



Constructing quantum dots sensitized TiO₂ nanotube p-n heterojunction for photoelectrochemical hydrogen generation

This is the peer reviewed (post-print) version of the following article:

Original

Constructing quantum dots sensitized TiO₂ nanotube p-n heterojunction for photoelectrochemical hydrogen generation / Abdelkarim, O., Mirzaei, A., Selopal, G.S., Yurtsever, A., Bassioni, G., Wang, Z.M., Chaker, M., Rosei, F.. - In: CHEMICAL ENGINEERING JOURNAL. - ISSN 1385-8947. - 446:(2022), pp. 137312-137312. [10.1016/j.cej.2022.137312]

Availability:

This version is available at: 11368/3087016 since: 2024-08-30T21:56:16Z

Publisher:

Published

DOI:10.1016/j.cej.2022.137312

Terms of use:

Some rights reserved. More details in the PostPrint rights section below.

License:

Attribution-NonCommercial-NoDerivatives 4.0 International

Publisher copyright

--

(Article begins on next page)

Constructing quantum dots sensitized TiO₂ nanotube p-n heterojunction for photoelectrochemical hydrogen generation

Omar Abdelkarim^{a,1}, Amir Mirzaei^a, Gurpreet S. Selopal^{a,b,*}, Ayca Yurtsever^a, Ghada Bassioni^c, Zhiming M. Wang^{b,d}, Mohamed Chaker^a, Federico Rosei^{a,*}

^a Institut National de la Recherche Scientifique, Centre Énergie, Matériaux et Télécommunications, 1650 Boul. Lionel Boulet, Varennes, Québec J3X 1P7, Canada

^b Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, PR China

^c Ain Shams University, Faculty of Engineering, Chemistry Division, Cairo P. O. Box 11517, Egypt

^d Institute for Advanced Study, Chengdu University, Chengdu, Sichuan 610106, PR China

ARTICLE INFO

Keywords:

Nanotubes
Quantum dots
Water splitting
P-n heterojunctions
Carrier dynamics

ABSTRACT

Photoelectrochemical (PEC) water splitting is a promising approach to convert solar radiation into hydrogen (H₂) as a clean fuel. The PEC device performance depends on the light harvesting efficiency of the photoanode and the carrier dynamics (i.e. separation/transport rate) at the photoanode/electrolyte interface. Herein, we report a photoanode architecture consisting of self-organized TiO₂ nanotubes (NTs) sensitized by CdS/CdSe quantum dots (QDs) and treated with a Cu-based solution to create a p-n heterojunction. Our results demonstrate that the TiO₂ NTs/QDs PEC device yields a photocurrent density of 4.18 mA.cm⁻² at 0.5 V vs RHE, which is 51 times higher than the device based on TiO₂ NTs only (i.e., 0.08 mA.cm⁻²) and 7 times compared to TiO₂/QDs nanoparticles (NPs) (i.e. 0.45 mA.cm⁻²) under one sun illumination. The p-type CuSe coating over the TiO₂/QDs NTs photoanodes forms a p-n heterojunction that improves the carrier dynamics. The resulting PEC device shows a 13% improvement in the photocurrent density. In addition, employing longer TiO₂ NTs improves the device's stability. Our results offer a simple and scalable method for the design and optimization of the photoanodes to enhance the performance of PEC and other optoelectronic devices.

1. Introduction

Sustainable development dictates an urgent transition from fossil fuels to renewable energy technologies, both due to the scarcity of the former and their carbon emissions byproduct, which is at the origin of climate change [1-4]. That is why the United Nations (UN) identifies the demand for a clean and sustainable source of energy as one of the sustainable development goals (SDGs) in the 21st century [5].

Photovoltaic cells transform solar radiation into electrical power [6]. However, solar energy is intermittent; one of the unresolved challenges is its efficient storage [7,8]. Improving solar electricity storage can be obtained through two approaches: i) improving the storage capacity of batteries and reducing their production cost [9]; ii) directly storing the solar energy as a clean chemical fuel [e.g. hydrogen (H₂)] [10,11].

Solar-driven photoelectrochemical (PEC) cells are considered a promising approach to generate H₂ from water splitting [12]. Typically, a PEC device consists of a photoanode, cathode, and electrolyte solution.

The photoanode is composed of a semiconductor that absorbs photons, which creates electron-hole pairs (i.e. exciton), where holes oxidize water to generate oxygen at the photoanode surface, while electrons transfer to the cathode, through an external circuit, and reduce water to generate H₂ [13]. In the last few years, considerable efforts have focused on improving the conversion efficiency of PEC devices to reach industrial-scale requirements [14-19].

The conversion efficiency of the PEC devices depends mainly on three factors: i) the light harvesting efficiency (LHE), ii) the photo-injected charge transfer efficiency within the photoanode, and iii) the interfacial charge transport efficiency at the surface of the photoactive material [20]. Different strategies were implemented in several articles to improve the conversion efficiency by focusing on each of the mentioned factors [21]. For instance, the LHE of the wide bandgap semiconductors was enhanced by doping with a transition metal [22,23], decorating with plasmonic nanoparticles [24-26], the addition of a scattering layer [27,28], or sensitizing with organic and inorganic

* Corresponding authors.

E-mail addresses: gurpreet.selopal@inrs.ca (G.S. Selopal), federico.rosei@inrs.ca (F. Rosei).

¹ (this is a note): On leave from Ain Shams University, Faculty of Engineering, Design and production Division, Cairo, Egypt P. O. Box 11517.

light harvesting materials [29-36]. While the charge transport of the photoinjected electron within the photoanode was optimized by designing one-dimensional (1D) nanostructured materials [37-39] and introducing carbon-based materials inside the wide bandgap semiconductor [40-42]. Finally, the charge transport efficiency was enhanced through surface modification and treatments, such as coating or using passivation materials [43-45], which reduces the influence of the surface states as trap sites and consequently enhances the carrier dynamics at the photoanode/electrolyte interface [46,47].

To date, numerous studies aimed to enhance the PEC device

performance by exploring each specific factor individually. However, an attempt to optimize all the factors together in terms of improving the performance of PEC devices is still lacking. In addition, focusing only on the conversion efficiency of the PEC devices without considering the complexity of the fabrication processes hinders the transition of this technology from lab scale to commercial products. Therefore, we report the fabrication of a simple photoanode architecture that is designed to enhance the PEC device performance. The photoanodes were fabricated with a simple cost-effective solution-based processes under ambient conditions. The photoanode consists of 1D TiO_2 nanotubes (NTs)

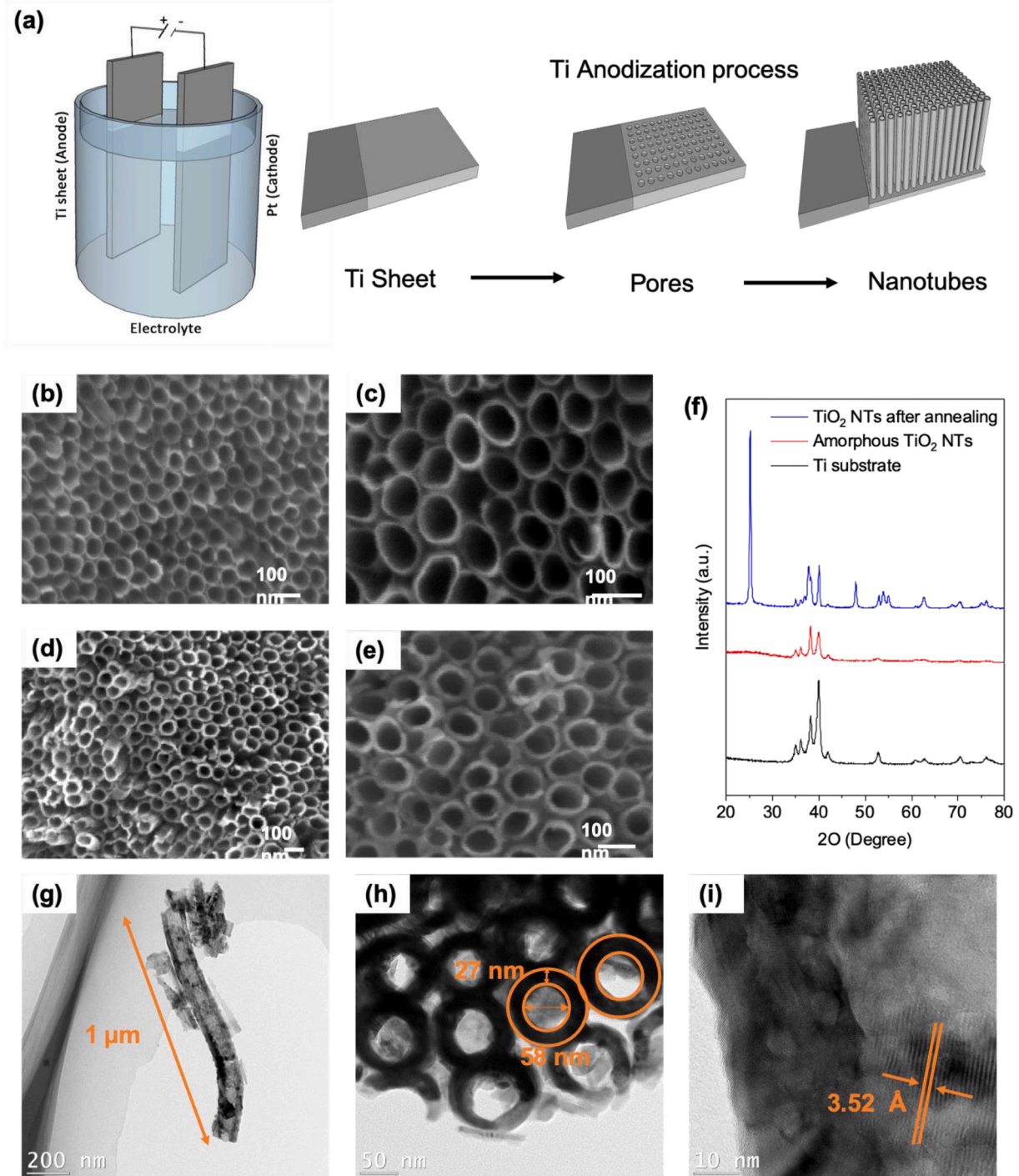


Fig. 1. (a) Schematic representation of the Ti Anodization process. Structural characterization of as-synthesized TiO_2 NTs: SEM images: (b) - (c) before annealing; (d) - (e) after annealing. (f) XRD pattern for Ti substrate (black color line) amorphous TiO_2 NTs (red color line) and crystalline TiO_2 NTs (blue color line). TEM images: (g) single TiO_2 NTs; (h) Top view of the TiO_2 NTs array; (i) high-resolution TEM showing the atomic resolution and interplanar spacing.

sensitized with CdS/CdSe QDs and CuSe coating to create a p-n heterojunction at the photoanode/electrolyte interface.

