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Role of surface engineering of hybrid structure for high performance quantum dots based photoelectrochemical hydrogen generation

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ABSTRACT

We report the synthesis of a TiO₂ hybrid structure, consisting of a combination of nanorods and nanoparticles, subsequently treated with hydrazine to enhance the performance of photoelectrochemical (PEC) hydrogen (H₂) generation. The optimized TiO₂ hybrid photoanode sensitized with Quantum dots (QDs), yields a saturated photocurrent density of 4.25 mA cm⁻² (at 0.8 V vs RHE), which is 172% higher than that of the reference sample. The optimized hybrid photoanode treated with hydrazine exhibits an additional 28% increase in the saturated photocurrent density, reaching 5.43 mA cm⁻² with CdS QDs, and 8.12 mA cm⁻² with CdS/CdSe QDs (at 0.8 V vs RHE), while maintaining 80% of the initial value of photocurrent density, after 2 h of continuous one sun illumination (AM 1.5 G, 100 mW cm⁻²). We used Density Functional Theory with Hubbard energy correction (DFT + U) calculations to describe the mechanism that underpins this significant improvement. DFT + U results highlighted that the concentration of the hydrazine treatment plays a crucial role and affects the sites (surface or interstitial) where nitrogen may be present. This eventually affects the recombination centers within the hybrid photoanode. Thus, the results of this work define a promising strategy to optimize the morphology of the hybrid photoanodes via hydrazine surface engineering to fabricate efficient and stable PEC water splitting devices for H₂ generation.

1. Introduction

Human civilization is fundamentally dependent on fossil fuels, which currently represent more than 85% of global energy consumption [1]. Besides being non-renewable, fossil fuels are also known to cause an overwhelming proportion of greenhouse gases, which in turn are the main cause of global warming [2]. In this context, solar technologies such as photovoltaics and photoelectrochemical (PEC) cells are promising towards replacing fossil fuels by converting solar energy directly into electrical power or clean chemical fuels such as hydrogen (H₂) [3].

Solar-driven PEC water splitting is a promising approach to convert solar energy into H₂ [4], which can be easily stored and reused. H₂ possesses a three times higher amount of energy per unit weight as compared to fossil fuels, and upon combustion in a fuel cell, it only

produces clean by-products, such as water vapor [5].

PEC cells typically use wide-bandgap semiconductors (e.g. TiO₂, ZnO, WO₃, etc.) since the pioneering discovery made by Honda & Fujishima [6]. However, wide-bandgap semiconductors can only absorb ultraviolet light, which accounts for a mere 5% of the solar spectrum, making them inefficient and inadequate photoabsorbers. In this context, nitrogen (N₂) doped TiO₂ represents a viable way to extend absorption to the visible region [7–9]. This approach was also used to narrow the bandgap of ZnO, consequently yielding a higher light-harvesting efficiency [10]. In the case of TiO₂, the location of the doped N atoms in the crystal lattice (i.e., interstitial or surface sites) is a function of the doping concentration [11]. In addition, depending on the concentration percentage of N₂ in the crystal lattice, recombination or trapping centers can be formed, thereby degrading the overall performance of the PEC

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device [12]. In parallel, the sensitization of wide bandgap semiconductors (e.g. TiO_2 , ZnO , SnO_2 , etc.) with quantum dots (QDs) has been shown to be an effective way to enhance the performance of PEC devices for water splitting [13,14]. Due to their tunable bandgap, QDs can harvest light from the visible to Near-infrared (NIR) regions of the solar spectrum to generate charge carriers [15]. In addition, QDs are synthesized through low-cost solution processing, with unique optoelectronic properties that depend on the size, shape, chemical composition, and the choice of capping ligand [16,17]. However, the overall performance of TiO_2 /QDs based PEC cells is still hindered by undesirable non-radiative carrier recombination within the wide bandgap semiconductor (e.g. TiO_2) and at the TiO_2 /QDs/electrolyte interface [18]. Briefly, there are four main non-radiative recombination routes occurring at the TiO_2 /QDs/electrolyte interface of the PEC system: i) Charge recombination inside the QDs at defect/trap states; ii) Photo-generated electrons in the Conduction band (CB) of QDs with the oxidized species in the electrolyte; iii) Back electron transfer from the CB of TiO_2 to the Valence band (VB) of QDs; iv) Recombination of photo-injected electrons in TiO_2 with oxidized species in the electrolyte [19]. In addition to these recombination routes, photo-injected electrons recombine due to deep and surface traps inside the TiO_2 mesoporous film, which further degrades device performance [20]. These traps occur due to the presence of impurities and lattice defects inside the semiconductor and are usually located in the forbidden bandgap. During device operation, these traps are dominant in the recombination process, which decreases the carrier mobility and collection efficiency, thus reducing overall device performance [21,22]. To date, plenty of studies have been reported to enhance PEC device performance by improving the charge transport efficiency and reducing the non-radiative carrier recombination processes. To this end, a promising approach consists in changing the morphology of TiO_2 into one-dimensional (1D) nanorods (NRs), nanotubes, or nanowires [23,24], providing a direct pathway for the charge carriers, enhancing charge transport and suppressing carrier recombination. Nevertheless, due to the low available surface area of 1D nanostructures compared to nanoparticles, the QDs loading is low [25]. In addition, the morphology does not have the proper porosity for the electrolyte to penetrate and be in contact with a large area of the TiO_2 surface, which affects the charge kinetics in the PEC device [26]. Therefore, it is highly desirable to design a photoanode architecture that combines fast charge carrier transfer as well as a porous structure with high specific surface area for high amount of QDs loading and proper electrolyte penetration. Moreover, surface modification through surface treatment is also crucial to improve the performance of the photoanode, as it suppresses the bulk- and surface trap sites and reduces the non-radiative carrier recombination processes.

In the present work, the hydrazine acts as a source of N_2 that does not form an internal band inside the semiconductor bandgap, which could eventually compete with the QDs for light-harvesting in the visible region. However, the N_2 source can be used to suppress the recombination sites without tuning the bandgap of TiO_2 NRs/NPs hybrid structured photoanode, for an efficient PEC water splitting device. In this work, we highlight the synergetic effect of TiO_2 NRs/NPs hybrid structure and the hydrazine treatment on the overall PEC device performance. A series of PEC devices was fabricated with different configurations of TiO_2 NRs/NPs hybrid photoanodes, sensitized with CdS and CdS/CdSe QDs, using the successive ionic layer adsorption and reaction (SILAR) method. The structure, composition and carrier dynamics of the photoanodes were studied using scanning electron microscopy (SEM), X-ray diffractometer (XRD), energy-dispersive X-ray spectroscopy (EDS), X-ray photoemission spectroscopy (XPS), electrochemical impedance spectroscopy (EIS), and transient photovoltage decay measurements. Understanding the function of the hydrazine treatment on the surface of TiO_2 NRs/NPs hybrid photoanodes is crucial for the rational design of advanced photoanodes for PEC devices. Therefore, a detailed computational study via Density Functional Theory with Hubbard energy correction (DFT + U) was conducted for various N-doped TiO_2 configurations. This work

defines a special opportunity to optimize the morphology and electronic band structure of TiO_2 NRs/NPs hybrid photoanodes, reducing the non-radiative carrier recombination processes and consequently improving the performance of PEC devices.

2. Experimental

2.1. Materials

Cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 98%), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 98\%$), sodium borohydride (NaBH_4), selenium powder (Se 99.5+%), disodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ $\geq 98\%$), titanium (IV) chloride ($\text{TiCl}_4 \geq 99.0\%$ (AT)), and hydrazine solution 35 wt% in H_2O were bought from Sigma-Aldrich Inc. Methanol, acetone, ethanol, concentrated hydrochloric acid (HCl, 36% – 38%), and sodium sulfite anhydrous (Na_2SO_3 , $\geq 98\%$), were bought from VWR chemicals. Titanium (IV) n-butoxide 99+% was bought from Alfa Aesar. All chemicals were used as received without further purification. TiO_2 paste composed of 20 nm-sized anatase nanoparticles (transparent, code 18 NR-T) and mixed TiO_2 paste of 20–450 nm-sized anatase particles (active opaque, code 18 NR-AO) were supplied by GreatCell Solar. Glass substrate, coated with Fluorine-doped tin oxide (FTO) film, with sheet resistance $\sim 15 \text{ Ohm (square)}^{-1}$, purchased from Pilkington glasses.

