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CdS/TiO₂ photoanodes via solution ion transfer method for highly efficient solar hydrogen generation

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Abstract
Cadmium sulfide (CdS) is a unique semiconducting material for solar hydrogen generation applications with a tunable, narrow bandgap that straddles water redox potentials. However, its potential towards efficient solar hydrogen generation has not yet been realized due to low photon-to-current conversions, high charge carrier recombination and the lack of controlled preparation methods. In this work, we demonstrate a highly efficient CdS/TiO₂ heterostructured photoelectrode using atomic layer deposition and solution ion transfer reactions. Enabled by the well-controlled deposition of CdS nanocrystals on TiO₂ inverse opal (TiIO) nanostructures using the proposed method, a saturation photocurrent density of 9.1 mA cm⁻² is realized which is the highest ever reported for CdS-based photoelectrodes. We further demonstrate that the passivation of a CdS surface with an ultrathin amorphous layer (~1.5 nm) of TiO₂ improves the charge collection efficiency at low applied potentials paving the way for unassisted solar hydrogen generation.

Introduction
One of the greatest challenges facing humanity in the 21st century is securing environmentally clean, renewable energy sources. Among the various choices towards addressing this challenge, energy derived from hydrogen is considered the most promising source for the future as it can be produced from clean and renewable energy sources and offers a clean life cycle. Hydrogen fuel produced by the direct conversion of solar energy is also an effective approach to tackle the problems of storage and transport associated with the intermittent nature of various renewable energy sources [1, 2]. The production of hydrogen from water using solar energy can be achieved in a photoelectrochemical system with the help of a semiconductor, which is first excited by incident photons to create photogenerated charge carriers. The generated charge carriers then participate in a redox chemical reaction with water at the semiconductor surface and split water molecules to hydrogen and oxygen [3–6]. For the reactions to occur without any external energy input, the minimum energy equivalent to an electrical potential of 1.23 eV is required. Considering the losses involved in the reaction kinetics, a single semiconductor material with a bandgap energy of 2.0–2.2 eV, having conduction and valence band-edge energies that straddle the electrochemical redox potential of water can propel the water splitting reaction to produce hydrogen and oxygen with an overall solar to chemical energy conversion efficiency of up to 15% [7–9].

The lack of semiconductor materials with efficient light absorption, and band-edge energetics matching with the H₂ and O₂ evolution reactions prompted several strategies to overcome the issue of high voltage requirements and achieve the target solar-to-hydrogen conversion efficiency of above 10%. One approach makes use of a dual electrode cell configuration where an n-type photoanode with a sufficiently positive valence band drives water oxidation with a reasonable photocurrent, and a p-type photocathode with a sufficiently
negative conduction band drives water reduction [7, 10–12]. The use of two semiconductor materials with bandgaps tuned to absorb complementary portions of the solar spectrum provides an attractive option for capturing a large portion of the solar spectrum. However, due to the integrated nature of the components in a dual electrode system, an appropriate combination of photoanode and photocathode to provide the necessary photoelectrochemical performance is required to capture a large portion of the solar spectrum. Although this technique based on multi-junction silicon solar cells [13, 14], III–V based solar cells [15, 16], and tandem CIGS and perovskite solar cells [17, 18], has proven to be the most efficient, the associated costs and complexity warrant the design of simpler systems. Single bandgap semiconductor based photoelectrolytic cells could provide the basis for a simplified device architecture for practical applications if a suitable semiconductor material with an appropriate bandgap and band-edge positions is developed.