Nanoparticles (NPs) are widely employed in PEC applications due to their high active surface area that improves the catalytic activity [48]. However, the performance is still inadequate due to the undesirable carrier recombination that occurs inside the system. On the other hand, 1D TiO₂ NTs can provide a directional pathway for the photoinjected carriers [49], as well as a high specific surface area for QDs deposition [50], which makes them a promising candidate for PEC applications [51-54]. The self-organized growth of TiO₂ NTs has unique features such as controllable morphology and low contact resistance at the NTs/substrate interface [55]. In addition, the growth of TiO₂ NTs was carried out with the electrochemical anodization process, using a metallic titanium

substrate [56], which is potentially scalable and suitable for commercialization [Fig. 1 (a)]. The TiO₂ NTs photoanodes of different lengths were sensitized with CdS/CdSe QDs using successive ion layer adsorption and reaction (SILAR) [Fig. 2 (a)]. SILAR is a metal-organic decomposition (MOD) technique, which requires only a metal precursor decomposable in organic solvents. The QDs were directly grown on the photoanode (i.e. TiO₂ NTs) using solution-processable methods near ambient conditions without harsh pressure, temperature, vacuum, and inert environment. The simplicity of this method makes it desirable for up-scaling applications [57]. In comparison with other sensitization methods, the SILAR process is faster as compared to the chemical bath deposition process for the direct growth of QDs. In addition, the process is simpler than the hot injection method for the sensitization of colloidal

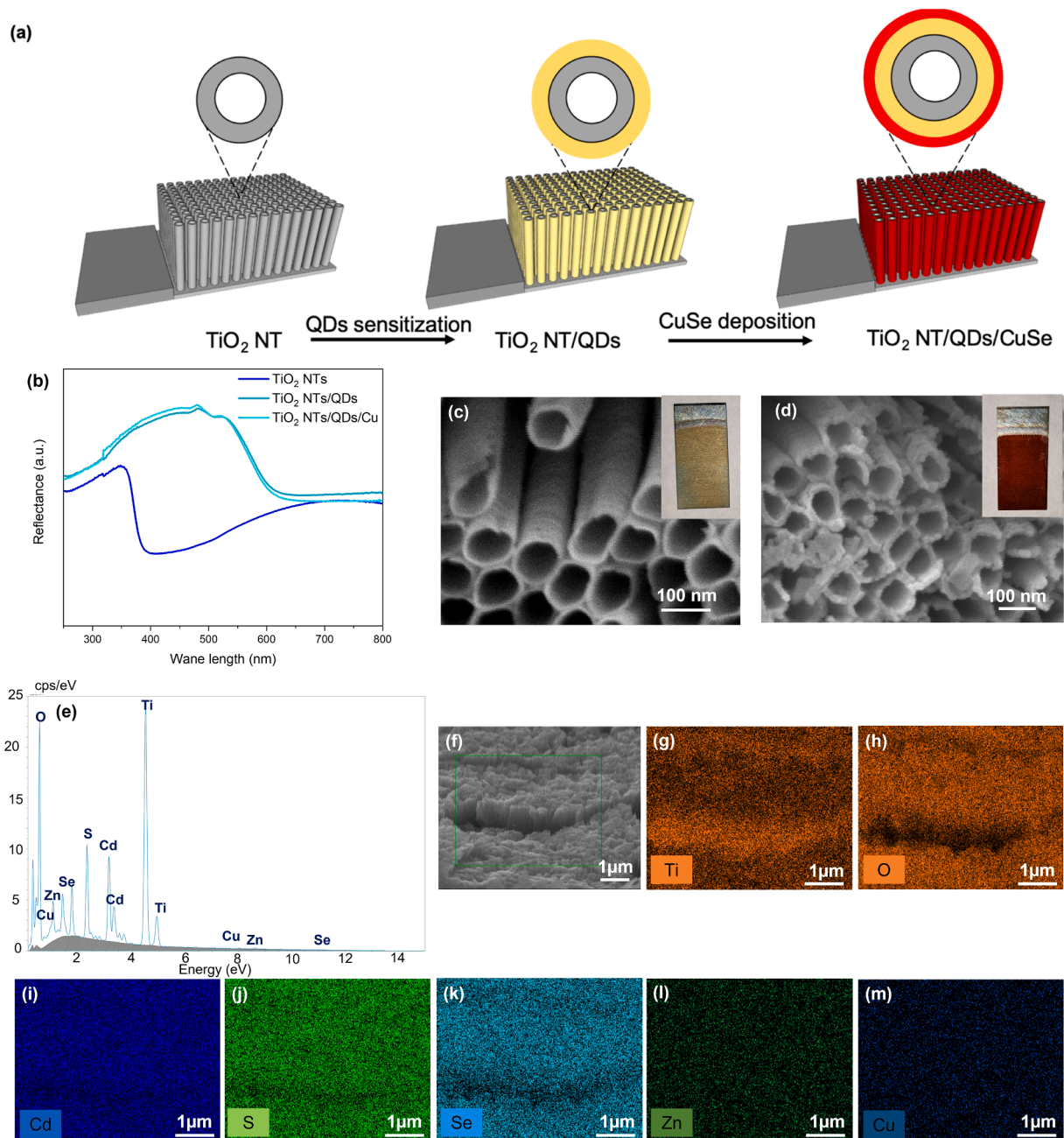


Fig. 2. (a) Schematic of QDs sensitization of TiO₂ NTs and CuSe deposition. (b) UV-Vis reflectance spectrum of TiO₂ NTs with QDs and CuSe deposition. Structural characterization of TiO₂ NTs before and after-sensation by CdS/CdSe QDs: SEM images of the TiO₂ NTs (c) before; (d) after CdS/CdSe QDs deposition (the inset images are visual inspection of the corresponding photoanodes). EDS analysis and elemental distribution of QDs and CuSe deposition on the TiO₂ NTs photoanode: (e) elemental map spectrum (f) EDS selected area for mapping; elemental distribution of (g) Ti; (h) O; (i) Cd; (j) S; (k) Se; (l) Zn; (m) Cu.

QDs, since this approach requires a complex reaction setup, high reaction temperature (250 °C), and an inert environment (Ar/N₂ atmosphere) during QDs synthesis. Furthermore, for the deposition of colloidal QDs, electrophoretic deposition (EPD) is used to disperse the as-synthesized colloidal QDs onto the electron transport layer, which requires high voltage (200 V) for long duration times (e.g., 2 h). The quantization effect of the QDs leads to a size-dependent optoelectronic property, such as tunable bandgap [31], multiple excitation generations (MEG) [58], and extraction of hot charge carriers before thermalization [59]. To further enhance the charge separation in the photoanode, the TiO₂ NTs sensitized by CdS/CdSe QDs were coated with the CuSe layer to create a p-n heterojunction at the photoanode/electrolyte interface. The CuSe layer was deposited with a simple approach, after the sensitization of CdS/CdSe QDs, by dipping the photoanodes in a Cu-based solution for a few seconds. This built-in p-n heterojunction enhances the surface potential and consequently improves the charge separation efficiency of the photogenerated electron-hole pairs [60-62].

In this work, we fabricate a series of devices to investigate our design concept for enhanced PEC H₂ generation. We also report the effect of the TiO₂ NTs length on the PEC device stability and examine it for longer TiO₂ NTs. This work provides a systematic way to design an efficient and cost-effective solar-driven PEC system for H₂ generation.

2. Experimental

2.1. Materials

Ti foils (0.89 mm thickness) with 99.7% purity were purchased from Alfa Aesar, USA. Ammonium fluoride (NH₄F ≥ 98%, Acros Organic, USA) and ethylene glycol (C₂H₆O₂ ≥ 99%, Fisher Scientific, Canada) were used for electrolyte preparation. The TiO₂ NPs paste, composed of 20 nm-sized anatase nanoparticles (transparent, code 18 NR-T), was supplied by GreatCell Solar.

The materials used for the QDs growth are cadmium acetate dihydrate (Cd (CH₃COO)•2H₂O, 98%), disodium sulfide nonahydrate (Na₂S•9H₂O ≥ 98%), sodium borohydride (NaBH₄), selenium powder (Se 99.5+ %), and zinc acetate dihydrate (Zn (CH₃COO)₂•2H₂O, ≥ 98%). All chemicals were bought from Sigma-Aldrich Inc. The solutions used for the QDs deposition are methanol and ethanol and were bought from VWR chemicals.

The material used for the CuSe deposition is copper (II) nitrate trihydrate (Cu (NO₃)₂•3H₂O, 98.0%) that was purchased from Sigma-Aldrich Inc.

The electrolyte used in the PEC measurement consists of sodium sulfite anhydrite (Na₂SO₃ ≥ 98%) and disodium sulfide nonahydrate (Na₂S•9H₂O ≥ 98%). The chemicals were obtained from VWR and Sigma-Aldrich Inc., respectively. All the chemicals were used as received without any purification.

2.2. Photoanode preparation

TiO₂ NTs were directly grown on Ti foil by anodization [63]. Briefly, Ti foil was cut into 10 × 25 mm² sizes and used as a working electrode, while Pt foil (10 × 10 mm²) served as cathode. Before anodization, Ti foils were cleaned with acetone, then isopropanol, and finally with deionized (DI) water in an ultrasonic bath for 10 min each and dried with high purity nitrogen gas. The anodization process was performed at room temperature in an electrolyte (97 vol% ethylene glycol, 3 vol% DI water with 0.5 wt% ammonium fluoride). A constant potential of 50 V was applied for 30 and 60 min (to investigate the effect of the TiO₂ NTs length on the PEC performance). After anodization, the TiO₂ NTs were washed in isopropanol for 2 min in an ultrasonic bath and dried with a nitrogen stream. The as-prepared TiO₂ NTs were then annealed at 500 °C for 1 h in an ambient atmosphere.

The TiO₂ NPs photoanode was prepared using the spin coating method. In particular, 200 mg of the TiO₂ mesoporous transparent paste

was mixed with 1.2 ml of ethanol and sonicated for 30 min to obtain a homogenous mixture. A 100 µl of the as-prepared mixture was poured on the same Ti sheet used for NTs and spin-coated for 1 min at 6,000 rpm. The samples were subsequently annealed at 120 °C for 6 min, then at 500 °C for 30 min. The final film thickness was measured using scanning electron microscopy (SEM); the thickness of the TiO₂ mesoporous film was 1 µm to match the same thickness as the TiO₂ NTs for relevant PEC device performance comparison.

2.3. Sensitization of the photoanode with CdS/CdSe QDs

SILAR is a solution-based low-cost process that was used to grow directly the CdS/CdSe QDs on the wide bandgap semiconductor. Briefly, the photoanode was dipped into the cationic and anionic precursor solutions one after the other. The immersion time was 1 min. The photoanode was then washed with the same solvent that was used in the corresponding precursor and subsequently dried with nitrogen. The quantity of QDs depends on the number of SILAR cycles.

For CdS QDs the precursors were 0.05 M Cd(CH₃COO)•2H₂O in 20 ml of methanol used as Cd²⁺ source, and 0.05 M of Na₂S•9H₂O in 20 ml of DI water/methanol (1:1) used as S²⁻ source.