2.2. Photoanode preparation

FTO glass substrates were first cleaned using soap and water then immersed in acetone and deionized (DI) water followed by sonication for 20 min and 10 min, respectively, then dried with N_2 gas. Finally, all cleaned FTO glass substrates were treated in the ozone chamber for 20 min, to remove any organic contamination on the surface. A thin compact TiO_2 blocking layer was then deposited on the FTO surface, by dipping the samples in 40 mM TiCl_4 in DI water for 30 min at 70°C . The samples were then washed with DI water, ethanol, and dry air, and subsequently annealed at 500°C for 30 min. The 1D TiO_2 NRs were grown by hydrothermal synthesis [27]. In a typical procedure, 30 ml of DI water and 30 ml of concentrated HCl were mixed and stirred for 10 min then 1 ml of titanium (IV) butoxide was added. After vigorously stirring for another 10 min, FTO substrates with the TiO_2 blocking layer were placed against the wall of the Teflon-liner stainless steel autoclave, with the conducting side of the FTO substrate facing downwards. After that, the solution was slowly transferred into the autoclave and heated at 150°C for (3, 4, and 5 h) to obtain different NRs growth. Subsequently, the samples were washed with DI water, dried in ambient condition, then annealed at 500°C for 30 min. After the TiO_2 NRs deposition two layers of (transparent and/or mixed) mesoporous TiO_2 (m- TiO_2), with 20 nm particle size for the transparent film, and 20–450 nm particle size for the mixed film, were tape cast on the FTO. After applying the first layer, the samples were left to dry at room temperature for 10 min, then annealed at 125°C for 6 min. The same procedure was used for the second layer, then the samples were annealed at 500°C for 30 min. For hydrazine treated samples, the samples with the hybrid structure were then dipped in 0.25 M, 0.5 M, and 1 M aqueous solution of hydrazine. The solution was heated first at 70°C , then the samples were dipped for 30 min. The samples were then dried in ambient conditions and finally annealed at 500°C for 30 min.

2.3. Sensitization of TiO_2 NRs/NPs hybrid structure with CdS and CdS/CdSe QDs

SILAR method was used to deposited CdS and CdS/CdSe QDs on the photoanode [28]. The TiO_2 photoanode samples were immersed in a solution containing 0.05 M of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in 20 ml of methanol for 1 min, as Cd^{2+} source, washed with the same solution (methanol), then dried with N_2 gas. For the S^{2-} source, the samples were immersed in

a solution containing 0.05 M of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in 20 ml of DI water/methanol (1:1) for 1 min, then washed in the same solution of DI water/methanol (1:1), then dried with N_2 gas. This procedure was used for CdS deposition. For CdSe, the solution for the Cd^{2+} source is 20 ml of 0.03 M ethanolic $\text{Cd}(\text{CH}_2\text{COO})\cdot 2\text{H}_2\text{O}$, while the solution for Se^{2-} source is a mixture of 0.03 M of Se powder and 0.06 M of NaBH_4 in 40 ml ethanolic solution. For ZnS, used as a passivation for the QDs, the Zn^{2+} source is 0.1 M $\text{Zn}(\text{CH}_2\text{COO})\cdot 2\text{H}_2\text{O}$ in 20 ml of methanolic solution, while the S^{2-} source is 0.1 M of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in 20 ml of DI water/methanol (1:1). The photoanodes were prepared using two methodologies: One with 5 CdS and 2 ZnS cycles and the other is with 5 CdS, 3 CdSe, and 2 ZnS cycles.

2.4. Characterization

Structural analysis for the photoanode. SEM Tescan LYRA 3 equipment was used for examining the morphology of the TiO_2 NRs, and the whole TiO_2 hybrid structure. EDS was used for elemental analysis for the sensitized TiO_2 hybrid structure with CdS QDs. XPS spectra were acquired using a XPS VG Scientific Escalab 220i-XL system. A monochromatic aluminum energy source of 1486.6 eV was used. The results were analyzed using Casa XPS software to obtain the elemental composition, bonding and position of the valence band maximum (VBM) of the TiO_2 with and without hydrazine treatment [29]. XRD patterns were acquired for the TiO_2 NRs using a Philips X'pert diffractometer, equipped with a Cu K_α radiation source ($\alpha = 0.15406$ nm). Ultra-violet–visible spectroscopy (UV–Vis) was used to study the absorption spectrum of the reference and treated samples with hydrazine. The UV–Vis data was then used to calculate the optical bandgap of the photoanodes.

PEC measurements. PEC measurements were carried out using a three-electrode cell configuration. The working electrode consisted of the TiO_2 hybrid structure (reference and treated with hydrazine). The counter electrode consists of Pt. The reference electrode consisted of saturated Ag/AgCl. The electrolyte used, acting as a hole scavenger, was a mixture of 0.25 M $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and 0.35 M Na_2SO_3 with pH ~ 13 . N_2 was applied to the electrolyte, for 30 min, to remove dissolved oxygen before using it. The photoanode was covered with epoxy to an area of $0.15 \sim 0.2$ cm^2 . The potential measured was with respect to Ag/AgCl, then converted to the reversible hydrogen electrode (RHE) using equation (1).

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.197 + \text{pH} \times (0.059) \quad (1)$$

We used a class AAA solar simulator (model SLB-300A by Science-tech Inc.) equipped with a 300 W xenon arc lamp as a light source, with an AM 1.5 G filter under one sun illumination. The light intensity was calibrated, with the power meter adjusted to 100 mW cm^{-2} , before each measurement. All measurements were carried out in three conditions, dark, continuous illumination, and chopped illumination.

Carrier dynamics. The carrier dynamics of the TiO_2 hybrid structure were studied by using transient open-circuit voltage (V_{oc}) decay measurement in the three-electrode configuration cell. The photoanode was illuminated for 50 s to achieve a flat band potential, then the light was turned off, and the open circuit potential was measured with respect to time. The potential decay was then used to calculate a comparative study for the electron lifetime, which indicates the recombination rate, using Eq. (2) [30].

$$\tau = -k_B T / e \times (dV_{\text{oc}}/dt)^{-1} \quad (2)$$

Where τ is the photoelectron lifetime, k_B is Boltzmann's constant $= 1.381 \times 10^{-23} \text{ J K}^{-1}$, T is the temperature in K, $e = -1.602 \times 10^{-19} \text{ C}$, and dV_{oc}/dt is the first derivative of the open-circuit voltage with respect to time.

To examine the hydrazine treatment effect on the carrier dynamics of the photoanode after device optimization, EIS was carried out under dark conditions for the reference and treated samples. The equipment

used was SOLARTRON 1260 A Impedance/Gain-Phase Analyzer, with a bias voltage of 200 mV. The frequency range used for every measurement is from 10 mHz to 300 kHz, and the AC signal was 10 mV in amplitude. An appropriate equivalent circuit, using Z-View software (v3.5, Scribner Associate, Inc.), was used to analyze and simulate the impedance measurements.

3. Results and discussion

3.1. Structural characterization of photoanode

The hydrothermal nucleation and growth process of TiO_2 NRs depends on several parameters including growth time, temperature, reactant concentration and the additives chosen to prepare the NRs [31]. Another key factor that plays an important role in nucleation and growth of the NRs is the interface of rutile TiO_2 NRs with the substrate [32]. The lattice mismatch can affect the NRs growth and crystallinity. However, in our case, the compact film of TiO_2 nanoparticles, so-called blocking layer, acts as a seed for the nucleation of the TiO_2 NRs favoring the nucleation and growth process. However, not all TiO_2 NRs are aligned and normal to the FTO surface. Some NRs grow off-normal angles, run into and collide by nearby NR, and stop the epitaxial growth. This misalignment is due to the polycrystalline nature of the TiO_2 blocking layer, coated on FTO substrates. Since the FTO glass substrate has highly textured grains on the surface, then the polycrystalline grains of the TiO_2 blocking layers are not all perfectly aligned and normal to the surface, leading to the misalignment of the grown TiO_2 NRs [32]. Fig. 1 shows the morphological characterization of the TiO_2 NRs grown over the TiO_2 blocking layer coated FTO substrates, at different growth duration. Fig. 1 (a)–(c) displays the top view of the TiO_2 NRs distribution for 3, 4, and 5 h, respectively. The inset image displays a high-resolution SEM micrograph of the corresponding NRs that confirms the well-aligned NRs arrays, obtained after 4 and 5 h growth, with a square end tubular structure, a well-known feature of tetragonal-faceted TiO_2 NRs [27]. The short-time (i.e. 3 h) hydrothermal synthesis was insufficient to grow a well-aligned array of NRs. The TiO_2 NRs surface density (in μm^{-2}) decreases as the growth time is increased. Briefly, for 4 h growth time, the density was $44 \text{ NRs } \mu\text{m}^{-2}$, while for 5 h growth time was $24 \text{ NRs } \mu\text{m}^{-2}$. However, for 3 h growth time, it was difficult to calculate the density of the TiO_2 NRs, as the NRs were grown with random orientation. This shows that with longer growth time, fewer NRs are going to be in contact with the TiO_2 NPs at the interface of the hybrid structure. The distribution of the TiO_2 NRs diameter grown at different duration is shown in Fig. 1 (e)–(g). The results indicate that for 3 h NRs growth, there is a broad distribution of the NRs diameter with average values of ~ 41 nm. While for 4 and 5 h growth duration, the NRs were observed to grow homogeneously over the FTO substrates with an average diameter of ~ 79 and ~ 145 nm, respectively. To investigate the length of the NRs, we acquired cross-sectional SEM images of the TiO_2 NRs photoanodes. Figure S1 (a)–(c) displays cross-sectional SEM images of the TiO_2 NRs for 3, 4, and 5 h NRs growth, respectively. The average length of the TiO_2 NRs was ~ 500 nm, ~ 1 μm , and ~ 2 μm for 3, 4, and 5 h NRs growth duration under identical experimental conditions, respectively. The NRs growth was not perfectly aligned and perpendicular to the substrate in the case of 3 h and shows a randomly oriented structure [Figure S1 (a)]. However, the NRs start to align with each other for extended growth duration [Figure S1 (b) and (c)]. Fig. 1 (d) displays the cross-sectional SEM image of the hybrid structure of TiO_2 NRs/NPs grown over the FTO. The effect of hydrothermal growth time on the TiO_2 NRs diameter and length is shown in Fig. 1 (h). A linear growth ratio was obtained between the length and diameter of the TiO_2 NRs over the growth duration time.