CdS is a unique inorganic semiconductor material that has ideal bandgap properties for overall water splitting—it has a bandgap of ∼2.2 eV which is tunable via quantum confinement and CdS₆Se₁₋ₓ alloy formation [19–22], with valence and conduction band-edges that overlap water redox potentials. However, low photoconversion efficiency and corrosion hinder its progress for practical solar water splitting application. While recent studies showed that the addition of a co-catalysts such as Co-Pi and IrOₓ [10, 23], can suppress photocorrosion of CdS, higher photocurrent conversions above 8 mA cm⁻² at sufficient voltages still need to be achieved before the 10% solar-to-hydrogen conversion efficiency can be realised. CdS has typically been combined with wide bandgap nanostructured semiconductors such as TiO₂ or ZnO to form heterostructures with a type II band alignment favouring efficient light absorption, charge separation and transfer [24–30]. Despite a wide range of in situ and ex situ methods such as chemical bath deposition [31], electrodeposition [32], successive ionic layer adsorption and reaction (SILAR) [28, 33], chemical vapour deposition [20] and spray pyrolysis deposition [34] which have been developed to combine CdS with wide bandgap semiconductors, poor control over thickness and uniformity in high aspect ratio nanostructures has led to high internal recombination losses and low photocurrent conversions.

Here, we report a novel method of combining CdS with nanostructured TiO₂ using atomic layer deposition (ALD) and solution ion transfer (SIT) reactions. In fact, ion exchange reactions have been used increasingly in recent years as a versatile synthetic tool to develop nanomaterials with compositions, morphologies, and crystal phases that are not readily accessible by conventional synthetic methods [35–38]. A conformal, sacrificial layer of ZnO is deposited on nanostructured TiO₂ inverse opal (TiO) using ALD, followed by anion (sulfidation) and cation (cadmiumation) SIT steps to convert ZnO to ZnS and CdS, respectively. The resulting CdS/TiO₂ heterostructures showed a significantly improved photoelectrochemical performance compared to those prepared by the conventional SILAR method. This work provides a basis for the development of a single bandgap semiconductor based photoelectrochemical system towards practical applications.

Results and discussion

The fabrication procedure for the CdS-sensitized TiO₂ heterostructure is schematically illustrated in figure 1. First, TiO nanostructure was fabricated by vertical self-assembly of monodispersed polystyrene particles into an opal template, followed by infiltration of the opal template with TiO₂ using ALD. Subsequent heat treatment produces an inverse opal nanostructure with interconnected, three-dimensional and periodic pore geometry as shown in figure 2(a). More details can be found in literature from our earlier works [21, 39, 40]. The as-fabricated TiO was coated conformally with 10 nm ZnO using ALD and further subjected to anion and cation exchange SIT steps to convert the ZnO film into ZnS and CdS, respectively. Figures 2(b)–(d) confirms the decoration of TiO with CdS nanocrystals with highly uniform distribution across the entire pore structure. It is noted that the conformal film of ZnO is transformed into nanocrystal morphology after the SIT reactions and annealing at 400 °C. Transmission electron microscopy (TEM) imaging of the nano-heterostructure confirms that the internal surfaces of pores in the TiO structures are decorated with CdS nanoparticles (figure 2(e)).

Electron dispersive x-ray (EDX) analyses of these structures in scanning TEM (STEM) mode further confirm this as shown in the EDX maps in the supplementary information (figure S1 is available online at stacks.iop.org/ NANOFT/2/015004/mmedia). High resolution TEM image of the CdS nanoparticle on TiO₂ surfaces shows that both the TiO₂ and CdS are crystalline in nature and have good interfacial contacts as shown in figure 2(f). The crystal phases of TiO₂ and CdS were confirmed as anatase and hexagonal, respectively, using x-ray diffraction (XRD) measurements (figure S3). For a comparison of photoelectrochemical characteristics, we also prepared CdS/TiO nanostructures using conventional SILAR method. Pore blocking and non-uniform distribution of CdS on TiO surface with non-uniform distribution is observed in these nanostructures when prepared using the SILAR method (figure S4).
Current–potential ($J–E$) characteristics of CdS/TiO$_2$ photoanode prepared via SIT were measured in a three-electrode configuration with a polysulfide solution as an electrolyte in comparison with that of the photoanode prepared using the conventional SILAR method. It has been widely reported that the addition of a passivation layer on quantum dots surface can greatly suppress charge recombination at the semiconductor-electrolyte interface and improve photoconversion efficiency [25, 41, 42]. Thus, we deposited 1.5 nm of amorphous TiO$_2$ conformally on the SIT CdS/TiO$_2$ photoanode and characterised its $J–E$ curves (figure 3(a)).