For CdSe QDs the precursors were 0.03 M Cd(CH₃COO)•2H₂O in 20 ml of methanol used as Cd²⁺ source, and a mixture of 0.06 M of NaBH₄ and 0.03 M of Se powder in 40 ml of ethanol were used as Se²⁻ source. The Se²⁻ solution was prepared in a 250 ml glass flask sealed with a cap. Then the mixture was stirred vigorously under nitrogen flow for 45–50 min. Once the solution becomes transparent, it reveals that the Se is completely dissolved in the ethanol solution, and henceforth it was used for SILAR deposition.

A ZnS capping layer was used to passivate the surface and reduce the number of surface trap sites in the QDs. The deposition of ZnS was made through the same SILAR procedure. The precursors were 0.1 M Zn (CH₃COO)•2H₂O in 20 ml of methanol used as Zn²⁺ source, and 0.1 M Na₂S•9H₂O in 20 ml of DI water/methanol (1:1) used as S²⁻ source.

The number of cycles used was five for CdS, three for CdSe, and two for ZnS.

2.4. p-n heterojunction formation

To enhance the surface potential for a better separation efficiency of the photogenerated carriers, a p-n heterojunction was formed by depositing the CuSe layer. To form this layer, a solution of 2.5 mM of Cu (NO₃)₂•3H₂O in 40 ml of DI water was used. After the three SILAR cycles of the CdSe, the Se²⁻ was deposited on the photoanode, then immediately immersed in the as-prepared solution for 5, 10, 15, and 20 s. The CuSe layer was grown after the CdS/CdSe QDs sensitization. The ZnS layer was grown afterwards, to passivate the photoanode. Different immersion time was used to investigate the effect of the CuSe layer thickness on the performance of the PEC device.

2.5. Characterization

2.5.1. Structural analysis of the photoanode

Different techniques were applied to analyze the structure of the photoanode. The morphology of the TiO₂ NTs and NPs was investigated using SEM (JEOL JSM-7401F) and transmission electron microscopy (TEM) (JEOL 2100F). The chemical composition and elemental analysis of TiO₂ NTs sensitized by CdS/CdSe QDs with CuSe were determined by energy-dispersive X-ray spectroscopy (EDS) using a Tescan LYRA 3 system and X-ray photoelectron spectra (XPS) operating by a VG Scientific Escalab 220i-XL system. A monochromatic aluminum source with 1486.6 eV energy was used in the XPS experiments. The analysis of XPS peaks was carried out using the CasaXPS software. The crystal structure of the TiO₂ NTs, before and after annealing, with QDs and CuSe deposition, was examined by X-ray diffraction (XRD). XRD patterns were acquired using a Philips X'pert diffractometer, with Cu K_α (α = 0.15406

nm) radiation source. Diffuse reflectance configuration ultraviolet–visible spectroscopy (UV–Vis) equipped with an integrating sphere was used to acquire the absorption spectrum for the TiO₂ NTs and TiO₂NTs/QDs with and without CuSe.

2.5.2. PEC measurements

A three-electrode configuration cell was used to perform PEC measurements. The working, counter, and reference electrodes consist of the TiO₂ photoanode (NTs and NPs), Pt, and saturated Ag/AgCl, respectively. The electrolyte used was an alkaline-based solution (sulfide aqueous media), acting as hole scavenger, with a pH of ~ 13 . The electrolyte solution consists of 0.25 M Na₂S·9H₂O and 0.35 M Na₂SO₃. The solution was purged with nitrogen for 30 min, before the PEC measurement, to remove the dissolved oxygen. The photoanodes samples were covered with epoxy, from the back and front, while keeping an active surface area of 0.15 $\sim$ 0.2 cm² to be in contact with the electrolyte. Class AAA sun simulator (model SLB-300A by Sciencetech Inc.) was used to stimulate the solar spectrum by using a light source of 300 W xenon arc lamp and filtered with AM 1.5 G filter. The intensity of the light was calibrated using a silicon cell connected to a power meter to adjust the intensity at 100 mW cm⁻². The electrochemical measurements were performed using a Gamry potentiostat (interface 1010 E). The current density–voltage (*j*-*V*) curves were recorded using linear sweep voltammetry (LSV) measurement with potential range -1.3 to 0.1 V vs Ag/AgCl, with a scan rate of 20 mV/s, under dark, light, and chopped illumination. The transient photovoltage decay was performed to investigate the carrier dynamic. The open-circuit voltage (*V*_{oc}) was measured for 300 s, starting with 50 s under light and then the light was turned off for the rest of the experiment, to measure the *V*_{oc} decay rate. The electron lifetime of different photoanodes, which represent the recombination rate, was calculated from the *V*_{oc} decay measurement using the following Eq. (1) [64]:

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

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

The stability of the PEC devices was measured at -0.5 V vs Ag/AgCl under chopped illumination for 300 s by switching between light and dark every 30 s, and under contentious one sun illumination for 2 h.

In all PEC measurements, the potential was converted from Ag/AgCl to the reversible hydrogen electrode (RHE) using Eq. (2) [65].

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times \text{pH} + E_{Ag/AgCl}^o \quad (2)$$

2.5.3. Surface potential measurements

Kelvin probe force microscopy (KPFM) was used to measure the surface potential of the photoanodes, with and without CuSe deposition, to investigate the effect of the designed p-n heterojunction. The measurements were acquired under low and high LED light intensity inside the KPFM to stimulate the difference between light and dark responses of the photoanodes. KPFM was performed using an Enviroscope AFM system (Veeco Instruments, now Bruker) operating in tapping mode at room temperature, equipped with a magnetic Co/Cr-coated tip (MF-M01, NT-MDT) with a radius at the apex ~ 40 nm. We used the double-pass technique, mechanically oscillating the cantilever at its first resonance (71.9 kHz) for topography imaging in the first pass, and minimizing the electrostatically excited oscillations of the cantilever (at the same frequency) in the second pass while tracing the topography at a lift height of 50 nm. The amplitude of the AC excitation applied was 1 V.

3. Results and discussion

3.1. Growth and structural characterization of TiO₂ NTs

The anodization process of the Ti sheet is schematically presented in Fig. 1 (a). Briefly, Ti foil was used as a working electrode, Pt foil as a cathode, and a solution of 97 vol% ethylene glycol and 3 vol% DI water with 0.5 wt% ammonium fluoride as the electrolyte. A constant potential of 50 V was applied for 30 and 60 min (details reported in experiment section). Fig. 1 presents the structural characteristics of as-synthesized TiO₂ NTs before and after annealing. Fig. 1 (b) and (c) show the amorphous TiO₂ NTs before annealing. The anodization process of Ti foil results in the self-organized growth of amorphous TiO₂ NTs with controllable morphology. After annealing, the amorphous TiO₂ NTs crystallized, with insignificant differences in the morphology of the TiO₂ NTs as shown in Fig. 1 (d) and (e). The morphology of the self-organized TiO₂ NTs arrays through the anodization process has important features that affect the PEC performance. The consistent inner porous diameter of the TiO₂ NTs provides a high surface area for the QDs deposition. This porous structure also provides better electrolyte penetration that improves the carrier kinetics at the photoanode/electrolyte interface along with the directional pathway for the photogenerated carriers transfer, which enhances the charge transport efficiency. Another unique feature of as-synthesized TiO₂ NTs is that each NTs has its separate wall. This feature leads to the creation of mesoporous voids when the exterior walls of the NTs brought together. These mesoporous voids further increase the probability of QDs deposition and electrolyte penetration for the TiO₂ NTs based photoanode [Fig. 1 (b) and (d)]. XRD patterns were acquired to determine the crystallinity of the TiO₂ NTs before and after annealing. Fig. 1 (f) shows the XRD patterns for the Ti substrate, amorphous TiO₂ NTs, and crystalline TiO₂ NTs after annealing. The new peaks that appear at $2\theta = 25.2^\circ$ and 48° subsequent to the annealing process are mainly associated with the diffraction patterns of the crystalline TiO₂ anatase phase (JCPDS: 01-071-1167). The sharp (004) peak located at 37.8° suggests the directional growth of TiO₂ NTs in the *c* direction perpendicular to the Ti substrate. For a detailed structural analysis, high-resolution TEM images of the as-synthesized crystalline TiO₂ NTs were acquired. Fig. 1 (g) shows a TEM of a single TiO₂ NTs with an average length of ~ 1 μ m. Fig. 1 (h) displays the TEM top view of TiO₂ NTs film supported on the Cu-grid. It is observed that the as-synthesized TiO₂ NTs have an average inner diameter of ~ 58 nm and a wall thickness of ~ 27 nm, which are consistent with the SEM results. Fig. 1 (i) displays the atomic resolution image of the crystalline TiO₂ NTs. The lattice spacing is ~ 3.52 Å, which corresponds to the (101) plane of the tetragonal anatase phase of TiO₂ [66].

XPS was used for elemental analysis of the as-synthesized TiO₂ NTs. Figure S1 (a) and (b) display the survey scan spectra for the TiO₂ NTs before and after annealing, respectively. The N 1S peak at 400 eV and the F 1S peaks at 684.3 and 687.9 eV [Figure S1 (g) and (h)] are found before annealing, due to the presence of ammonium fluoride in the electrolyte during the preparation of TiO₂ NTs. However, after the annealing process, both the N and F 1S peaks were eliminated due to the oxidation of the TiO₂ NTs. Moreover, the Ti 2p peaks (Ti⁴⁺ 2p_{3/2} and Ti⁴⁺ 2p_{1/2}) are slightly shifted due to the annealing process [Figure S1 (c) and (d)]. This change in binding energy is related to the change in chemical bonding. The removal of valence charge electron, due to the oxidation process, increases the binding energy of the Ti 2p spectrum [67]. The content of the chemical species in the O 1S peaks (OH¹⁻ at 531.7 eV and O²⁻ 529.9 eV) changes during the annealing in the oxygen atmosphere [68]. The concentration of OH¹⁻ has decreased with respect to O²⁻ after annealing while maintaining the same peak position, as shown in Figure S1 (e) and (f).

3.2. QDs and CuSe deposition on TiO₂ NTs

CdS/CdSe QDs were deposited by SILAR on the TiO₂ NTs

photoanodes to increase the LHE and broaden the absorption range. The SILAR process involved five cycles of CdS QDs, followed by three cycles of CdSe, and finally two cycles of the ZnS passivation layer [Fig. 2 (a)]. UV-Vis spectroscopy was used to investigate the broadening effect of light-harvesting of the photoanodes sensitized with QDs. Fig. 2 (b) presents the reflectance spectrum of the reference photoanode (i.e. TiO₂ NTs), and QDs sensitized TiO₂ NTs with and without CuSe deposition. The reflectance spectrum presents a significant difference between the photoanode sensitized with QDs and reference photoanodes in the visible region, while an insignificant difference occurs with CuSe deposition. This difference is attributed to the photocatalytic activity of the CdS/CdSe QDs in the visible region. SEM images and visual inspection before and after sensitization with QDs are presented in Fig. 2 (c) and (d). The SEM images before and after sensitization display the difference in morphology of the TiO₂ NTs. The surface of the TiO₂ NTs before sensitization shows a smooth structure as compared to after sensitization. Moreover, the presence of QDs all over the surface of the TiO₂ NTs is obvious in the SEM image [Fig. 2 (d)]. Upon visual inspection, the TiO₂ NTs colour changed from light grey into dark red, which confirms the deposition of the CdSe QDs homogeneously in the TiO₂ NTs photoanode [inset Fig. 2 (c) and (d)]. To confirm the QDs decoration of the TiO₂ NTs walls from inside and outside, SEM images were acquired at higher magnification. The walls of the TiO₂ NTs are smooth [Figure S2 (a)], while after QDs deposition over the TiO₂ NTs [Figure S2 (b)] they become rough with the accumulation of nanoparticles outside and inside of the NTs walls.

