exchange is based on the solubility of the material which allows only a critical selection of the target materials. Very recently ion exchange reaction has also been employed to fabricate nanowire p-n junctions for photovoltaics26, as well as photosensitizer layers on ZnO nanowires for semiconductor-sensitized solar cells28,29. Due to its amphipathic property, ZnO is unstable for PEC in acidic or alkaline electrolyte solution, which is the bottleneck for practical applications. On the other hand, the amphipathicity of ZnO makes it an ideal template for nanofabrications28.

In order to have the merit of ALD without the highly toxic source for the QD sensitization, in this work, ALD ZnO thin films were deposited on various TiO2 nanostructures as the sacrificial templates to convert to short bandgap semiconductor sensitizers by ion exchange reaction (we call the whole process ALDIER). The thickness and the size of the sensitizers could be controlled by the thickness of the ZnO layer and the condition of ion exchange reaction. The reproducible photocurrent levels >15 mA/cm2 is obtained using the TiO2 inverse opals (TiIO), which is so far the highest among all nanostructure TiO2-based PEC cell for hydrogen generation.

Results

Figure 1(a) illustrates the flowchart of the ALDIER based on the example of TiIO obtained by replicating a self-assembled multilayer polystyrene spheres29,30. However, the TiO2 host structures for the 3-D homogeneous photosensitization can include a wide range of common types, for example, hydrothermal-grown nanorods, anodized nanotubes, and commercial P25 nanoparticles. In the first step, the host is coated with a layer of ZnO of tunable thicknesses using ALD. The second step is the ion exchange reaction. In this process the ALD ZnO layer serves as the sacrificial reactant which transforms first into ZnSe through anion exchange with the Se2− precursor and then to the final CdSe via cation exchange with Cd2+ source31. The ion exchange reaction is based on the solubility product constant (Ksp) of the material. As the constant of ZnO (Ksp = 6.8 × 10−27) is much larger than ZnSe (3.6 × 10−30), ZnO can be converted into ZnSe by anion exchange reaction with Se2− anions. With the same principle, ZnSe can be further exchanged into CdSe (6.31 × 10−30).

The sensitized TiIO is tested as the PEC photoanode in a three-electrode system for hydrogen generation. Figure 1(b) shows the diagram of the PEC cell where a piece of Pt foil was used as the cathode. H2 gas bubbles are generated on the cathode through the water reduction reaction 2H+ + 2e− → H2, whereas the holes are scavenged by the sulfide electrolyte. As CdSe has a wider light absorption range and better conduction band edge alignment with TiO2 than ZnSe (see Fig. 1c), the photocurrent level of TiO2/CdSe is much higher than TiO2/ZnSe, as also reported in previous work32. Thus in this experiment we focus on CdSe photosensitizer on TiIO.

The composition transformation from ZnO to CdSe is confirmed using X-ray diffractometer (see Fig. 2a). The blue solid lines are the calculated XRD peaks for Anatase TiO2 (PDF#21-1272), and the green dashed lines are the calculated XRD peaks for SnO2 (PDF#41-1445). All the diffraction peaks of TiO2 structure on FTO correlate well with the calculated positions. The diffraction peaks of ZnO (PDF#36-1451) appear only for the TiIO samples after the deposition of ZnO. After the first step anion exchange reaction, the ZnSe peaks (PDF#37-1463) can be detected while the ZnO peaks disappear, implying that the ALD ZnO layer is totally converted to ZnSe. After the complete exchange reaction, the peaks can be indexed to hexagonal CdSe (PDF#08-0459). The peak intensities of the CdSe
increase from the 60-cycle sample to 120-cycle one, in accordance with the increased loading of CdSe.