We measured XRD patterns to investigate the crystalline structure of the TiO_2 NRs. Fig. 2 (a) displays the XRD pattern of the TiO_2 NRs grown for 4 h on the TiO_2 blocking layer deposited over the FTO substrate. All TiO_2 rutile NRs peaks belong to the tetragonal structure (JCPDS

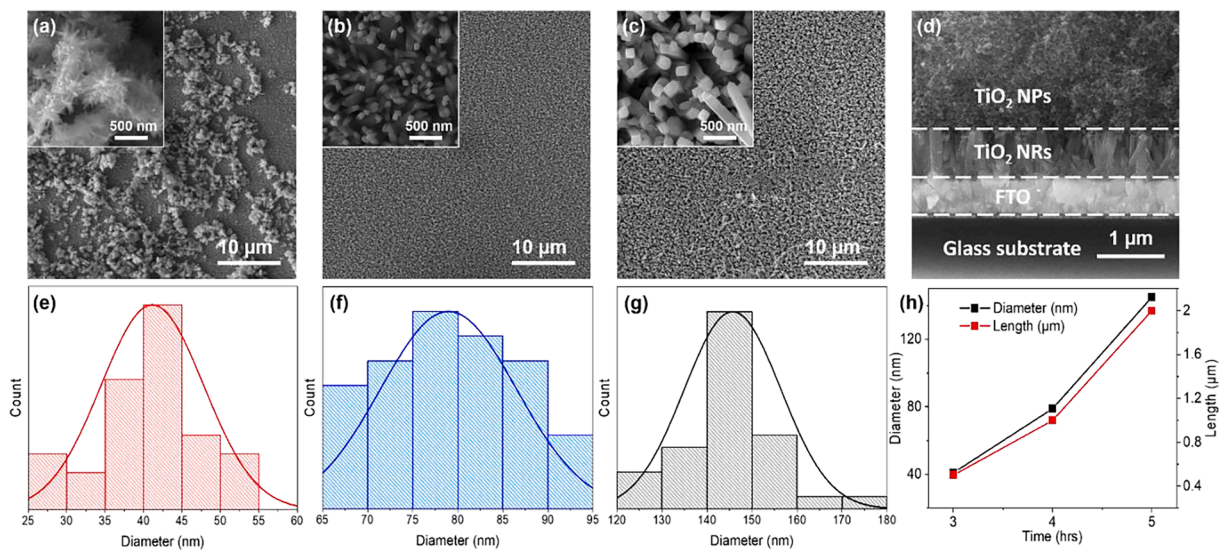


Fig. 1. Structural characterization. SEM images of the TiO₂ NRs obtained at different growth time (a) 3 h (b) 4 h and (c) 5 h. (d) The cross-sectional view of TiO₂ NRs/NPs hybrid structure. Distribution of TiO₂ NRs growth for: (e) 3 h; (f) 4 h and (g) 5 h. (h) Variation of TiO₂ NRs length and diameter as the function of growth time.

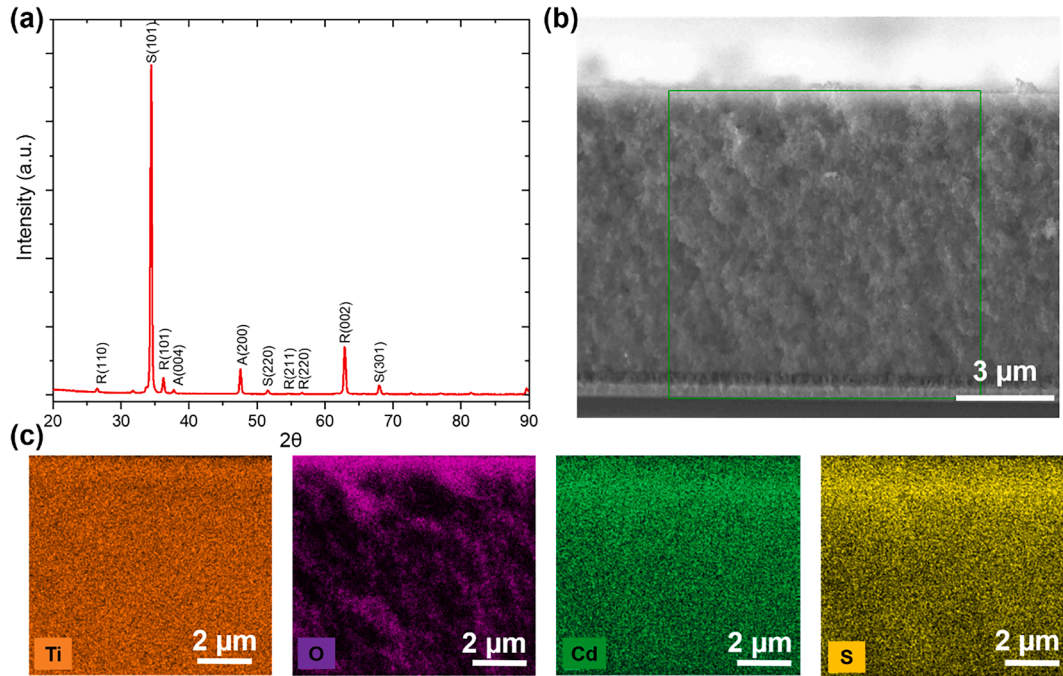


Fig. 2. Structural characterization of TiO₂ NRs by (a) XRD (b) Cross-section SEM image of the TiO₂ hybrid structure (c) elemental maps of Ti, O, Cd, S.

No.88–1175). The highest peak of the rutile NRs is (002), which indicates that the NRs are oriented and perpendicular to the surface and grow along the [001] direction [27]. The anatase phase (A) peaks (004) & (200) are related to TiO₂ blocking layer, while the other (S) peaks (101) (220), and (301) originate from the FTO substrate. As the homogeneity of the distribution of the QDs is important for device performance, EDS elemental mapping was performed to confirm the deposition of CdS QDs. Fig. 2 (b) shows an SEM image of the cross-section (the selected area is shown in the green rectangle) of the TiO₂ hybrid structure grown over FTO for elemental mapping. Fig. 2 (c) shows that the Cd and S elements are distributed all over the TiO₂ NPs and the NRs, which confirms the homogenous distribution of the QDs within the TiO₂ NRs/NPs hybrid photoanode.

3.2. Photoelectrochemical and carrier dynamic measurements

Several photoanodes were prepared using different sized TiO₂ NRs with two mixed layers of TiO₂ NPs. The PEC performance of the devices based on the hybrid TiO₂ photoanode, with different NRs growth, sensitized by CdS QDs, were measured under dark, chopped, and continuous illumination (AM 1.5G, 100 mW cm⁻²). A typical three-electrode configuration cell was used with as-designed photoanodes as working electrode, Ag/AgCl (saturated with KCl) as reference electrode, and Pt as counter electrode. Fig. 3 (b)-(e) displays the saturated photocurrent density (*J*) vs potential (*V* vs RHE) curves for the TiO₂ NPs-only and the TiO₂ × NRs/NPs photoanodes, (where × corresponds to the different growth time in h), respectively. There is a significant improvement in the saturated photocurrent density of the PEC device