The photoanodes were immersed in a Cu (NO₃)₂·3H₂O solution for different immersion times to construct a p-n heterojunction at the surface (more details are provided in the experimental section). EDS elemental mapping was used to confirm the deposition and homogenous distribution of the CdS/CdSe QDs inside the TiO₂ NTs photoanodes.

Fig. 2 (e) represents the EDS chemical composition spectrum for the TiO₂ NTs photoanodes, coated with CuSe. The elemental mapping was measured through the cross-sectional image of the TiO₂ NTs photoanodes sensitized by CdS/CdSe QDs, with CuSe deposition, and ZnS passivation layer. Fig. 2 (f) shows the cross-sectional SEM image of the photoanode and the green rectangle represents the elemental mapping scanning area. These images [Fig. 2 (g) – (m)] confirm the homogenous distribution of elemental Ti, O, Cd, S, Se, Zn, Cu inside the TiO₂ NTs/QDs photoanodes.

XPS spectra were acquired to further analyze the surface elemental composition and investigate the bonding nature and oxidation state of the TiO₂ NTs photoanodes sensitized with CdS/CdSe QDs and CuSe coating. Fig. 3 (a) displays the survey scan acquired from TiO₂ NTs photoanodes, which confirms the presence of elemental Ti, O, Cd, S, Se, Zn, and Cu. The high-resolution spectra for each element are displayed in Fig. 3 (b) – (h). The high-resolution Ti 2p spectrum consists of 2 peaks located at binding energies of 458.6 and 464.3 eV for Ti⁴⁺ 2p_{3/2} and Ti⁴⁺ 2p_{1/2} species, respectively [Fig. 3 (b)] [69]. The O 1s peaks located at binding energies of 529.9 and 513.7 eV are attributed to O⁻² and OH⁻¹ of the TiO₂ NTs, respectively [Fig. 3 (c)] [70]. Both the Ti 2p and O 1s spectrum were the same before and after QDs sensitization [Figure S1 (d) and (f)]. The elements of the QDs deposited on the TiO₂ NTs photoanode are identified in the high-resolution scans. The Cd 3d exhibits two peaks located at 405 and 411.7 eV, which are related to the Cd 3d_{3/2} and Cd 3d_{5/2} peaks, respectively [71] [Fig. 3 (d)] and the S 2p spectrum was fitted in two characteristic peaks, S 2p_{3/2} and S 2p_{1/2}, with binding energies of 161.2 and 162.4 eV, respectively [Fig. 3 (e)]. The shoulder appearing in Fig. 3 (e) at binding energies 159.8 eV is due to the overlap between the Se 3p and S 2p peaks [72].

Se 3d_{5/2} was also fitted into two characteristic peaks located at 53.8 and 54.4 eV, respectively [Fig. 3 (f)]. Zn 2p_{1/2} and 2p_{3/2} peaks are

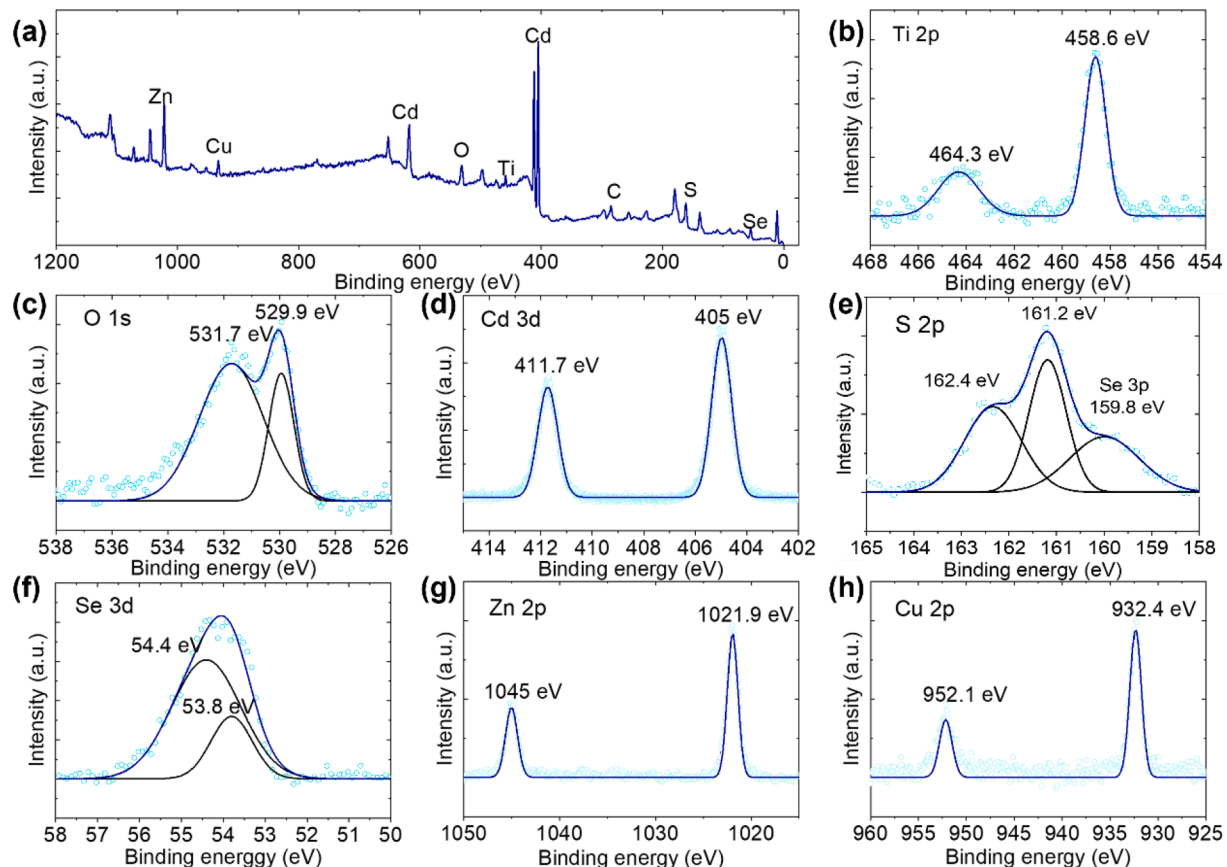


Fig. 3. XPS spectra acquired for TiO₂ NTs/CdS/CdSe/CuSe/ZnS photoanode: (a) full survey scan; (b) Ti 2p; (c) O 1s; (d) Cd 3d; (e) S 2p; (f) Se 3d; (g) Zn 2p; (h) Cu 2p.

located at 1021.9 and 1045 eV [Fig. 3(g)]. Finally, the Cu 2p peak positions are centered at 932.4 and 952.1 eV, referenced as Cu 2p_{3/2} and 2p_{1/2}. At those binding energies, the peaks are related to Cu (I) state [Fig. 3(h)] [73,74]. Based on these results, the Cu (I) state is combined with the 53.8 eV Se 3d_{5/2} peak to confirm the deposition of the CuSe layer [72,75]. The XPS spectra for the TiO₂ NTs photoanode without CuSe layer deposition are presented in Figure S3.

XRD patterns acquired from the photoanodes made of TiO₂ NTs, TiO₂ NTs/QDs, and TiO₂ NTs/QDs/CuSe, along with Ti foil are shown in Figure S4. All diffraction peaks detected from TiO₂/NTs are compatible with the anatase phase of TiO₂ (JCPDS: 01-071-1167) with the (101) main peak at 25.2° [76]. The Ti substrate main peak (101), located at about 40°, is detected in all photoanodes. Most of the diffraction peaks of CdS, CdSe, ZnS, and CuSe overlap with TiO₂ NTs (anatase) and Ti substrate, as shown in Figure S4. There is a difference in the diffraction peaks of TiO₂ NTs as compared to the sample with QDs and CuSe in the range of 26-30° and 44°. These differences are associated with (101) and (102) at 26.6° and 28.1° for CuSe (JCPDS:00-34-0171) [77], (220) at 44° for CdS (JCPDS:01-077-2306) [78], (002) at 25° for CdSe (JCPDS:00-019-0191) [79], and (220) at 44° for ZnS (JCPDS: 05-0566) diffraction pattern peaks [80].

3.3. PEC performance

A series of PEC devices were fabricated and investigated to characterize: i) the effect of sensitization of the TiO₂ NTs with CdS/CdSe QDs, ii) the difference in performance between the TiO₂ NTs and NPs with the same photoanode thickness and QDs deposition, iii) surface potential influence on device performance with different CuSe deposition time, and iv) the effect TiO₂ NTs length on the device stability. The PEC performance measurements were carried out under dark, continuous light, and chopped light (AM 1.5 G, 100 mW.cm⁻²). A three-electrode configuration cell was used. The working electrode was the as designed photoanodes, the counter electrode was Pt, and the reference electrode was Ag/AgCl (saturated with KCl).

Figure 4 (a) displays the *j*-V (vs RHE) of PEC devices based on three types of photoanode structures (i.e. TiO₂ NTs, TiO₂ NTs with QDs, and TiO₂ NPs with QDs). To highlight the effect of the QDs sensitization of

the TiO₂ NTs photoanode, we fabricated a PEC device with only TiO₂ NTs as a reference sample. The latter (i.e. TiO₂ NTs) yield a photocurrent density of 0.08 mA cm⁻² at 0.5 V vs. RHE under one sun illumination (AM 1.5 G, 100 mW.cm⁻²). After CdS/CdSe QDs sensitization (i.e. TiO₂ NTs/QDs), the photocurrent density is significantly enhanced and reaches 4.18 mA cm⁻² under identical measurement conditions, which is 51 times higher than that of the reference sample (i.e. TiO₂ NTs). This significant enhancement in the PEC device performance is mainly attributed to the broadening of the light-harvesting range of the QDs sensitized photoanode that generates more charge carriers under one sun illumination. The photoactivity variation with QDs sensitization in the visible region was apparent from the UV-Vis results in Fig. 2 (b). From these results, we highlight the effect of LHE on the overall device performance.