Typically, all the electrodes exhibit an onset potential of $\sim -0.3$ V versus reversible hydrogen electrode (RHE) and approach photocurrent plateau at 0.4 V versus RHE. The photoanode prepared via the newly proposed SIT method showed a marked increase in photocurrent conversion efficiency reaching a saturation current density of above 9 mA cm$^{-2}$, which is almost double that of the photoanode prepared via the conventional SILAR method. To our knowledge, this is the highest reported photocurrent for CdS based photoelectrochemical hydrogen generation.

We also investigated the effect of the thickness of ZnO sacrificial film (figure S6) on the photocurrent generation, finding $\sim 10$ nm of ZnO (60 ALD cycles) as optimal and using this throughout the study. It is noteworthy that the amorphous TiO$_2$ passivation resulted in pronounced improvement in the charge collection efficiency at lower applied potentials, presenting a remarkable 6.6 mA cm$^{-2}$ at 0 V versus RHE, demonstrating a great promise towards realizing efficient, unbiased photoelectrochemical solar hydrogen generation.

Electrochemical impedance spectroscopy measurements were carried out at open circuit conditions to investigate charge separation, transfer and recombination processes. Typically, the smaller the diameter of the Nyquist plot, the lower the charge transfer impedance at the TiO$_2$/CdS/electrolyte interface [43]. Lowest impedance is observed for the SIT photoanode, implying an improved charge separation while the impedance is slightly increased with the addition of amorphous TiO$_2$ coating (figure 3(c)). For a quantitative analysis of the impedance, we fitted the Nyquist plots with two-RC circuit as in the inset in figure 3(c). Here, $R_s$ is the series resistance of the electrochemical device. $R$ and $C$ represent the resistance and capacitance of space charge region, respectively. $R_p$ and $C_p$ are the resistance and capacitance of the Pt cathode, respectively. The fitted values of $R$ is 120.2, 182.4 and 259.7 for pristine TiO-CdS SIT, TiO-CdS SIT-TiO$_2$, TiO-CdS SILAR photoelectrodes, respectively. The lowest space charge resistance of SIT CdS/TiO$_2$ photoanodes can be attributed to the highly controlled and uniformly decorated CdS on the TiO$_2$ surface with a well-defined nanocrystal morphology.

The characteristic peak frequency (below 100 Hz) shifts to a higher value for the CdS/TiO$_2$ electrode prepared via SIT method. Higher characteristic peak frequency is indicative of a shorter electron lifetime than that in the SILAR photoelectrode. The decreased electron lifetime can be attributed to the significantly increased CdS/electrolyte interfacial area originating from the nanocrystal morphology that provides extended pathways for charge recombination. However, the
characteristic frequency peak shifted to a much lower value when passivated with a thin conformal TiO$_2$ film, indicating a greatly improved electron lifetime. This is consistent with the increased charge transfer resistance with the addition of TiO$_2$ passivation layer and confirms the beneficial effect of passivating CdS surface in improving its photoelectrochemical performance at lower applied potentials. Mott–Schottky plots (figure S8) were obtained based on the capacitances derived from the electrochemical impedance, from which flat-band potential can be calculated. The flat-band potential of SIT electrode and SILAR electrode are determined to be 0.25 and $-0.1$ V versus RHE. The flat-band potential of SIT electrode increased compared that of SILAR electrode. This Fermi level shift is attributed to the changes in electronic properties of CdS obtained from different methods.