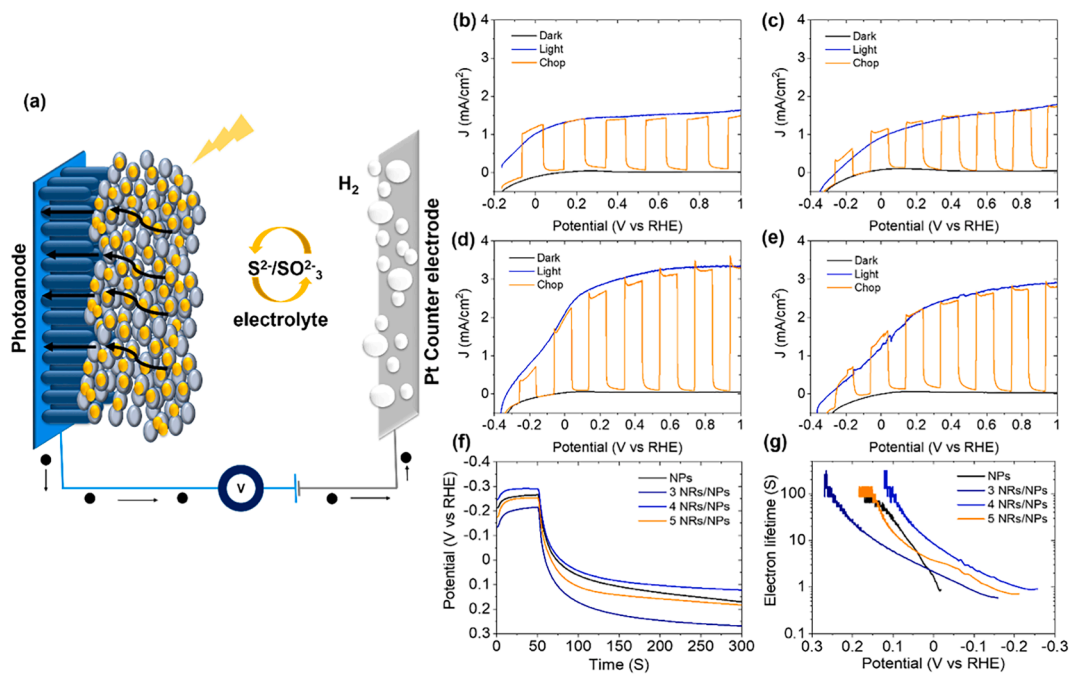


Fig. 3. (a) PEC device schematic representation and carrier dynamics. PEC performance under dark, light, and chopped for the $\text{TiO}_2/\text{CdS}/\text{ZnS}$ photoanode with (b) NPs-only, (c) 3 NRs/NPs, (d) 4 NRs/NPs and (e) 5 NRs/NPs photoanodes. Transient photovoltage decay measurement: (f) V_{oc} decay, and (g) calculated electron lifetime.

based on TiO_2 4 NRs/NPs photoanode ($J = 3.33 \text{ mA cm}^{-2}$ at 0.8 V vs RHE) representing a 113% increase compared to the PEC device based on the reference photoanode made with only TiO_2 NPs ($J = 1.56 \text{ mA cm}^{-2}$). For the TiO_2 3 NRs/NPs photoanode there was no significant improvement as compared to TiO_2 NPs-only. The inhomogeneous distribution of the TiO_2 NRs and its small size do not improve the charge transfer of the photogenerated electrons being injected from the QDs into the TiO_2 film. On the other hand, for TiO_2 5 NRs/NPs, the performance ($J = 2.83 \text{ mA cm}^{-2}$ at 0.8 V vs RHE) was better than that of the reference sample but lower than the TiO_2 4 NRs/NPs photoanode. The overgrowth of the TiO_2 NRs reduces the overall device performance due to several factors; i) it decreases the collection of the photogenerated electrons, as the TiO_2 NRs density decreases with increasing the growth time; ii) it decreases the surface area of the TiO_2 NRs for QDs loading; and iii) it increases the overall photoanode thickness, where the photogenerated electrons take longer time to reach the back contact of the photoanode and eventually enhances the possibility of recombination of the photogenerated electrons.

Fig. 3 (f) and (g) display the V_{oc} decay curve and the calculated electron lifetime for the PEC devices based on different TiO_2 NRs/NPs hybrid structured photoanodes. This measurement is important to support our conclusion about the PEC performance and evaluate the electron lifetime. The illumination of the photoanode sensitized with QDs leads to the generation of electron-hole pair (exciton). Under continuous illumination, the holes move towards the semiconductor/electrolyte interface and are consumed by the hole scavenger in the electrolyte. On the other hand, due to an open circuit condition, the electrons accumulate in the bulk of the semiconductor and create a field opposite to the electric field of the space charge region, shifting the measured potential (Fermi level) of the semiconductor into a more cathodic potential [33]. When the light is turned off, the photogenerated electrons recombine with the oxidized species in the electrolyte. The rate of the potential decay represents the recombination rate of the photoexcited electrons [34]. In addition, the potential dependent electron lifetime was calculated from the V_{oc} decay measurements by using equation (2). The first derivative of the potential decay with respect to time (i.e., dV_{oc}/dt) represents the rate of the recombination process that occurs between the

photogenerated electrons accumulated in the bulk of the photoanode under illumination and the oxidized species in the electrolyte. Therefore, the evaluated electron lifetime value of the PEC device directly depends on the rate of the carrier recombination. The prolonged electron lifetime represents a lower recombination rate of the photogenerated electrons at the $\text{TiO}_2/\text{QDs}/\text{electrolyte}$ interface. The V_{oc} decay for all devices with different TiO_2 hybrid structure is shown in Fig. 3 (f). The PEC device based on TiO_2 NPs shows a higher potential decay rate as compared to TiO_2 4 NRs/NPs. The potential decay for all the hybrid structure devices tends to reach a plateau, while the potential decay of the device based on only TiO_2 NPs continues to decrease with time. These results demonstrate that TiO_2 hybrid structure devices have a lower recombination rate as compared to the device based on TiO_2 NPs only. The photogenerated electrons lifetime is shown in Fig. 3 (g), at the same voltage, the electron lifetime of TiO_2 4 NRs/NPs is higher than all other PEC devices. The calculated electron lifetime of TiO_2 NPs decreases sharply as compared to all other TiO_2 NRs/NPs hybrid structures, which indicates that the non-radiative photogenerated electron recombination of the hybrid structures at the $\text{TiO}_2/\text{QDs}/\text{electrolyte}$ interface is reduced. At 0.1 V vs RHE potential, the electron lifetime of the pristine sample (i.e. TiO_2 NPs) is higher than the lifetime values of the TiO_2 3 NRs/NPs and TiO_2 5 NRs/NPs based PEC devices. For the TiO_2 3 NRs/NPs sample, the growth of TiO_2 NRs was inhomogeneous and incomplete as confirmed by the SEM image [Fig. 1 (a)]. This reduces the photoinjected electrons transport efficiency within the TiO_2 3 NRs/NPs photoanode due to poor interface contact between the TiO_2 NRs and TiO_2 NPs layers. Therefore, at 0.1 V vs RHE the electron lifetime of TiO_2 3 NRs/NPs PEC device is lower than the pristine sample. In the case of TiO_2 5 NRs/NPs, the overgrowth of the TiO_2 NRs reduces the collection probability of the photoinjected electrons. The TiO_2 5 NRs/NPs photoanode has a longer electron transport layer thickness. This increase in the photoanode thickness ($\sim 2 \mu\text{m}$) leads to an increase in the diffusion length that results in a longer path of the photoinjected electrons to reach the back contact of the photoanode. A longer diffusion length then increases the recombination probability of the photoinjected electrons and eventually decreases the electron lifetime. From these data, we confirm that the optimized duration for TiO_2 NRs growth is 4 h, which

yields a lower recombination rate and improved performance.

Further optimization of the TiO₂ NRs/NPs hybrid structured photoanodes was carried out with TiO₂ NPs of different sizes. Figure S2 (a)-(d) displays the PEC performance of the different photoanode structure. The PEC device based on two transparent layers of TiO₂ (20 nm particle size) yields a saturated photocurrent density of 4.25 mA cm⁻² (at 0.8 V vs RHE), which is 28% higher than the PEC device with two mixed layers of TiO₂ (20–450 nm particle size). A detailed explanation of the effect of different NPs on the PEC device performance is provided in supporting information. These results indicate that the optimum device structure consists of a first layer of TiO₂ NRs of ~ 79 nm NRs diameter and 1 μm thickness and a second layer of TiO₂ NPs (20 nm particle size) with 10 μm thickness. The average thickness of optimized photoanode was 11 μm.

To highlight the effect of the ZnS passivation layer, the PEC devices were fabricated using an optimized TiO₂/CdS hybrid photoanode with and without ZnS passivation layers. The PEC device, with ZnS passivation layers, yields a saturated photocurrent density of 4.25 mA cm⁻² (at 0.8 V vs RHE), which is 44% higher than the PEC device without ZnS (2.4 mA cm⁻² at 0.8 V vs RHE), as shown in Figure S3. These results emphasize the importance of the ZnS coating, which reduces the surface traps on the QDs surface, and improves the PEC device performance significantly.

In addition, the stability of the PEC device was examined with respect to the pH and the temperature of the electrolyte. Three different aqueous electrolytes were prepared; i) 0.25 M Na₂S·9H₂O and 0.35 M Na₂SO₃ with pH ~ 13, ii) 0.35 M Na₂SO₃ with pH ~ 7, and iii) 0.1 M HCl with pH ~ 1. The measurements were performed under continuous one sun illumination conditions (AM 1.5 G, 100 mW/cm²) for 1 h at 0.6 V vs RHE. Figure S4 (a) displays a comparison of the long-term stability of the devices with different pH values. The PEC device maintains the highest stability with the electrolyte of pH ~ 13 (i.e., 0.25 M Na₂S·9H₂O and 0.35 M Na₂SO₃) and maintains 70% of the initial value of photocurrent density after 1 h of continuous illumination. The stability of the PEC device degraded significantly and maintained only 64% and 13% of the initial photocurrent density after 1 h of continuous illumination by changing the pH of the electrolyte to ~ 7 (i.e., 0.35 M Na₂SO₃) and ~ 1 (i.e., 0.1 M HCl), respectively. These results confirm the importance of the sulfide ions in the hole scavenger process that reduces photo-corrosion and enhances the oxidation–reduction reaction rate of the PEC devices. We also examined the effect of temperature on the long-term stability of PEC devices using 0.25 M Na₂S·9H₂O and 0.35 M Na₂SO₃ electrolyte (pH ~ 13). The PEC device maintains 70% of the initial photocurrent density after 1 h of continuous illumination at room temperature. However, the PEC device stability reduces significantly with increase in temperature from 25 °C to 75 °C as shown in Figure S4 (b). Briefly, the PEC device lose 40% of the initial photocurrent density after only 45 min at 75 °C. The sealant was not stable at 75 °C and peeled off after 45 min.