A 20 nm particle-sized titania paste was used to prepare the TiO₂ NPs photoanode with 1 μm thickness, using a spin coating technique, to match the same thickness of the TiO₂ NTs (details are reported in the experimental section). SEM images [Figure S5] confirmed the successful deposition of a homogenous mesoporous layer of TiO₂ NPs. The photocurrent density of the TiO₂ NPs, sensitized with CdS/CdSe QDs, was 0.45 mA cm⁻² at 0.5 V vs. RHE. The PEC device based on TiO₂ NTs photoanode shows a 7 times higher photocurrent density as compared to the TiO₂ NPs due to the enhancement in charge transport efficiency. The photogenerated carriers in the case of TiO₂ NTs have a directional pathway toward the backend of the photoanode, which improves the collection efficiency and reduces non-radiative carrier recombination. On the other hand, the TiO₂ NPs photoanode has a higher surface area as compared to the TiO₂ NTs photoanode. Consequently, a larger amount of QDs is deposited into the TiO₂ NPs photoanode, generating more charge carriers upon illumination. However, the zigzag pathway of the photoinjected charge carrier within the TiO₂ NPs photoanode increases non-radiative recombination processes, eventually deteriorating the overall device performance [81]. Fig. 4 (b) and (c) shows the dark, light, and chop *j*-V curve for the TiO₂ NTs and TiO₂ NTs with QDs, respectively.

The systematic comparison shows the effect of LHE on the PEC performance of TiO₂ NTs, which absorb only in the UV region (E_g = 3.2 eV), and the extended absorption range of the CdS/CdSe QDs sensitized

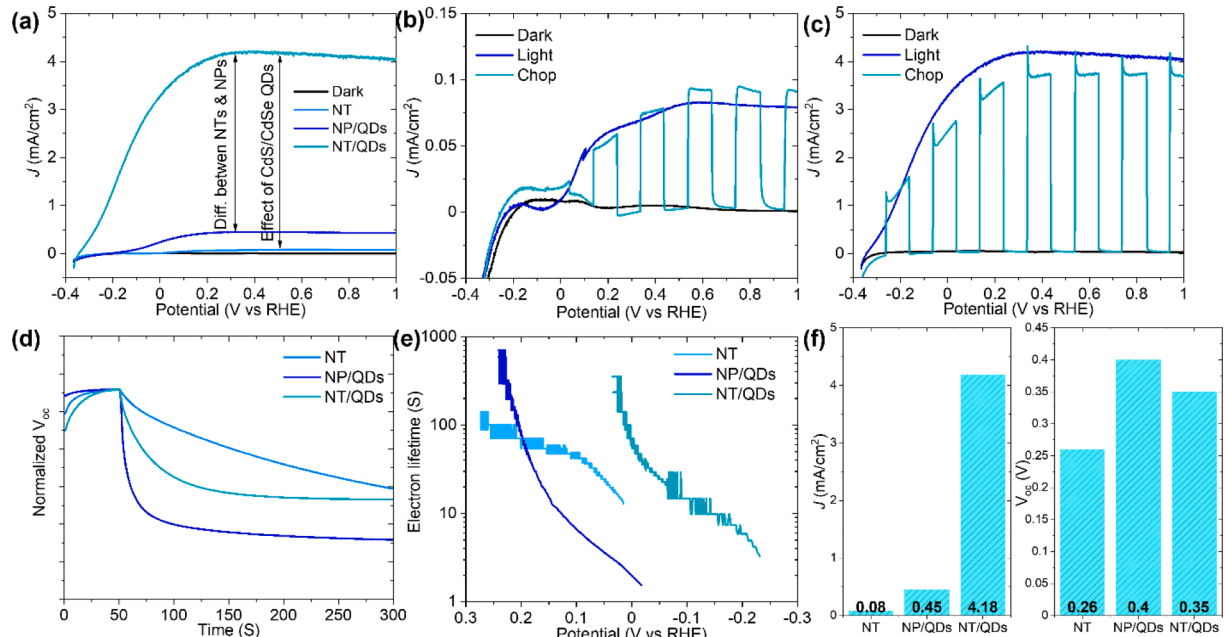


Fig. 4. (a) PEC performance of TiO₂ NTs, TiO₂ NPs/QDs, and TiO₂ NTs/QDs photoanodes under dark and light conditions. PEC performance of (b) TiO₂ NTs and (c) TiO₂ NTs/QDs under Dark, light and chopped conditions. (d) Normalized open-circuit voltage decay measurement. (e) Electron lifetime calculation. (f) Saturated photocurrent density at 0.5 V vs. RHE and photovoltage.

TiO₂ NTs towards the visible region. The open-circuit potential measurement can represent the amount of photovoltage that the device can produce through splitting the quasi-Fermi level under one sun illumination. To measure the photovoltage of the device, we performed transient photovoltage decay measurements. First the device was illuminated under one sun illumination for 50 s, then the light was turned off for 250 s and the potential decay was recorded [Fig. 4 (d)]. The difference between the potential under light and dark (when it reached the plateau) conditions is the photovoltage of the device. Fig. 4 (e) displays the electron lifetime calculations from the V_{oc} decay measurement. In open-circuit conditions, upon illumination, the photogenerated electrons are being accumulated in the conduction band of the photoanode. After turning off the light, these electrons start to recombine, which is reflected by the decay of the open circuit potential [Fig. 4 (d)]. The decay rate of the curve represents the tendency of photogenerated electrons to recombine with the oxidized species in the electrolyte and by internal traps inside the photoanode itself. Therefore, the electron lifetime calculations from the V_{oc} decay measurement can reflect the non-radiative carrier recombination for different photoanode designs. At any given potential, the electron lifetime of the device based on TiO₂ NTs/QDs is higher as compared to the case of TiO₂ NPs/QDs. This electron lifetime calculation shows that the carrier recombination inside the device based on QDs sensitized NTs is lower as compared to the NPs, which is consistent with the obtained j - V performance of the corresponding devices. Fig. 4 (f) represents the photovoltage and photocurrent density at 0.5 V vs. RHE of the three PEC devices. The photovoltage of the TiO₂ NPs with QDs shows a slightly higher photovoltage (0.05 V) as compared to TiO₂ NTs with QDs because i) it has a higher surface area with a higher amount of QDs deposition, which generates more charge carriers under illumination, and ii) the mesoporous structure of the photoanode leads to higher electrolyte penetration inside the device.

The surface potential enhancement is crucial to improve the charge separation process, which eventually improves the overall device performance. Creating a p-n heterojunction at the surface of the photoanode generates an electric field that can favor the separation of photogenerated carriers. The CuSe layer was formed by immersing the photoanode in Cu (NO₃)₂·3H₂O solution with different immersion times (details are provided in the experimental section). Fig. 5 (a) shows a schematic representation of the QDs sensitized TiO₂ NTs photoanode with CuSe coating. Fig. 5 (b) and (c) represent the j - V curve for the reference sample and the one with 15 s of CuSe deposition, respectively. A 13% improvement in the photocurrent density is recorded with CuSe deposition compared to the reference device. Fig. 5 (d) shows the effect

of CuSe deposition immersion time (s) on the photocurrent density of TiO₂ NTs/CdS/CdSe photoanode. By increasing the immersion time from 0 to 15 s, the photocurrent density increases from 4.18 to 4.72 mA·cm⁻² and then decreases from 4.72 to 3.16 mA·cm⁻² with a further increase in the immersion time from 15 to 20 s. The decrease in the photocurrent density can be attributed to the recombination of the photogenerated carriers that occurs at the surface of the photoanode, due to the generation of more photogenerated holes by the p-type semiconductor (CuSe). The stability of the PEC devices was investigated under chopped illumination for 300 s by switching between light and dark every 30 s [Fig. 5 (e)]. The potential used was at 0.4 V vs RHE. The photocurrent density for both samples was decreased at the end of the stability test. The reference device maintains 89.44% of the initial photocurrent density (from 3.6 to 3.22 mA·cm⁻²), while the device based on 15 s CuSe maintains 95.94% of its initial value (from 4.19 to 4.01 mA·cm⁻²). In addition, the long-term stability was investigated under continuous one sun light illumination (AM 1.5 G, 100 mW·cm⁻²) for 2 h at 0.4 V vs RHE, as shown in Fig. 5 (f), for PEC devices based on TiO₂ NTs/QDs and TiO₂ NTs/QDs/Cu. The long-term stability is consistent with the short chopped one and shows an improvement in device stability with the addition of the CuSe layer. The results show that the reference device maintains 62% of the initial photocurrent density, while the device made of TiO₂ NTs/QDs/Cu maintains 66% of the initial value after 2 h of continuous light illumination under one sun (AM 1.5 G, 100 mW·cm⁻²).

The device stability depends on the rate of the photocorrosion process. The main cause of photocorrosion is the accumulation of photogenerated holes at the surface of the photoanode. Holes are strong oxidants that can oxidize the QDs, and eventually, degrade the operational stability of the device. The CuSe layer enhances the carrier separation and the hole transfer efficiency from the QDs to the electrolyte, which prevents hole accumulation, and enhances the device stability. The V_{oc} decay measurements and the calculated electron lifetime are presented in Fig. 5 (g). The p-n heterojunction on the surface of the photoanode enhances the charge separation and injection in a closed-circuit cell [Fig. 5 (c) and (e)]. However, in an open-circuit measurement, the photogenerated carriers are being generated and separated, yet are still accumulated on the photoanode bulk (with no collection of the charge carriers) due to an open-circuit condition. When the light is turned off, more holes exist as compared to the reference device, due to the deposition of the CuSe layer. These holes in addition to the oxidized species in the electrolyte both increase the recombination rate of the photogenerated carriers on the surface of the photoanode. The results

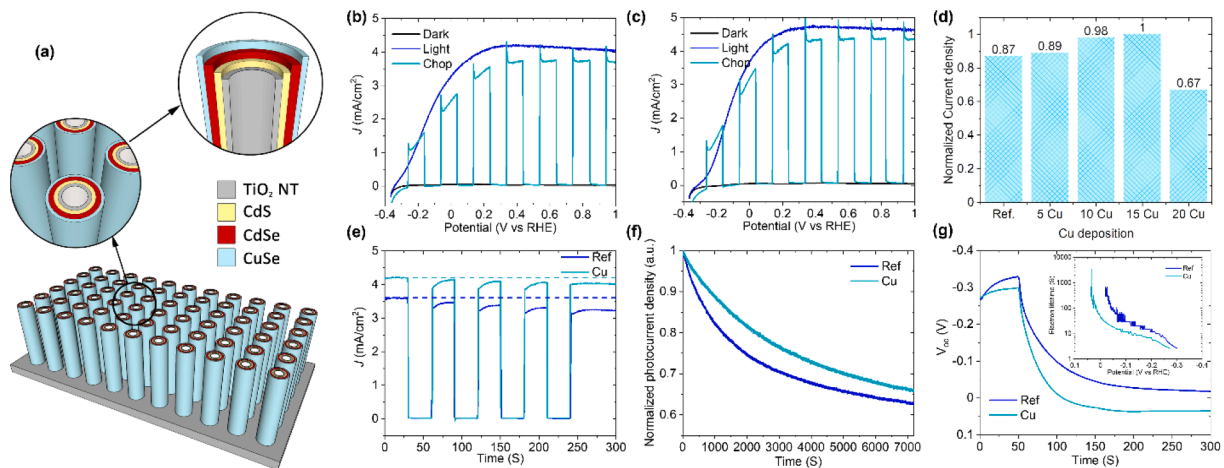


Fig. 5. (a) A schematic representation of the as designed photoanode. PEC performance under dark, light, and chopped conditions; (b) TiO₂ NTs/QDs (reference); (c) TiO₂ NTs/QDs/15s CuSe. (d) Normalized photocurrent density of photoanodes with $\times$ S CuSe deposition time. (e) Chopped illumination stability test. (f) Long-term stability test for the devices based on TiO₂ NTs/QDs and TiO₂ NTs/QDs/Cu. Transient photovoltage decay measurement: (g) Open-circuit voltage decay and inset electron lifetime calculation from open-circuit voltage decay.

indicate that the electron lifetime at any given potential is shorter in the case of CuSe as compared to the reference device.