Figure 4(a) shows the diffuse reflectance spectra of the different nanostructures. It is noticeable that the TiO nanostructure has very high diffuse scattering which is extremely beneficial for light harvesting efficiency. This is attributed to Mie scattering originating from the porous structure of these nanostructures which is at the same
length scale as that of the incident light. The absorption wavelength is redshifted with the addition of CdS while the nanostructure with SIT CdS shows strongly absorbing characteristics. Interestingly, SIT CdS exhibits a reduced optical bandgap ($\sim 2.18$ eV) than that prepared using the SILAR method (figure S7), thus favoring photon absorptions at longer wavelengths. This anomalous bandgap reduction has been observed in many other previous works as well [44] and can be caused by non-stoichiometry and the presence of intermediate states. Incident photon-to-current conversion efficiency (IPCE) measurements were carried out in a three-electrode...
setup at 0.5 V versus RHE to identify the wavelength-dependent light harvesting ability of the photoanodes.

Maximum IPCE values of ∼80% and 50% were observed for photoanodes prepared via SIT and SILAR methods, respectively, with the SIT photoanode having superior quantum efficiency in the entire wavelength range as shown in figure 4(b). This result is consistent with the corresponding J–E and optical absorption characteristics.

The practical hydrogen generation rate has been quantified by gas chromatography at an applied bias of 0.1 V (versus RHE) under AM1.5 irradiation. The current–time plot obtained concurrently is also shown in figure 5. The photocurrent density decreased by about 3.7% after 100 min of irradiation, indicating a good long-term photostability in the polysulphide electrolyte. The hydrogen generation rate is determined to be 141.3 μmol cm⁻² h⁻¹, corresponding to a Faradaic efficiency of around 96%.

In summary, we have demonstrated a novel method to combine CdS with wide bandgap high aspect ratio nanostructures using solution ion transfer reactions with highly controlled surface coverage and well-defined morphology. A remarkable saturation photocurrent density of ∼9.0 mA cm⁻² has been realized under AM1.5G illumination using CdS nanocrystal decorated TiO₂ inverse opal as a photoanode which is attributed to the improved interfacial charge transfer and high quantum efficiency in the visible light region. We have further illustrated that the addition of an ultrathin amorphous TiO₂ passivation film on CdS can greatly suppress charge recombination and improve the photoconversion efficiency. A photocurrent density of 6.6 mA cm⁻² at 0 V versus RHE applied potential was realized showing the promise towards efficient, unassisted photoelectrochemical solar hydrogen generation. We believe this is the highest ever reported performance for any single bandgap photoelectrodes in non-tandem configuration and it can be further improved with the addition of co-catalysts. Based on the newly developed CdS/TiO₂ photoanodes, a hydrogen gas generation rate of 141.3 μmol cm⁻² h⁻¹ at 0.1 V versus RHE has been verified.

**Experimental section**

**Fabrication of TiO₂ inverse opal**

Carboxylate-modified, monodispersed polystyrene particles of 400 nm diameter from Thermo Scientific were assembled onto fluorine-doped SnO₂ (FTO) coated glass substrates via a vertical deposition process at 90 °C [45]. The thickness of the opal templates was confirmed to be ∼6 μm. The self-assembled polystyrene opal templates were then infiltrated with TiO₂ using a Picosun R200 ALD system at 85 °C in stop-flow method, using titanium tetrachloride (99.99%, Sigma Aldrich) and DI water as the sources for Ti and O, respectively. The ALD infiltrated opal structures were calcined in air at 500 °C for 1 h to form TiO₂ structures. This was followed by inductively coupled plasma reactive ion etching (Versaline, Plasma-Therm) to remove the top surface and open up the pores.