3.3. Optical and structural characterization of hydrazine treated photoanode

The optimized TiO₂ NRs/NPs hybrid photoanode was then treated with hydrazine, as a source of N₂, to screen the surface and bulk traps, and to reduce the related non-radiative carrier recombination processes in the device. Usually, the absorption of TiO₂ can be tuned by introducing an intermediate bandgap from N₂ doping [7–9]. However, this is not a favourable behavior in our case, as we do not want the TiO₂ to compete in light harvesting with the QDs. In addition, the overall performance of the PEC device based on N₂ doping TiO₂ was reduced due to the introduction of the intermediate bandgap, which is responsible for more recombination events of the photogenerated carriers [12]. For the hydrazine treatment, the photoanodes were dipped in a 0.25 M, 0.5 M, and 1 M of hydrazine solution for 30 min at 70 °C then annealed to deposit the N₂ (see more details in the Experimental section). To ensure

that the deposition methodology does not introduce an intermediate bandgap, that can act as photoactive material in the visible region in the TiO₂ device, we acquired UV–Vis spectra [Fig. 4 (a)]. The absorption spectrum of the treated samples does not change as compared to the reference sample. In addition, there is no absorption in the visible region. The inset image shows the Tauc plot of the calculated bandgap for the reference sample and the treated one. The bandgap changes slightly, varying by less than 0.1 eV between the treated and untreated samples.

XPS spectra were acquired to confirm the deposition of N₂ and its nature of bonding inside the treated samples. Fig. 4 (b), (c), and (d) display high-resolution spectra for the main peak of N 1 s. The XPS spectra show a binding energy of 400 eV for the 0.25 M and 0.5 M hydrazine treated samples. The absence of the peak at 396 eV confirms that no Ti-N interaction occurs, which is attributed to the formation of the internal bandgap in the TiO₂ [35]. However, the presence of the peak at 400 eV is attributed to the Ti-O-N or N-Ti-O molecularly chemisorbed γ-N₂ bonding [36], which indicates the successful deposition of N₂ from the decomposition of hydrazine hydrate as described in equation (3). The Ti 2p and O 1s high-resolution spectra are shown in Figure S5 (a) and (b). XPS results confirm that the hydrazine treatment does not affect the TiO₂ bonding or change the chemical formula. Fig. 4 (e) displays the high-resolution spectra of the valence band for the reference and treated samples. From the valence band spectra, we can identify the VBM, through linear extrapolation of the peak to the baseline [29]. The band edge position of the reference and treated samples is the same and has the same value of 2.45 eV below the Fermi level. From the XPS and UV–Vis results, we can confirm that the hydrazine treatment does not change the valence band and conduction band position in the electronic band structure of the photoanode. In addition, it does not introduce the (Ti-N) internal bandgap that may responsible for light harvesting in visible region, and its counterproductive part of reducing the performance due to the formation of recombination sites.



Figure S6 (a), (b), and (c) show the SEM images for the reference, 0.25 M, and 0.5 M hydrazine treated samples, respectively. These images show that the hydrazine treatment process does not change the morphology of the TiO₂ NRs/NPs hybrid structured photoanode, with no induced crack due to the thermal treatment or the annealing process.

3.4. Photoelectrochemical and carrier dynamics measurements of hydrazine treated photoanode

Fig. 5 (a) and Figures S7 (a-c) display the saturated photocurrent density versus potential (V vs RHE) curves for the 0.25 M and the reference, 0.5 M, and 1 M hydrazine treated samples, respectively. The saturated photocurrent density of the PEC device (at 0.8 V vs RHE) shows a significant improvement for the 0.25 M hydrazine treated TiO₂ NRs/NPs hybrid photoanode based device and reaches 5.43 mA cm⁻², which is 28% higher than the reference device. However, the devices based on hybrid photoanodes treated with 0.5 M and 1 M hydrazine show a saturated photocurrent density values of 3.84 and 3.8 mA cm⁻², respectively. The degradation in the PEC performance is mainly attributed to the increase of trap sites due to the excess nitrogen doping. A systematic comparison of the saturated photogenerated current density with different hydrazine treatments at 0.8 V vs RHE and the J-V curves under continuous illumination are shown in Fig. 5 (b) and Figure S7 (d), respectively. Long-term stability measurements were conducted to study the effect of hydrazine treatment on the operational stability of the PEC devices. The tests were performed under continuous one sun illumination (A.M. 1.5, 100 mW.cm⁻²) for 2 h at 0.6 V vs. RHE. As shown in Figure S7 (e), the PEC device based on hybrid photoanode treated with 0.25 M hydrazine maintains 67% of the initial photocurrent density, which is comparable to the reference PEC device (without hydrazine treatment). We therefore conclude that the hydrazine treatment does

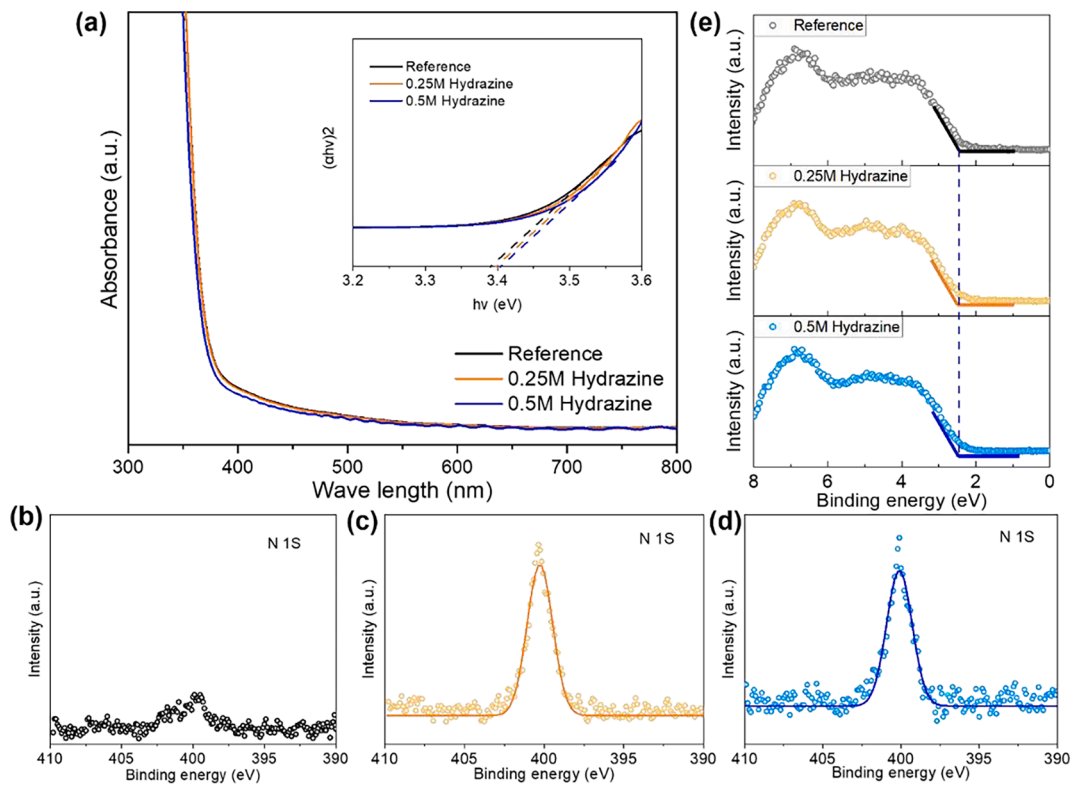


Fig. 4. (a) Comparison of the UV–visible absorption spectra of TiO₂ (black color line) and TiO₂ with 0.25 M hydrazine treatment (orange color line), and TiO₂ with 0.5 M hydrazine treatment (blue color line). The inset image is the calculated bandgaps. N 1S XPS high-resolution spectra acquired for (b) reference, (c) 0.25 M hydrazine treated, and (d) 0.5 M hydrazine treated samples. (e) The valence band spectra for the reference, 0.25 M hydrazine treated, and 0.5 M hydrazine treated samples.

not affect the long-term stability of PEC devices.