To understand the effect of QDs sensitization and CuSe deposition on the flat band potential of different devices, Mott-Schottky plots ($M-S$ plots) were recorded [Figure S6 (a)]. The flat band potential is identified through the extrapolation of the slope obtained in the measurement. All devices show a positive slope, which reflects the dominance of the n-type semiconductor on the photoanode design, due to the presence of TiO_2 and CdS/CdSe QDs. In the case of TiO_2 NTs/QDs/Cu, the $M-S$ plot shows the same behavior as compared to TiO_2 NTs/QDs with less $\frac{1}{C_{sc}}$ due to the presence of the p-n junction. Similarly, The TiO_2 NTs substrate was sensitized with CuSe by depositing the photoanode in the same Se precursor used in the SILAR method for 1 min and then 15 s in the Cu-based solution. The CuSe is considered a p-type semiconductor and should indicate a negative slope in the $M-S$ plot. However, since the CuSe deposited layer is very thin compared to the quantity of TiO_2 , a positive slope was obtained with less $\frac{1}{C_{sc}}$ as with respect to the TiO_2 NTs substrate. The flat band potential of the devices sensitized with QDs was shifted by 0.1 V due to the change in the electronic band structure. To confirm the deposition and the effect of the CuSe layer on the TiO_2 NTs substrate, the photocurrent density was measured as shown in Figure S6 (b). The deposition of CuSe shows a significant improvement in photocurrent density under illumination as compared to the bare TiO_2 NTs. However, the obtained value (0.28 mA.cm^{-2}) is considerably lower as compared to the devices based on TiO_2 NTs/QDs and TiO_2 NTs/QDs/Cu.

We studied the influence of the length of the TiO_2 NTs on the overall device performance. Figure S7 (a) displays the difference in the photocurrent density at 0.5 V vs RHE between the short (1 μm) and long (2 μm) TiO_2 NTs photoanodes, with and without 15 s CuSe deposition. The photocurrent density decreases, from short to long TiO_2 NTs, for both devices based on TiO_2 NTs/QDs by 11%, from 4.18 to 3.72 mA cm^{-2} , and TiO_2 NTs/QDs/CuSe by 14%, from 4.72 to 4.05 mA cm^{-2} . Figure S7 (b) and (c) present the $j-V$ curves for the long TiO_2 NTs/QDs and TiO_2 NTs/QDs/CuSe devices, respectively. The photocurrent density was reduced for both samples as compared to the short one as the mean free path length for the photogenerated carriers increases with a longer TiO_2 NTs, which increases the probability of charge carrier recombination and eventually degrades the photocurrent density of the PEC device. Figure S7 (d) displays the difference between the stability of short and long TiO_2 NTs based devices in the chopped test measurement. The photocurrent stability for both devices increased with longer TiO_2 NTs. The thickness of the photoanode has a dual effect. As the thickness increases, the available active surface area increases, which increases the amount of QDs deposition. On the other hand, the non-radiative carrier recombination of the photogenerated carriers increases, as it takes more time to reach the back contact of the photoanode, and the probability of the charge carriers to be recombined with the oxidized species in the electrolyte or by internal trap sites inside the photoanode increases. Figure S7 (e) presents the chopped illumination for the 300 s stability test. The increase in the photoanode thickness improves the stability of the device as shown in Table 1.

The photocorrosion process occurs as explained before. However, the

Table 1
Stability of different PEC devices.

PEC device	Thickness (μm)	Initial photocurrent density (mA.cm^{-2})	Final photocurrent density (mA.cm^{-2})	Stability (%)
TiO_2 /QDs	1	3.6	3.22	89.44
TiO_2 /QDs/CuSe	1	4.19	4.01	95.94
TiO_2 /QDs	2	3.53	3.46	98.01
TiO_2 /QDs/CuSe	2	3.91	3.85	98.46

excess availability of QDs and the additional electrolyte penetration inside the photoanode enhance the kinetics of the hole scavenger process at the photoanode/electrolyte interface. Both these parameters improve the operational stability of the device. Figure S7 (f) presents the V_{oc} decay measurement with an almost comparable decay rate between the reference and the TiO_2 NTs/QDs/CuSe devices. The electron lifetime calculation is presented in the inset of Figure S7 (f). The results are consistent with the shorter TiO_2 NTs photoanode but with a lower effect of the CuSe coating layer on the electron lifetime of the PEC device, as the impact of photogenerated holes from the p-type semiconductor (CuSe) is reduced as compared to the excess availability of the n-type semiconductors (CdS/CdSe QDs). A systematic comparison of the photocurrent density of the previously reported PEC devices, based on TiO_2 NTs sensitized with CdS/CdSe, and the results of this work are presented in Table S1.

3.4. Surface potential measurements

KPFM was used to measure the influence of surface potential created by the p-n heterojunction. This was conducted by measuring the difference in work function (Φ) at the surface of the photoanode with and without CuSe deposition, in both light and dark conditions (details reported in the experimental section). Fig. 6 (a) shows the AFM topography image, using tapping mode, of the reference sample (without CuSe), while Fig. 6 (b) shows the same image with different light intensity to stimulate dark and light conditions. Fig. 6 (c) and (d) represent the AFM topography and difference in lighting conditions for the photoanode with CuSe coating, respectively. Fig. 6 (e) illustrates the results of the KPFM line scan for both samples under light and dark conditions. The Φ difference for the reference sample between dark and light is ~ 35.1 mV, while the sample with CuSe shows a higher Φ difference, reaching ~ 52.7 mV, as compared to the reference sample. The higher difference in Φ indicates a higher surface potential difference, between light and dark, which leads to a higher separation and injection efficiency of the photogenerated carriers in the operational conditions of the PEC device. However, the surface potential is not very stable due to the charging effect [82]. The band diagram for the n-type semiconductor and p-n-heterojunction under dark (left) and illumination (right) is shown in Fig. 6 (f). The splitting of the quasi-Fermi-level occurs according to the predominant charge carriers. In the case of p-n heterojunctions, both electrons (from n-type semiconductors) and holes (from p-type semiconductors) are generated upon illumination. This dual photogeneration increases the splitting of the quasi-Fermi-level as compared to only electrons in the n-type semiconductor. As the difference in the quasi-Fermi-level increases, a larger photovoltage is generated in the PEC device. From the KPFM results, we conclude that the photoanode with p-n heterojunction has a higher surface potential, which results in better separation/injection of charge carriers. This demonstration is consistent with the PEC results of the corresponding photoanodes. A schematic of the effect of p-n heterojunction at the surface of CdS/CdSe QDs sensitized TiO_2 NT photoanode on the carrier dynamics is shown in Fig. 6 (g). Suitable engineering of the band alignment of the CdS/CdSe with the TiO_2 enhances the generation and injection of the charge carriers. When the CuSe layer is added, a p-n heterojunction forms at the interface. This p-n heterojunction further enhances the carrier kinetics and increases the charge separation/injection rate, which results in better PEC performance.

4. Conclusions and perspectives

In summary, we investigated different strategies to enhance the performance of TiO_2 photoanodes in PEC H_2 generation. The fabrication methods use simple low-cost solution-based processes under the ambient condition that makes it easy for commercialization. Ti substrates were used to grow self-organized TiO_2 NTs that are used as a template for the CdS/CdSe QDs sensitization process by SILAR. The

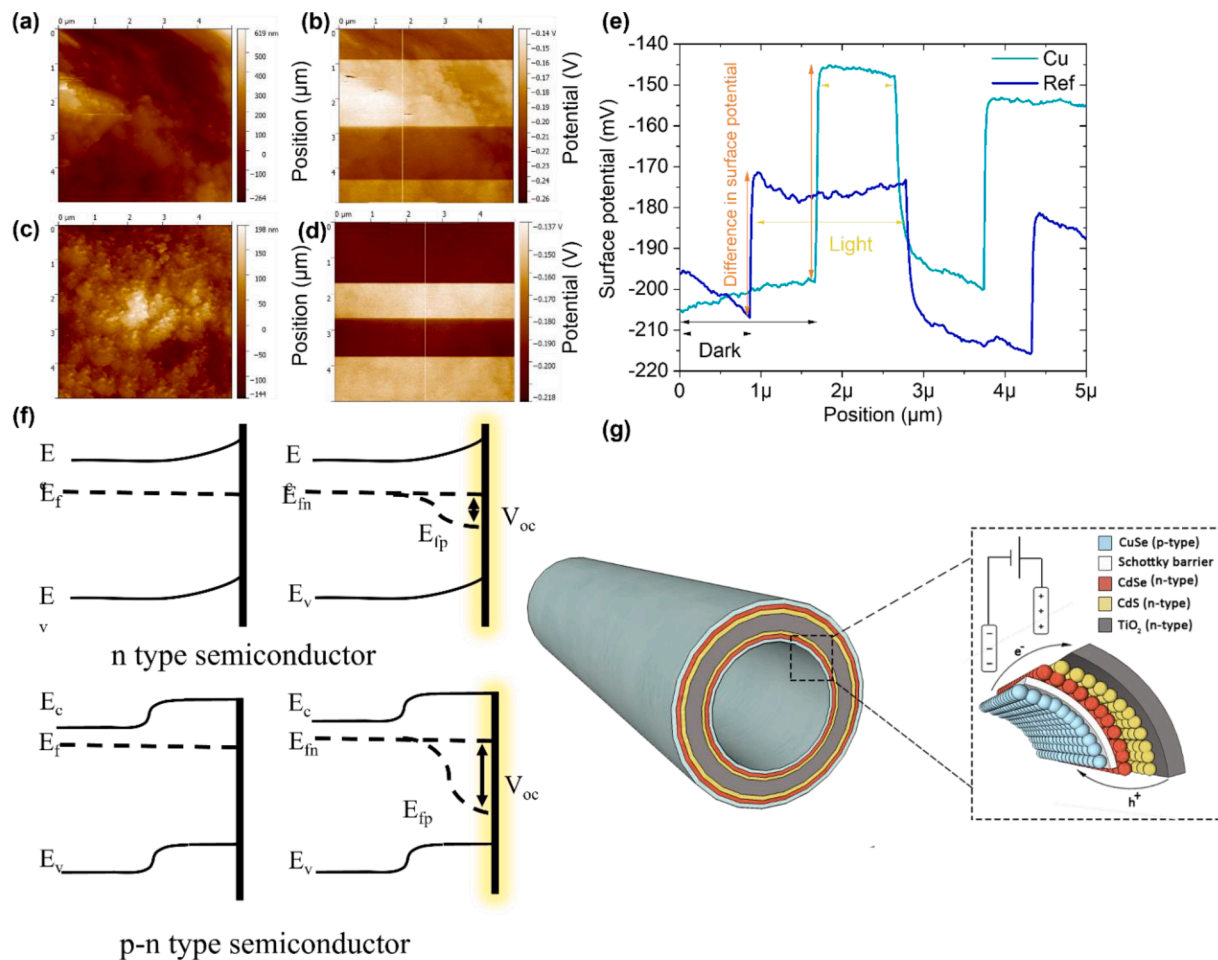


Fig. 6. Standard and chopped illuminated AFM topography images: (a)-(b) TiO₂ NTs/QDs; (c)-(d) TiO₂ NTs/QDs/CuSe, respectively. (e) KPFM surface potential line scan. (f) Band diagram representation of the TiO₂ NTs/QDs (n-type) and TiO₂ NTs/QDs/CuSe (p-n type) under dark and light. (g) A schematic representation of the effect of the p-n heterojunction in PEC device carrier dynamics.