**Solution ion transfer deposition of CdS**

Conformal sacrificial ZnO films were deposited onto the TiO₂ surface using ALD with Diethylzinc (DEZ, 99.99%, Sigma Aldrich) and H₂O as the Zn and O precursors, respectively. The ZnO coated TiO₂s were then annealed in air at 450 °C for 30 min to improve the crystallinity. The ZnO films were subjected to SIT steps via anion exchange (sulfidation) in 0.25 M Na₂S solution at 60 °C for 4 h, followed by cation exchange (cadmiation) in 0.1 M CdCl₂ at 120 °C for 12 h, to convert ZnO to ZnS and CdS, respectively. By controlling the reaction

![Figure 5. (a) Current-time curve, (b) hydrogen gas evolution measurements at 0.1 V versus RHE for CdS/TiO₂ heterostructures using SIT with TiO₂ surface passivation.](image)
temperature, the composition of the Zn\textsubscript{1-x}Cd\textsubscript{x}S could be tuned. The samples were then washed with deionized water and absolute ethanol and annealed in argon ambient at 400 °C for 45 min to improve crystallinity.

A modified SILAR process from previous reports was used to prepare reference samples [46]. In a typical procedure, the TiO\textsubscript{2} samples were dipped in a 0.1 M cadmium acetate dihydrate (Cd\textsubscript{2}Ac\textsubscript{2}2H\textsubscript{2}O, Alfa Aesar 98%) in methanol solution for 1 min, and then washed with methanol and dried with N\textsubscript{2} stream. After that the samples were immersed in a sodium sulfide nonahydrate (Na\textsubscript{2}S\textsubscript{9}, Alfa Aesar 99.9%) in equal amounts of methanol-water solution (0.1 M) for 1 min, where the preadsorbed Cd\textsuperscript{2+} ions react with S\textsuperscript{2-} to form CdS. The samples were then washed again with methanol and dried with N\textsubscript{2} stream. This procedure was repeated 15 times to increase the CdS film thickness for optimum photoelectrochemical performance. Finally, the samples were annealed in Ar at 400 °C for 45 min.

Materials characterizations
The morphology and microstructure of the nanostructured films were characterized using an FEI Helios 600 NanoLab DualBeam focused ion beam (FIB) system. Detailed TEM investigations were carried out using a JEOL 2100F operated at 200 keV and equipped with both STEM capabilities and an EDX detector. TEM samples were prepared by FIB sectioning using an FEI Helios Nanolab 600. The XRD patterns were recorded by Shimadzu 2100F operated at 200 keV and equipped with both STEM capabilities and an EDX detector. TEM samples were prepared in a JEOL FIB system. Diffuse reflectance and transmittance were measured using a Perkin Elmer spectrophotometer equipped with an integrating sphere.

Photoelectrochemical characterizations
Photoelectrochemical performance of the photoanodes was evaluated in a three-electrode configuration using a potentiostat (Autolab, PGSTAT302N). Ag/AgCl in saturated KCl and a Pt wire were used as reference and counter electrodes, respectively in 0.25 M Na\textsubscript{2}S and 0.35 M Na\textsubscript{2}SO\textsubscript{3} mixed aqueous solution as a sacrificial electrolyte. Photoresponse characteristics were measured using a solar simulator (from Newport) equipped with a 150 W Xe lamp and an AM 1.5G filter, calibrated with a standard Si solar cell. Photocurrent stability tests were conducted by measuring the photocurrent produced under chopped light irradiation (light/dark cycles of 50 s) at an applied bias of 0 V versus Ag/AgCl. The IPCE measurements were taken as a function of wavelength from 300 to 800 nm using a 1000 W Xe lamp equipped with gratings to generate a monochromatic beam, with a three-electrode configuration. The incident light intensity was calibrated by a standard silicon photodiode. The H\textsubscript{2} gas evolved was quantified using gas chromatography (SRI Instruments, Educational GC) equipped with a thermal conductivity detector. The electrode potential versus Ag/AgCl was converted to the RHE potential according to the Nernst equation [8]: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \, \text{pH} + \frac{E^0_{\text{Ag/AgCl}}}{\text{RHE}}$, where $E_{\text{RHE}}$ is the converted potential versus RHE, $E^0_{\text{Ag/AgCl}} = 0.1976$ V at 25 °C, and $E_{\text{Ag/AgCl}}$ is the experimental potential measured against the Ag/AgCl reference electrode.

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