EIS measurements were carried out to understand the charge carrier dynamics and illustrate our conclusions for the results of the PEC performance for the reference and treated photoanodes. The EIS measurements characterize the charge transport and trapping within TiO₂ NRs/NPs hybrid structured photoanode, and the charge transfer at the TiO₂/electrolyte interfaces [37]. The impedance characteristics of the device were measured over a 10 mHz to 300 kHz frequency range, while applying a 200 mV potential bias, in dark condition, and the data were analyzed using an equivalent circuit. The sulfide based aqueous solution was used as electrolyte with same composition as used in the PEC measurements. Fig. 5 (c) shows the EIS results and the fitting for PEC devices based on the reference photoanode, 0.25 M, and 0.5 M hydrazine treated photoanodes. The equivalent circuit is shown in Fig. 5 (c). The electronic components represent the FTO ohmic resistance (R_1), the charge transport resistance inside the TiO₂ photoanode (R_2), the space charge capacitance (C_{sc}) are calculated from the constant phase element (CPE₁), the charge transfer resistance at the interface of the TiO₂/electrolyte (R_3), and Helmholtz capacitances (C_H) are calculated from the constant phase element (CPE₂) [38]. To calculate the C_{sc} and C_H , we used the following Eq. (4).

$$C_i = \frac{(R_i Q_i)^{\frac{1}{n}}}{R_i} \quad (4)$$

R_i is the charge transfer resistance (R_3), Q_i is the constant phase element of each capacitance (CPE _{x}), and n is the similarity between the CPE of each capacitance and a real capacitor.

The data for each of the parameters is shown in Table 1. The 0.25 M hydrazine treated photoanode shows a higher R_3 at the TiO₂/electrolyte interface, compared to the reference and 0.5 M hydrazine treated photoanodes. A higher R_3 value means a higher resistance for the electrons

transfer from the TiO₂ photoanode to the electrolyte. This leads a higher recombination resistance for the photogenerated carriers upon excitation at the photoanode/electrolyte interface. Therefore it reduces the overall non-radiative carrier recombination and yield better device performance, which is consistent with the obtained performance of the corresponding PEC devices. On the other hand, the 0.25 M hydrazine treatment shows a decrease in the R_2 compared to the reference and 0.5 M hydrazine treated samples. From these results, we demonstrated that the 0.25 M hydrazine treated sample enhanced the carrier dynamics by offering; i) lower trapping of electrons inside the TiO₂ that gives lower charge transport resistance inside the TiO₂ film, and ii) higher recombination resistance with higher R_3 at the TiO₂/electrolyte interface, as compared to the reference and 0.5 M hydrazine treated sample [39]. The higher R_2 and lower R_3 of the 0.5 M hydrazine photoanode, compared to the reference and 0.25 M hydrazine treated photoanodes indicates a higher number of traps, inside the TiO₂, and lower recombination resistance at the TiO₂/electrolyte interface, which reduces the overall device performance. These results are aligned with the PEC performance measurements discussed in the previous section and are described theoretically through DFT calculations (see detail in section 3.5.).

To further improve the performance of the PEC device, CdS/CdSe QDs were used as light harvesters instead of CdS QDs. Fig. 5 (d) presents the saturated photocurrent density versus potential (V vs RHE) curves. The saturated photocurrent density at 0.8 V vs RHE shows significant improvement by changing the QDs from CdS to the CdS/CdSe QDs. This change results in a saturated photocurrent density of 8.12 mA cm⁻², which represents a 50% improvement compared to the sample with CdS QDs (5.43 mA cm⁻²) [Fig. 5 (a)]. Moreover, the device with CdS/CdSe QDs maintains 80% of the initial photocurrent density, after 2 h of continuous one sun illumination, which is 13% higher than the device based on CdS QDs, as shown in Fig. 5 (e). This increase in the photocurrent density and long-term stability of the PEC devices based on CdS/

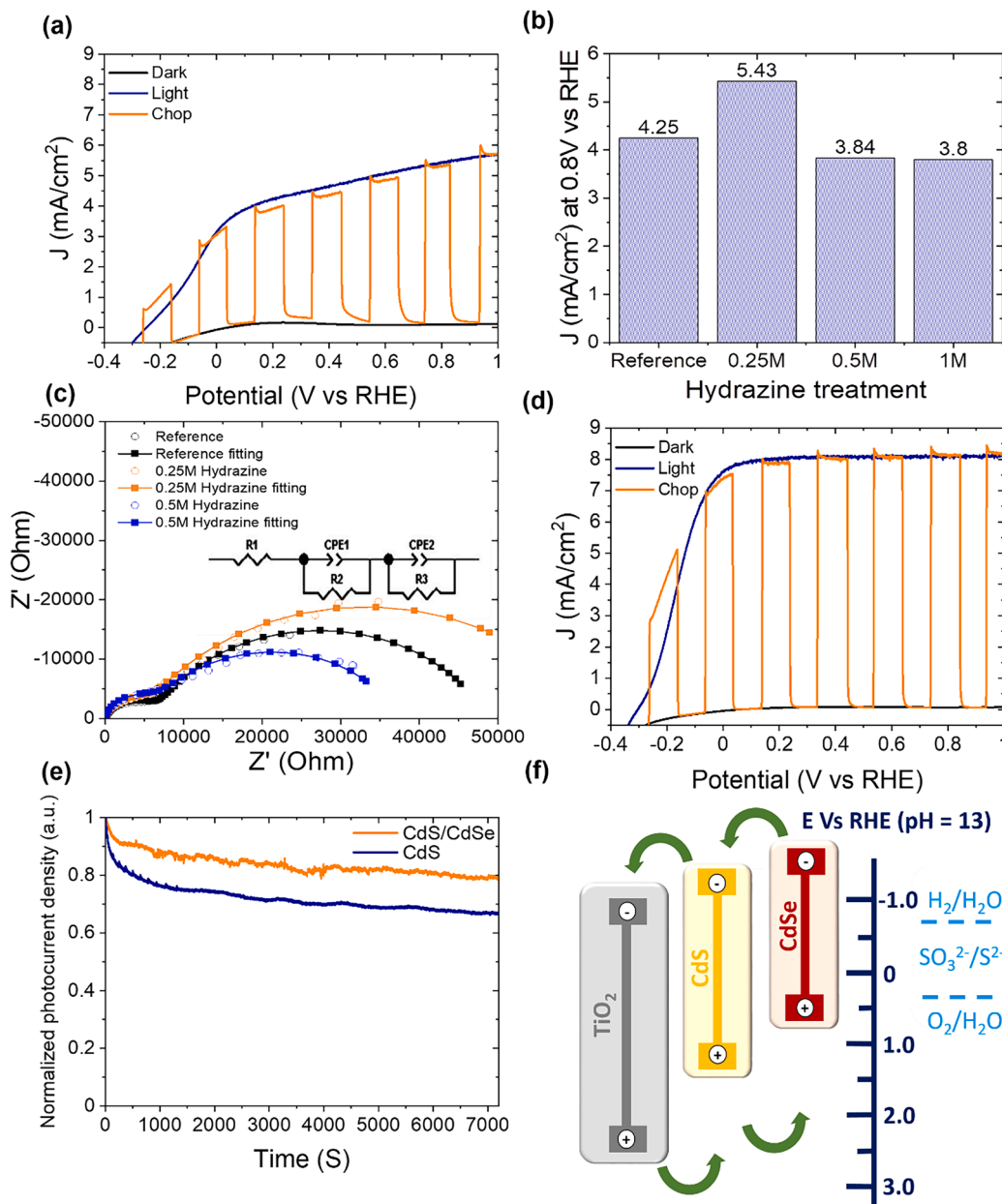


Fig. 5. PEC performance of the hybrid $\text{TiO}_2/\text{CdS}/\text{ZnS}$ photoanode in dark, light, and chop performance: (a) with 0.25 M hydrazine treatment (b) Comparison of the photocurrent density values of different PEC devices (at 0.8 V vs RHE). (c) EIS results in original data and its fit for the TiO_2 reference, 0.25 M and 0.5 M hydrazine treated samples with the equivalent circuit used to simulate the impedance spectra of the photoanode. (d) PEC performance of the hybrid $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$ in dark light, and chop. (e) Comparison of the long-term stability of PEC devices sensitized with CdS and CdS/CdSe QDs. (f) A schematic representation for the proper band alignment of the PEC device based on CdS/CdSe QDs.

Table 1

EIS measurement under the dark condition for TiO_2 with different hydrazine treatments.

Electronic component	Reference	0.25 M hydrazine	0.5 M hydrazine
R_1 (ohm)	13.72	12.84	13.87
R_2 (ohm)	5.09×10^3	4.83×10^3	5.9×10^3
C_{sc} (F)	9.81×10^{-6}	1.11×10^{-5}	9.01×10^{-6}
R_3 (Ohm)	3.79×10^4	4.68×10^4	2.93×10^4
C_H (F)	3.96×10^{-4}	1.57×10^{-4}	1.04×10^{-4}

CdSe QDs is due to the increase in the light-harvesting efficiency and improved carrier kinetics at the TiO_2/QDs interface. In particular, the injection rate of the photogenerated carriers was achieved with proper engineering of the band alignment of the QDs, as illustrated in Fig. 5 (f).