sensitization leads to an increase in the photocurrent density that reaches $4.18 \text{ mA} \cdot \text{cm}^{-2}$ (at one sun illumination, AM 1.5 G, $100 \text{ mW} \cdot \text{cm}^{-2}$), which is 51 times higher than the control device. The change in the photoanode structure, between TiO₂ NPs and NTs, with the same thickness and QDs sensitization, yields an improvement of the photocurrent density by a factor of 7 when using TiO₂ NTs as compared to TiO₂ NPs. These results highlight the effect of enhancing the LHE and carrier transport efficiency on the overall PEC device performance. In addition, the deployment of nanoscale p-n heterojunction at the surface of the photoanode was performed with a fast and simple approach. The process requires dipping the photoanode in a Cu-based solution for 15 s after depositing the CdS/CdSe QDs. The deposition of CuSe (p-type semiconductor) enhances the photocurrent density by 13%, reaching $4.72 \text{ mA} \cdot \text{cm}^{-2}$. The surface potential for the reference device and the one based on the p-n heterojunction was investigated through KPFM measurements under dark and light conditions. This work demonstrates the potential of utilizing one-dimensional NTs as an electron transport layer and template for QDs deposition that can be used in other solar energy conversion devices. The employment of one-dimensional NTs and p-n heterojunction at the surface of the photoanode offer better carrier dynamics. Overall, this work provides a pathway to optimize the photoanode structure to further improve the performance of PEC H₂ generation and other emerging optoelectronic devices in a cost-effective way that can be easily scaled up for industrial applications.

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.

Acknowledgments

The authors acknowledge funding from the Natural Science and Engineering Research Council of Canada (M.C. and F.R., individual Discovery Grants) and the Canada Foundation for Innovation (CFI) for infrastructure and its operating funds. M.C. and F.R. acknowledge partial salary support and funding from the Canada Research Chairs program. O.A. acknowledges the UNESCO Chair in MATECSS for a Ph.D. Excellence Scholarship. A.M. is grateful to the Fonds de recherche du Québec - Nature et technologies (FRQNT) for an individual fellowship (282732). G.S.S. acknowledges the UNESCO Chair in MATECSS for a PDF Excellence Scholarship and is grateful to the University of Electronic Science and Technology of China and the China Postdoctoral Science Foundation (Grant No. Y02006023607941). Z.M.W. acknowledges the National Key Research and Development Program of China (2019YFB 2203400) and the "111 project" (B20030).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2022.137312>.