UV-visible diffuse reflection spectra are recorded to reveal the light harvesting capability of the pristine TiO\(_2\), ZnSe and CdSe sensitized TiO\(_2\) photoanodes (results shown in Fig. 2b). The pristine TiO\(_2\) can only absorb light with a wavelength below 400 nm. The absorption range broadens up to 550 nm after the exchange to ZnSe, and 700 nm after the final exchange into CdSe, consistent with their bandgaps. More diffuse reflection spectra for the samples at intermediate conversion stage are shown in Supplementary Fig. S1. The composition change after anion and cation exchange reactions and the light harvesting ability can also be revealed from the photographs of the samples in Fig. 2b inset. The samples with CdSe coating appear dark brown compared with the bright yellow coloured ZnSe and white pristine TiO\(_2\).

Morphologies of the photoanodes prior to and after the ion exchange reactions with different ALD ZnO cycles are shown by SEM images in Fig. 3. The original TiO\(_2\) surfaces are smooth. After ALDIER, the open surfaces are coated with a granular layer of CdSe. The SEM image in Fig. 3e provides an entire cross-sectional view of the structure with 60 ALD cycles (lager scale SEM images are provided in Supplementary Fig. S2). Clearly the ion exchange reactions proceed along the whole depth of 10\(\mu\)m, owing to the effectiveness of ALD in creating conformal coatings on the surfaces of high aspect-ratio nanostructures. The morphology is further characterized using transmission electron microscopy (TEM). Figure 4a provides clear evidence of the attachment of nanoparticles on the available surfaces of TiO\(_2\) pores. High-resolution TEM image in Fig. 4b shows that the particles are crystalline, and the lattice spacing can be indexed into (0-11) and (1-1-1) planes of hexagonal CdSe. Pure elements of Cd and Se are confirmed by the X-ray energy dispersion spectrum shown in Fig. 4c.

The PEC performance of the ALDIER photoanodes is investigated by conducting the current density vs potential (J-V) measurements under the dark and simulated sunlight illumination (AM 1.5) in the three-electrode cell configuration (Fig. 1b). First of all, all the electrodes are fabricated from 500 nm polystyrene spheres and have the same height of 10\(\mu\)m. For ion exchange reaction, temperature is a critical parameter that affects the size and morphology of the resulting sensitizer layer. Hence the first step is to optimize the reaction temperature for CdSe exchange reaction while keeping ALD ZnO thickness the same (~10 nm by 60 ALD cycles). As shown in Supplementary Fig. S3, the electrode obtained from the reaction at 120 \(^\circ\)C exhibits the highest photocurrent level (15.7 mA/cm\(^2\) at zero bias vs Ag/AgCl) compared to those from reactions at 90 \(^\circ\)C (4.6 mA/cm\(^2\)) and 140 \(^\circ\)C (10.5 mA/cm\(^2\)). Therefore, for the rest experiments, the reaction temperature is fixed at 120 \(^\circ\)C. Figure 5a presents the J-V
curves of TiO/CdSe anodes obtained from different ZnO ALD cycles. All the photoanodes present negligible dark currents while showing current densities above 10 mA/cm$^2$, upon illumination. This implies an efficient light harvesting by the sensitizers (see also IPCE below) and charge separation at the TiO$_2$ and CdSe interface rendered by the type-II band alignment (see Fig. 1c). All the samples show similar onset potentials ($-1.0$ V vs Ag/AgCl), as a result of similar surface flat bands. The photocurrents saturate...
with increasing bias voltage, indicating the good electrical conductivity of the TiO\textsubscript{2}/CdSe and the good contacts with the FTO.