The results from the long-term stability of the hydrazine treatment and changing the QDs, from CdS to CdS/CdSe [Figures S7 (f) and 5(e)], confirm that the stability of the device is influenced by the type of QDs rather than the concentration of hydrazine treatment of the hybrid TiO_2 NRs/NPs film. To highlight the effect of the CdS/CdSe core/shell QDs structure, the PEC device was fabricated using optimized hybrid TiO_2 4 NRs/NPs sensitized with CdSe QDs. The resulting PEC device yield a saturated photocurrent density of 1.7 mA cm^{-2} (at 0.8 V vs RHE, Figure S8), which is 4.7 times lower than the PEC device based on hybrid TiO_2 4 NRs/NPs sensitized with CdS/CdSe QDs (8.12 mA cm^{-2} at 0.8 V vs RHE). These results emphasize the importance of CdS/CdSe core/shell QDs structure compared to the bare CdS and CdSe QDs. Gas chromatography (GC) measurements were performed to evaluate H_2 evolution from the as-synthesized system. The rate of H_2 evolution was $49.5 \mu\text{mol h}^{-1}$ with an average faradic efficiency (FE) of 80.48%, as

shown in Figure S9 (a). In addition, a comparison between the wavelength-dependent incident photon-to-current efficiency (IPCE) for the PEC devices based on hybrid photoanodes TiO₂ 4 NRs/NPs, with and without 0.25 M hydrazine treatment, sensitized with CdS/CdSe QDs was performed. Figure S9 (b) shows the comparison of the IPCE values over the spectrum range from 350 to 800 nm. The calculated IPCE values show that the hydrazine treatment enhances the conversion efficiency over the entire wavelength range, which is consistent with the results from the PEC device performance. All calculation details for the GC, FE, and IPCE are reported in the supporting information. A systematic comparison of PEC performance of the previously reported QD sensitized TiO₂-based photoanodes and our system is presented in Table S1, highlighting the merits of the hybrid network system of this work.

3.5. Computational model and methods

For the computational study, we modeled the anatase (101) [40] surface of TiO₂ [Fig. 6] and investigated its interaction with N₂H₄, N₂, and N at the surface, as well as at the interstitial sites. In addition, we investigated the anatase (101) surface with two interstitial N atoms to analyze the effect of increased hydrazine concentration. The following four adsorption sites were considered on the surface: five-fold coordinated Ti (denoted as Ti5c), six-fold coordinated Ti (denoted as Ti6c), two-fold coordinated O (denoted as O2c), and three-fold coordinated O (denoted as O3c) [Fig. 6]. In addition, two interstitial N-doped supercells were prepared by embedding one and two N atoms into the interspace.

A periodic supercell slab of 144 atoms and a vacuum region greater than 12 Å were used to represent the anatase (101) surface. The Quantum-Espresso [41] software package within the plane-wave pseudopotential approach was utilized throughout. The interaction between the valence electrons and the ionic core was described by the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) formulation [42] with Vanderbilt ultrasoft pseudopotentials [43]. To overcome the well-known limitations of DFT of the underestimation of the bandgap and delocalization of d and f electrons, we used the DFT + U formalism with U value of 4.2 eV applied to the Ti d states. This U value has been obtained by fitting the experimental data and has been used previously for analyzing doped anatase and rutile surfaces [44–47]. The kinetic energy cut-offs of 40 Ry and 400 Ry were used for wave functions and charge density, respectively, and the self-consistent field convergence criterion was set to 1×10^{-5} Ry. Each system was relaxed until the magnitude of the residual Hellman-Feynman force on each atom was less than 1×10^{-2} Ry per Bohr. All calculations were spin-polarized. The supercells were relaxed using Brillouin zone integrations performed at the gamma k-point. For the density of states (DOS) calculations, the Monkhorst-Pack [48] mesh of k-points ($6 \times 6 \times 4$ points) was used to sample the Brillouin zone. The bulk lattice parameters for

zero pressure anatase structure obtained by variable cell relaxation using DFT + U, $a = b = 3.776$ Å, and $c = 9.486$ Å, were found to be in good agreement with the experimental values of $a = b = 3.782$ Å and $c = 9.502$ Å, respectively [49].

Stability of TiO₂ with adsorbents and dopants. The absorption energy for adsorbates (δH_{ads}) and formation energy (E_f) for dopants are important parameters to evaluate the relative difficulty for the incorporation of adsorbents and dopants into the host lattice, respectively. Therefore, estimating the relative stability of the materials with the adsorbed and doped species is essential. Assuming that N₂H₄ treatment not only results in the interaction of N₂H₄ with the anatase surface but also acts as a source of N₂ and N species, we investigated the adsorption of N₂H₄, N₂, and N species on the four unique sites of anatase (101) surface. The adsorption energies of N₂H₄, N₂, and N species on the anatase (101) surface were calculated as

$$\delta H_{\text{ads}} = E_{\text{tot}} - E_{\text{bare}} - E_{\text{ad}} \quad (5)$$

where E_{tot} (E_{bare}) is the energy of the surface with (without) adsorbate and E_{ad} is the energy of the isolated adsorbate species calculated in the same supercell. For the interstitial N-doped surface, the defect formation energies were calculated using the following equation:

$$E_f = E_{\text{tot}} - E_{\text{bare}} - m\mu_N \quad (6)$$

E_{tot} (E_{bare}) is the energy of the surface with (without) interstitial N atoms; μ_N represents the chemical potentials of the N; m is the number of doped nitrogen atoms. The chemical potential of N is calculated from the total energy of the N₂ molecule ($\mu_N = (E_{\text{N}_2})/2$). The smaller δH_{ads} (E_f) value indicates that the defected TiO₂ system, due to adsorbents or dopants, is more stable.

The calculated δH_{ads} for N₂H₄ molecule on O2c, O3c, Ti5c, and Ti6c sites were -0.009 , -0.006 , -0.065 , and -0.015 Ry, respectively. The negative values of E_{ads} suggest that the physisorbed N₂H₄ [Figure S10] is stable on the anatase (101) surface. The calculated adsorption energy of the N₂ molecule on O2c, O3c, Ti5c, and Ti6c sites were -0.0001 , 0.5490 , 0.4663 , and -0.0031 Ry, respectively. Figure S11 represents the N₂ adsorbed at various sites of the anatase (101) surfaces. The configurations with negative values of E_{ads} [Figure S11 (a) and (d)] are stable but have N₂ physisorbed on the surface. Whereas the configurations with positive values of E_{ads} [Figure S11 (b) and (c)] are less stable, but showed chemisorbed N₂ adsorption in which the N₂ molecule bonds with surface Ti and O atoms, thus confirming the experimental observation of the presence of γ -N₂ bonding. The configurations with chemisorbed N₂ adsorption showed a little distortion both in the structures of adsorbed N₂ and in the anatase surface. The bond length of the N₂ molecule undergoes only a very small elongation of 1.41 Å (on O3c site, Figure S11 (b)) and 1.45 Å (on Ti5c site, Figure S11 (c)) compared to that of the isolated N₂ molecule (1.1 Å). Further, for both chemisorbed

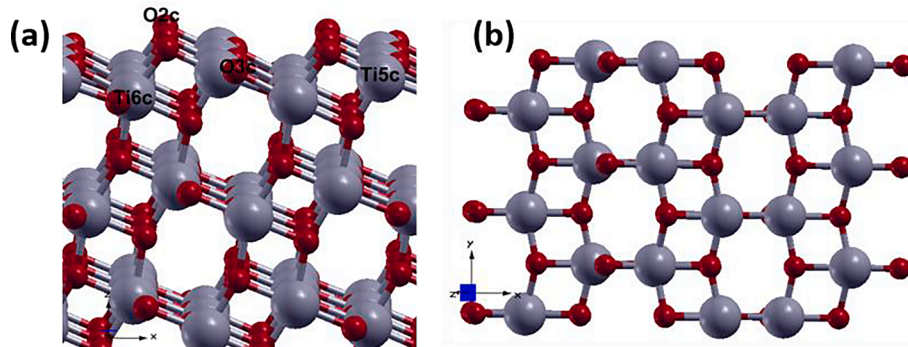


Fig. 6. (a) Side view and (b) top view of the anatase (101) surface representing the two-fold coordinated O (O2c), three-fold coordinated O (O3c), five-fold coordinated Ti (Ti5c), and six-fold coordinated Ti (Ti6c) sites considered for the adsorption of various adsorbents. Ti and O atoms are labeled as gray and red spheres, respectively.

configurations N₂ molecules interact with the Ti5c, O2c, and O3c atoms of the surface displacing them very slightly compared to the other surface atoms. This observation indicates that the chemisorbed N₂ molecules also have a very small influence on the surface structure. Lastly, Figure S12 represents the interaction of N atoms on the four sites of the anatase (101) surface, and Figure S13 represents the optimized geometry of the N atoms at the interstitial sites. As expected, N atoms chemisorb both on the surface and the interstitial sites. The E_{ads} values for N adsorption at O2c, O3c, Ti5c, and Ti6c surface sites are 0.255, 0.331, 0.321, and 0.322 Ry, respectively and at the interstitial site, E_{f} is 0.366 Ry for one N atom, and 0.678 Ry for two N atoms [Figure S13]. Clearly, N atoms at the surface or interstitial sites make TiO₂ slightly less stable.

Electronic structure. We calculated the electronic properties of the pristine anatase (101) surface, as well as doped anatase (101) surface with chemically adsorbed N₂, chemically adsorbed N, and interstitially doped N. Fig. 7 displays the total density of states (TDOS) and the projected density of states (PDOS) of various defective models. The bandgap (E_{g}) of the pure anatase surface is 2.8 eV as shown in Fig. 7 (a) and is significantly lower compared to the experimental value of 3.2 eV. The VB and CB of the anatase surface are mainly composed of delocalized O 2p electrons and Ti 3d states, respectively. The N₂ and N modified anatase surfaces also showed a similar bandgap of 2.8 eV [Fig. 7 (b-e)] with distinct mid-gap states. For the anatase surface with adsorbed N, N₂, and interstitial N atoms, two isolated N 2p states are localized at the top of the VBM and the bottom of the CB minimum (CBM). For the anatase surface with adsorbed N₂ [Fig. 7 (b)] and interstitial N [Fig. 7 (d)], the mid-gap state is at 1.0 and 1.8 eV below the CBM. However, for the surface with adsorbed N atoms, the N 2p states lie very close (0.55 eV) to the CBM. This indicates that the excess amount of N atoms on the anatase surface might result in the formation of recombination centers. Here electrons present in the TiO₂ CB (due to the neighboring QDs) can recombine with holes from TiO₂ nanorods, resulting in the reduced performance of the TiO₂/QD hybrid structure. For the surface with interstitial N, the position of the Fermi level indicates that this state might also be empty, although the distance between the mid-gap states and CBM is the maximum (1.8 eV). This might result in the formation of recombination centers. The DOS of the anatase surface with two interstitial N atoms [Fig. 7(e)] indicates that with the increase in the number of interstitial N atoms, the number of midgap states close to the CBM also increases, which can enhance the recombination centers significantly. Overall, one can conclude that the anatase surface with adsorbed or interstitially doped N can result in the creation of recombination centers, thereby reducing the performance of the TiO₂/QD system. However, the N₂-adsorbed surface seems to have the lowest possibility of forming recombination centers without competing with QDs for light harvesting. Therefore, the N₂-adsorbed surface might be responsible for the improved performance of hydrazine treated TiO₂. In other words, 0.25 M hydrazine treated samples might have increased the N₂ concentration, which enhances the performance of TiO₂ by not only preventing it from competing for visible light absorption with QDs but also creating no new counter-productive recombination sites. However, with the increase in the hydrazine concentration to 0.5 M, an increase in surface or interstitial N atoms is predicted, which then create the recombination centers, where electrons are transferred from the CB of QDs to CB of TiO₂ recombine with the holes present in TiO₂. This further increases light absorption in the visible region, due to the narrowing of the bandgap at a high concentration of N atoms, thus degrading the overall performance of the TiO₂/QD system.

In essence, we explored advanced surface engineering and doping techniques, which directly affect the optoelectronic properties in different applications (i.e. solar cells, photodetectors). Developing more efficient and stable optoelectronic devices, by understanding the importance of surface engineering, would facilitate the technological transition from the lab to the industrial scale. Future research directions may focus on tuning the electronic band structure to further suppress

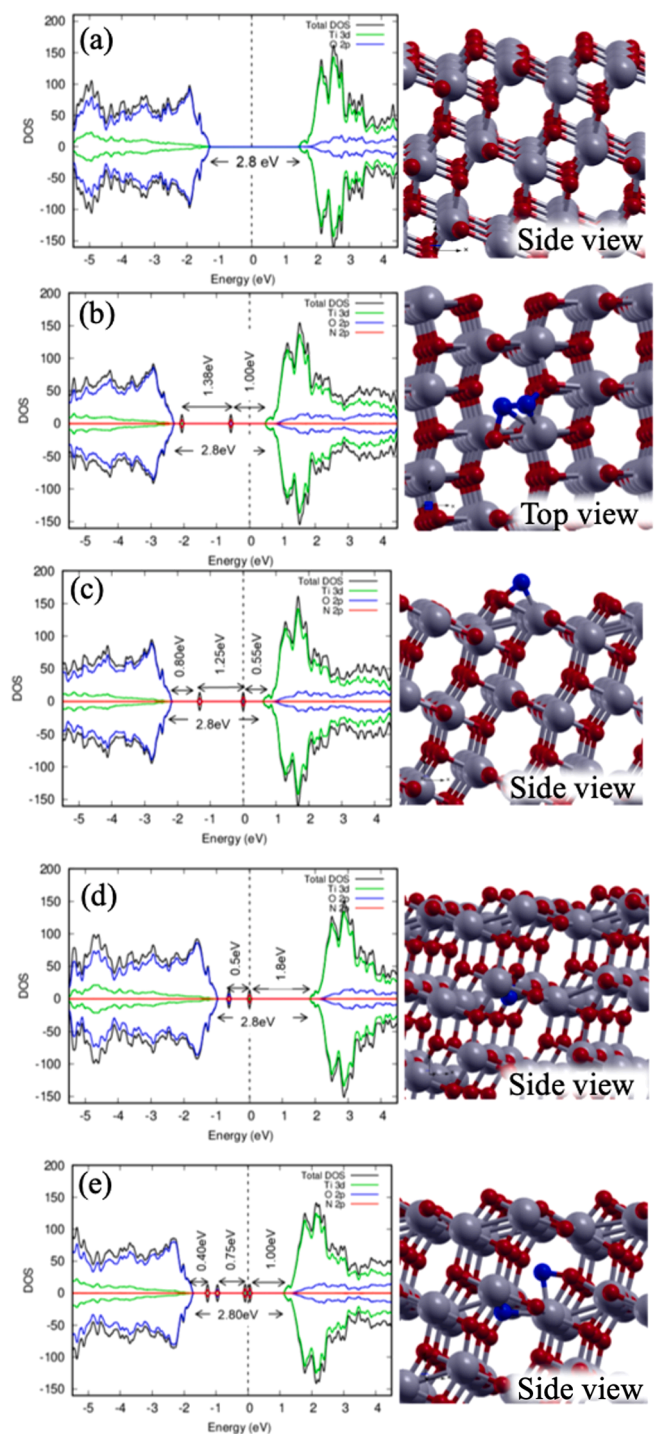


Fig. 7. The total density of states and projected density of states on the *p* and *d* orbitals of the anatase (101) surface with (a) no defects, (b) adsorbed N₂, (c) adsorbed N, (d) one Interstitial N atom, and (e) with two interstitial N atoms. The right panel represents the corresponding optimized structures for each surface.

trap sites that improve the carrier dynamics and the overall performance of the PEC devices.

4. Conclusion and prospective

In summary, we fabricated and optimized TiO₂ NRs/NPs hybrid structured photoanodes and used them in a solar-driven PEC water-splitting device for H₂ generation. A series of TiO₂ NRs arrays was

directly grown over the TiO₂ blocking layer coated FTO substrates by hydrothermal synthesis at constant temperature (150 °C) and reactant concentration, while using a different growth time (3–5 h). The optimization process of the TiO₂ NRs and TiO₂ NP leads to an improvement in device performance, using NPs with 10 µm thickness of 20 nm-sized and NRs with 1 µm thickness and ~ 79 nm diameter, to reach a saturated photocurrent density of 4.25 mA cm⁻² (at 0.8 V vs RHE), which represents a 172% improvement in performance as compared to the control device. We also highlight the effect of hydrazine treatment on device performance, with an optimum molar concentration of 0.25 M resulting in an additional improvement of 28% compared to the reference TiO₂ NRs/NPs hybrid structure. This enhanced performance was studied using EIS measurements to highlight the effect of nitrogen on the charge transport, inside the material, and charge transfer, between the photoanode and electrolyte. The hydrazine treated samples show higher R_{ct} with the electrolyte and lower internal R_{ox} of the electrons due to the trap screening effect. CdS/CdSe QDs were used instead of CdS QDs, to further improve device performance and stability. The saturated photocurrent density and stability were improved by 50% at 0.8 V and 13% after 2 h of continuous illumination, respectively. This significant improvement is attributed to the reduced non-radiative carrier recombination and enhanced photogeneration/injection rates of the charge carriers. Finally, a detailed computational study was conducted via DFT + U to understand the effect of hydrazine on the photoanode. It was found that the concentration of hydrazine affects the doping configuration in TiO₂. At 0.25 M hydrazine concentration, the N₂-adsorbed surface creates band states far below the CBM, thus having a low probability of acting as a recombination center while acting as a screen for the trap sites. However, at higher hydrazine concentration (i.e. 0.5 M) the surface or interstitial N doped TiO₂ creates bandgap states quite close to the CBM, which can easily act as recombination centers for the photoinjected electrons from the QDs to TiO₂. This work provides a new understanding of the role of N₂ doping, via hydrazine treatment, on the performance of the optimized TiO₂ NRs/NPs hybrid structured photoanodes, thereby providing a promising strategy to engineer the photoanode structure for enhanced performance of the PEC devices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ccej.2021.132425>.

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