We now discuss the effect of ALD ZnO thickness. Figure 5a-c show that the sample from 60 ALD cycles gives the highest photocurrents; further increment of the number of ALD cycles to 90 and 120 slightly bring the photocurrent down to ~13 mA/cm\textsuperscript{2}. The lowering of the current with higher ALD cycles might originate from adverse effects such as increased carrier recombination within the thicker CdSe layers. It is noted that a thicker ALD ZnO layer corresponds to a larger CdSe nanoparticle size. The photocurrent versus time (J–t) curves in Fig. 5c show that all the electrodes have good photoresponse and relatively good stability. For a comparison, a series of control samples of the same height are sensitized with CdSe via the SILAR method and measured under the same condition (see SEM images in Supplementary Fig. S4). Among samples with 3, 6, and 9 SILAR cycles, the highest photocurrent is ~6.5 mA/cm\textsuperscript{2} obtained from the 6-cycle SILAR sample (also presented in Fig. 5a). The CdSe nanoparticles appear to have a lower coverage than that by ALDIER based on SEM inspection, which is consistent with the diffuse reflectance data, that is, the SILAR samples have a higher diffuse reflectance compared to that of ALDIER samples (see Supplementary Fig. S5 and Fig. S1). It is noteworthy that the photocurrent level obtained from our ALDIER electrodes is very high among nano TiO\textsubscript{2} photoanodes, even higher than the previously reported TiO\textsubscript{2} nanocrystals with a homogeneous layer of CdSe photo-sensitizer. With the optimized ion exchange reaction temperature and ALD ZnO thickness, the highest photocurrent for the TiO\textsubscript{2}/CdSe electrode reaches 15.7 mA/cm\textsuperscript{2} at zero bias (versus Ag/AgCl), which is the highest value among TiO\textsubscript{2}-based photoelectrochemical cells for hydrogen generation. Further in-depth insights of the enhancement mechanism will be studied in more details. This sensitization method can be generalized to other sensitizers like CdS, PbS, and PbSe. It is optimistic that such ALDIER method is ready to be extended to other TiO\textsubscript{2} nanostructures including anodized nanotubes, and to other electron transporting materials like SnO\textsubscript{2}.

### Methods

#### Fabrication of TiO\textsubscript{2} Inverse Opals

Carboxylate-modified, monodisperse polystyrene spheres of 500 nm diameter (Duke scientific corporation) were assembled onto the Fluorine-doped SnO\textsubscript{2} (FTO) coated glass substrates via a vertical deposition process at 90 °C\textsuperscript{26}. The self-assembled polystyrene spheres opals were then infiltrated with TiO\textsubscript{2} using a stop-flow-reactor ALD system at 70 °C, for which tetrachloro (99.99%, Sigma Aldrich) and H\textsubscript{2}O were used as the Ti and O precursors, respectively. Finally, TiO\textsubscript{2} inverse opal structures were developed by burning the original polystyrene spheres in air at 450 °C for 2 h, which also improved the crystallinity of the TiO\textsubscript{2}. Last, reactive ion etching (RIE, NIE ES371) was used to weave the top surface and open up the pores.

#### Preparation of TiO\textsubscript{2} particle film

TiO\textsubscript{2} nanoparticle films were deposited on the FTO by successive screen-printing using a TiO\textsubscript{2} paste consisting of Degussa P25 TiO\textsubscript{2} powder and an ethyl cellulose binder in x-terpinol\textsuperscript{27}. The projected area of the TiO\textsubscript{2} layers was approximately 0.28 cm\textsuperscript{2} (circles with 0.6 cm diameter). Then, the TiO\textsubscript{2} electrodes were gradually heated to 450 °C where they were held for 15 min before being heated to 500 °C for a further 30 min.

#### ALD ZnO layer and Ion Exchange Reactions

ZnO layers with different thickness were conformally deposited onto the TiO\textsubscript{2} as the sacrificial layers for the ion exchange reaction by ALD with the Diethyl zinc (DEZ, 99.99%, Sigma Aldrich) and water (0.1 M as the Zn and O precursors, respectively. The ZnO coated TiO\textsubscript{2} electrodes were then annealed in air at 450 °C for 30 minutes to improve the crystallinity. TiO\textsubscript{2}/ZnSe core/shell structure was prepared by immersing the ZnO coated TiO\textsubscript{2} in a Se\textsuperscript{2-} ion solution (0.05 M, prepared by reacting 0.79 g Se powder with 0.8 g NaBH\textsubscript{4} in 200 ml deionized water) and kept at 60 °C for 5 hours in order to fully exchange the ZnO layer into ZnSe\textsuperscript{2-}. The samples were then washed with deionized water and absolute ethanol and dried in air. Due to the fact that Se\textsuperscript{2-} is vulnerable to oxygen, all the experiments containing Se\textsuperscript{2-} ions were done in glove box. The TiO\textsubscript{2}/ZnSe core/shell structures were then reacted with the 0.1 M CdCl\textsubscript{2}·2.5H\textsubscript{2}O aqueous solution at 90–140 °C for 10 hours to replace Zn\textsuperscript{2+} by Cd\textsuperscript{2+} in the ZnSe shell. By controlling the reaction temperature, the composition of the TiO\textsubscript{2}/ZnSe, and Se\textsuperscript{2-} core/shell structure could be tuned. Finally, TiO\textsubscript{2}/ZnO/CdSe core/shell nanostucture was annealed in argon ambient at 400 °C for 30 minutes to improve crystallinity.

#### Successive Ionic Layer Adsorption and Reaction (SILAR) of CdSe on TiO\textsubscript{2}

The SILAR process was modified from the previous report\textsuperscript{15,17}. In a typical procedure, the TiO\textsubscript{2} electrodes were immersed in a solution containing 0.05 M cadmium acetate dihydrate (Cd(Ac\textsubscript{2})·2H\textsubscript{2}O, Alfa Aesar, 98%) in ethanol for 1 min, to allow Cd\textsuperscript{2+} to adsorb onto the TiO\textsubscript{2} surface, and then rinsed with ethanol for 1 min to remove the excess Cd\textsuperscript{2+}. The electrodes were then dried for 2 min in an argon atmosphere. Subsequently, the dried electrodes were dipped in a solution containing 0.05 M Se\textsuperscript{2-} for 1 min. The Se\textsuperscript{2-} solution was prepared by mixing selenium (Se, Sigma-Aldrich, 99.8%) and sodium borohydride (NaBH\textsubscript{4}, Sigma Aldrich, 99.8%) in water. The electrodes were then rinsed in ethanol for 1 min and dried again in an argon atmosphere for another 2 min. This procedure was repeated several times to get desired CdSe loading.

### Materials Characterizations

The morphology and microstructure of the nanostructured films were examined using a JEOL JSM-7600F field emission scanning electron microscopy (FE-SEM), and a JEM 2100F transmission electron microscope (TEM). The X-ray diffraction (XRD) patterns were recorded by Shimadzu thin film XRD equipment using Cu K\textsubscript{α} radiation. The diffuse reflection spectra were taken using Zolix Solar Cell QE/IPCE Measurement System equipped with an integrating sphere and a silicon diode detector.

#### Photoelectrochemical Characterizations

The PEC performance measurements were conducted in three electrodes configuration with the as prepared nanostructured photoanodes as working electrodes, Ag/AgCl in saturated KCl as a reference electrode and Pt foil as the counter electrode. 0.24 M Na\textsubscript{2}S and 0.35 M
A mixed aqueous solution was used as the electrolyte. The current density vs potential ($J-V$) curves were measured in the dark and illumination with a 150 W Xe lamp (Science tech SS150) equipped with an AM1.5 G filter, calibrated with a standard Si solar cell to simulate AM1.5 illumination (100 mW/cm²). Photocurrent versus time ($J-t$) tests were carried out by measuring the currents under chopped light illumination (light/dark cycles of 30 s) at a fixed bias of 0 V versus Ag/AgCl. The incident photon-to-current conversion efficiency (IPCE) measurements were taken as a function of wavelength from 300 to 800 nm using a specially designed IPCE system for solar cells (Zolix Solar cell Scan100), with three electrodes configuration under zero bias versus Ag/AgCl. A 300 W Xe lamp equipped with gratings was used to generate a monochromatic beam. The incident light intensity was calibrated by a standard silicon photodiode.

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