- [1] C. Okkerse, H.V. Bekkum, From fossil to green, *Green Chem.* 1 (1999) 107–114, <https://doi.org/10.1039/A809539F>.
- [2] G. Bassioni, A study towards “greener” construction, *Appl. Energy* 93 (2012) 132–137, <https://doi.org/10.1016/j.apenergy.2010.09.012>.
- [3] V. Smil, *Energy: a beginner's guide*, Simon and Schuster, London, England, 2006.
- [4] J.S. Feser, G. Bassioni, A.K. Gupta, Effect of naphthalene addition to ethanol in distributed combustion, *Appl. Energy* 216 (2018) 1–7, <https://doi.org/10.1016/j.apenergy.2018.02.090>.
- [5] M.S. Dresselhaus, L.L. Thomas, Alternative energy technologies, *Nature* 414 (2001) 332–337, <https://doi.org/10.1038/35104599>.
- [6] N.S. Lewis, D.G. Nocera, Powering the planet: chemical challenges in solar energy utilization, *Proc Natl Acad Sci.* 103 (2006) 15729–15735, <https://doi.org/10.1073/pnas.0603395103>.
- [7] G.R. Timilsina, L. Kurdgelashvili, P.A. Narbel, Solar energy: Markets, economics and policies, *Renew. Sust. Energy. Rev.* 16 (2012) 449–465, <https://doi.org/10.1016/j.rser.2011.08.009>.
- [8] M. Abdelaal, M.H. Abdellatif, M. Riede, G. Bassioni, Studying the effect of high substrate temperature on the microstructure of vacuum evaporated TAPC: C60 organic solar thin films, *Materials* 14 (2021) 1733, <https://doi.org/10.3390/ma14071733>.
- [9] B. Nykvist, M. Nilsson, Rapidly falling costs of battery packs for electric vehicles, *Nat. Clim. Change.* 5 (2015) 329–332, <https://doi.org/10.1038/nclimate2564>.
- [10] L. Schlapbach, A. Züttel, Hydrogen-storage materials for mobile applications, *Mater. Sustain. Energy* (2011) 265–270, https://doi.org/10.1142/9789814317665_0038.
- [11] K.R.G. Burra, G. Bassioni, A.K. Gupta, Catalytic transformation of H₂S for H₂ production, *Int. J. Hydrog. Energy* 43 (2018) 22852–22860, <https://doi.org/10.1016/j.ijhydene.2018.10.164>.
- [12] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, *Nature* 238 (1972) 37–38, <https://doi.org/10.1038/238037a0>.
- [13] M. Grätzel, Photoelectrochemical cells, *Mater. Sustain. Energy* (2011) 26–32, https://doi.org/10.1142/9789814317665_0003.
- [14] F. Li, D. Benetti, M. Zhang, J. Feng, Q. Wei, F. Rosei, Modulating the 0D/2D interface of hybrid semiconductors for enhanced photoelectrochemical performances, *Small Methods* 5 (2021) 2100109, <https://doi.org/10.1002/smtd.202100109>.
- [15] Y. Hou, X. Zhuang, X. Feng, Recent advances in earth-abundant heterogeneous electrocatalysts for photoelectrochemical water splitting, *Small Methods* 1 (2017) 1700090, <https://doi.org/10.1002/smtd.201700090>.
- [16] Y. Tachibana, L. Vayssieres, J.R. Durrant, Artificial photosynthesis for solar water-splitting, *Nat. Photonics* 16 (2012) 511–518, <https://doi.org/10.1038/nphoton.2012.175>.
- [17] Y. Lin, S. Zhou, X. Liu, S. Sheehan, D. Wang, TiO₂/TiSi₂ heterostructures for high-efficiency photoelectrochemical H₂O splitting, *J. Am. Chem. Soc.* 131 (2009) 2772–2773, <https://doi.org/10.1021/ja808426h>.
- [18] R.J. Zomer, H. Neufeldt, J. Xu, A. Ahrends, D. Bossio, A. Trabucchi, M. van Noordwijk, M. Wang, Global tree cover and biomass carbon on agricultural land: the contribution of agroforestry to global and national carbon budgets, *Sci. Rep.* 6 (1) (2016), <https://doi.org/10.1038/srep29987>.
- [19] X. Li, J. Yu, J. Low, Y. Fang, J. Xiao, X. Chen, Engineering heterogeneous semiconductors for solar water splitting, *J. Mater. Chem. A* 3 (2015) 2485–2534, <https://doi.org/10.1039/C4TA04461D>.
- [20] J.H. Kim, D. Hansora, P. Sharma, J.W. Jang, J.S. Lee, Toward practical solar hydrogen production – an artificial photosynthetic leaf-to-farm challenge, *Chem. Soc. Rev.* 48 (2019) 1908–1971, <https://doi.org/10.1039/C8CS00699G>.
- [21] Z. Chen, H.N. Dinh, E. Miller, *Photoelectrochemical water splitting*, Springer, NY, USA, 2013.
- [22] T. Umabayashi, T. Yamaki, H. Itoh, K. Asai, Analysis of electronic structures of 3d transition metal-doped TiO₂ based on band calculations, *J. Phys. Chem. Solids* 63 (2002) 1909–1920, [https://doi.org/10.1016/S0022-3697\(02\)00177-4](https://doi.org/10.1016/S0022-3697(02)00177-4).
- [23] K. Ueda, H. Tabata, T. Kawai, Magnetic and electric properties of transition-metal-doped ZnO films, *Appl. Phys. Lett.* 79 (2001) 988–990, <https://doi.org/10.1063/1.1384478>.
- [24] F. Su, T. Wang, R. Lv, J. Zhang, P. Zhang, J. Lu, J. Gong, Dendritic Au/TiO₂ nanorod arrays for visible-light driven photoelectrochemical water splitting, *Nanoscale* 5 (2013) 9001–9009, <https://doi.org/10.1039/C3NR02766J>.
- [25] X. Zhang, Y. Liu, S.T. Lee, S. Yang, Z. Kang, Coupling surface plasmon resonance of gold nanoparticles with slow-photon-effect of TiO₂ photonic crystals for synergistically enhanced photoelectrochemical water splitting, *Energy Environ. Sci.* 7 (2014) 1409–1419, <https://doi.org/10.1039/C3EE43278E>.
- [26] W. Chen, Y. Lu, W. Dong, Z. Chen, M. Shen, Plasmon mediated visible light photocurrent and photoelectrochemical hydrogen generation using Au nanoparticles/TiO₂ electrode, *Mater. Res. Bull.* 50 (2014) 31–35, <https://doi.org/10.1016/j.materresbull.2013.10.017>.
- [27] H.J. Koo, J. Park, B. Yoo, K. Yoo, K. Kim, N.G. Park, Size-dependent scattering efficiency in dye-sensitized solar cell, *Inorganica Chim. Acta.* 361 (2008) 677–683, <https://doi.org/10.1016/j.ica.2007.05.017>.
- [28] H.J. Koo, Y.J. Kim, Y.H. Lee, W.I. Lee, K. Kim, N.G. Park, Nano-embossed hollow spherical TiO₂ as bifunctional material for high-efficiency dye-sensitized solar cells, *Adv. Mater.* 20 (2008) 195–199, <https://doi.org/10.1002/adma.200700840>.
- [29] M. Grätzel, Dye-sensitized solar cells, *J. Photochem. Photobiol. C* 4 (2003) 145–153, [https://doi.org/10.1016/S1389-5567\(03\)00026-1](https://doi.org/10.1016/S1389-5567(03)00026-1).
- [30] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-sensitized solar cells, *Chem. Rev.* 110 (2010) 6595–6663, <https://doi.org/10.1021/cr900356p>.
- [31] H. Zhao, F. Rosei, Colloidal quantum dots for solar technologies, *Chem* 3 (2017) 229–258, <https://doi.org/10.1016/j.chempr.2017.07.007>.
- [32] R. Plass, S. Pelet, J. Krueger, M. Grätzel, U. Bach, Quantum dot sensitization of organic–inorganic hybrid solar cells, *J. Phys. Chem. B* 106 (2002) 7578–7580, <https://doi.org/10.1021/jp020453l>.
- [33] E. Haque, J. Kim, V. Malgras, K.R. Reddy, A.C. Ward, J. You, Y. Bando, M. d. Shahriar, A. Hossain, Y. Yamauchi, Recent advances in graphene quantum dots: synthesis, properties, and applications, *Small Methods* 2 (2018) 1800050, <https://doi.org/10.1002/smtd.201800050>.
- [34] G.S. Selopal, H. Zhao, Z.M. Wang, F. Rosei, Core/shell quantum dots solar cells, *Adv. Funct. Mater.* 30 (2020) 1908762, <https://doi.org/10.1002/adfm.201908762>.
- [35] C. Zhang, D.B. Kuang, W.Q. Wu, A review of diverse halide perovskite morphologies for efficient optoelectronic applications, *Small Methods* 4 (2019) 1900662, <https://doi.org/10.1002/smtd.201900662>.
- [36] X. Liu, Y. Wang, X. Cui, M. Zhang, B. Wang, M. Rager, Z. Shu, Y. Yang, Z. Li, Z. Lin, Enabling highly efficient photocatalytic hydrogen generation and organics degradation via a perovskite solar cell-assisted semiconducting nanocomposite photoanode, *J. Mater. Chem. A* 7 (2019) 165–171, <https://doi.org/10.1039/C8TA08998A>.
- [37] J. Cai, J. Shen, X. Zhang, Y.H. Ng, J. Huang, W. Guo, C. Lin, Y. Lai, Light-driven sustainable hydrogen production utilizing TiO₂ nanostructures: A review, *Small Methods* 3 (2018) 1800184, <https://doi.org/10.1002/smtd.201800184>.
- [38] H.L. Feng, W.Q. Wu, H.S. Rao, L.B. Li, D.B. Kuang, C.Y. Su, T. three-dimensional hyperbranched TiO₂/ZnO heterostructured arrays for efficient quantum dot-sensitized solar cells, *J. Mater. Chem. A* 3 (2015) 14826–14832, <https://doi.org/10.1039/C5TA02269J>.
- [39] F. Navarro-Pardo, J. Liu, O. Abdelkarim, G.S. Selopal, A. Yurtsever, A.C. Tavares, H. Zhao, Z.M. Wang, F. Rosei, 1D/2D cobalt-based nanohybrids as electrocatalysts for hydrogen generation, *Adv. Funct. Mater.* 30 (2020) 1908467, <https://doi.org/10.1002/adfm.201908467>.
- [40] K.T. Dembele, G.S. Selopal, C. Soldano, R. Nechache, J.C. Rimada, I. Concina, G. Sberveglieri, F. Rosei, A. Vomiero, Hybrid carbon nanotubes–TiO₂ photoanodes for high efficiency dye-sensitized solar cells, *J. Phys. Chem. C* 117 (2013) 14510–14517, <https://doi.org/10.1021/jp403553t>.
- [41] K. Basu, G.S. Selopal, M. Mohammadnezhad, R. Akilimali, Z.M. Wang, H. Zhao, F. Vetrone, F. Rosei, Hybrid graphene/metal oxide anodes for efficient and stable dye sensitized solar cell, *Electrochim. Acta* 349 (2020), 136409, <https://doi.org/10.1016/j.electacta.2020.136409>.
- [42] R. Akilimali, G.S. Selopal, D. Benetti, M. Mohammadnezhad, H. Zhao, Z.M. Wang, B. Stansfield, F. Rosei, Graphene nanoribbon–TiO₂-quantum dots hybrid photoanode to boost the performance of photoelectrochemical for hydrogen generation, *Catal. Today* 340 (2020) 161–169, <https://doi.org/10.1016/j.cattod.2018.10.052>.
- [43] O. Abdelkarim, J. Kaur, J. Liu, F. Navarro-Pardo, H. Zarrin, A. Yurtsever, G. Bassioni, Z.M. Wang, G.S. Selopal, F. Rosei, Two-dimensional functionalized hexagonal boron nitride for quantum dot photoelectrochemical hydrogen generation, *J. Mater. Chem. A* 8 (2020) 20698–20713, <https://doi.org/10.1039/D0TA05260D>.
- [44] O. Abdelkarim, G.S. Selopal, K. Suresh, F. Navarro-Pardo, P. Kumar, K.K. Ghuman, A. Yurtsever, G. Bassioni, Z.M. Wang, F. Rosei, Role of surface engineering of hybrid structure for high performance quantum dots based photoelectrochemical hydrogen generation, *Chem. Eng. J.* 429 (2022), 132425, <https://doi.org/10.1016/j.cej.2021.132425>.
- [45] Z. Mou, Y. Wu, J. Sun, P. Yang, Y. Du, C. Lu, TiO₂ nanoparticles-functionalized N-doped graphene with superior interfacial contact and enhanced charge separation for photocatalytic hydrogen generation, *ACS Appl. Mater. Interfaces* 6 (2014) 13798–13806, <https://doi.org/10.1021/am503244w>.
- [46] S. Li, G. Yang, P. Ge, H. Lin, Q. Wang, X. Ren, S. Luo, D. Philo, K. Chang, J. Ye, Engineering heterogeneous NiS₂/NiS cocatalysts with progressive electron transfer from planar p-si photocathodes for solar hydrogen evolution, *Small Methods* 5 (2021) 2001018, <https://doi.org/10.1002/smtd.202001018>.
- [47] J.W. Ondersma, T.W. Hamann, Measurements and modeling of recombination from nanoparticle TiO₂ electrodes, *J. Am. Chem. Soc.* 133 (2011) 8264–8271, <https://doi.org/10.1021/ja201333u>.
- [48] A.M.A. Hussein, K.G. Burra, G. Bassioni, R.M. Hammouda, A.K. Gupta, Production of CO from CO₂ over mixed-metal oxides derived from layered-double-hydroxides, *Appl. Energy* 235 (2019) 1183–1191, <https://doi.org/10.1016/j.apenergy.2018.11.040>.
- [49] C. Wehrenfennig, C.M. Palumbiny, H.J. Snait, M.B. Johnston, L. Schmidt-Mende, L.M. Herz, Fast charge-carrier trapping in TiO₂ nanotubes, *J. Phys. Chem. C* 119 (2015) 9159–9168, <https://doi.org/10.1021/acs.jpcc.5b01827>.
- [50] N. Pugazhenthiran, S. Murugesan, S. Anandan, High surface area Ag-TiO₂ nanotubes for solar/visible-light photocatalytic degradation of cefixime sodium, *J. Hazard. Mater.* 263 (2013) 541–549, <https://doi.org/10.1016/j.jhazmat.2013.10.011>.
- [51] J.H. Park, S. Kim, A.J. Bard, Novel carbon-doped TiO₂ nanotube arrays with high aspect ratios for efficient solar water splitting, *Nano Lett.* 6 (2006) 24–28, <https://doi.org/10.1021/nl051807y>.
- [52] S. Zhu, Q. Wang, D. Cao, S. Zhao, W. Xu, C. Li, Y. Wang, CdTe and Ag nanoparticles co-modified TiO₂ nanotube arrays for the enhanced wastewater treatment and hydrogen production, *J. Environ. Chem. Eng.* 10 (2) (2022) 107207.
- [53] Q. Wang, H. Li, X. Yu, Y. Jia, Y. Chang, S. Gao, Morphology regulated Bi₂WO₆ nanoparticles on TiO₂ nanotubes by solvothermal Sb³⁺ doping as effective photocatalysts for wastewater treatment, *Electrochim. Acta* 330 (2020), 135167, <https://doi.org/10.1016/j.electacta.2019.135167>.

- [54] Z. Liu, Y. Song, Q. Wang, Y. Jia, X. Tan, X. Du, S. Gao, Solvothermal fabrication and construction of highly photoelectrocatalytic TiO₂ NTs/Bi₂MoO₆ heterojunction based on titanium mesh, *J. Colloid Interface Sci.* 556 (2019) 92–101, <https://doi.org/10.1016/j.jcis.2019.08.038>.
- [55] M. Ye, J. Gong, Y. Lai, C. Lin, Z. Lin, High-efficiency photoelectrocatalytic hydrogen generation enabled by palladium quantum dots-sensitized TiO₂ nanotube arrays, *J. Am. Chem. Soc.* 134 (2012) 15720–15723, <https://doi.org/10.1021/ja307449z>.
- [56] P. Roy, S. Berger, P. Schmuki, TiO₂ nanotubes: synthesis and applications, *Angew. Chem. Int. Ed.* 50 (2011) 2904–2939, <https://doi.org/10.1002/anie.201001374>.
- [57] Y. Jia, P. Liu, Q. Wang, Y. Wu, D. Cao, Q. Qiao, Construction of Bi₂S₃-BiOBr nanosheets on TiO₂ NTA as the effective photocatalysts: Pollutant removal, photoelectric conversion and hydrogen generation, *J. Colloid Interface Sci.* 585 (2021) 459–469, <https://doi.org/10.1016/j.jcis.2020.10.027>.
- [58] O.E. Semonin, J.M. Luther, S. Choi, H.Y. Chen, J. Gao, A.J. Nozik, M.C. Beard, Peak external photocurrent quantum efficiency exceeding 100% via MEG in a quantum dot solar cell, *Science* 334 (2011) 1530–1533, <https://doi.org/10.1126/science.1209845>.
- [59] W.A. Tisdale, K.J. Williams, B.A. Timp, D.J. Norris, E.S. Aydil, X.Y. Zhu, Hot-electron transfer from semiconductor nanocrystals, *Science* 328 (2010) 1543–1547, <https://doi.org/10.1126/science.1185509>.
- [60] P. Wu, Z. Liu, D. Chen, M. Zhou, J. Wei, Flake-like NiO/WO₃ p-n heterojunction photocathode for photoelectrochemical water splitting, *Appl. Surf. Sci.* 440 (2018) 1101–1106, <https://doi.org/10.1016/j.apsusc.2018.01.292>.
- [61] L. Meng, W. Tian, F. Wu, F. Cao, L. Li, TiO₂ ALD decorated CuO/BiVO₄ p-n heterojunction for improved photoelectrochemical water splitting, *J. Mater. Sci. Technol.* 35 (2019) 1740–1746, <https://doi.org/10.1016/j.jmst.2019.03.008>.
- [62] C. Hao, W. Wang, R. Zhang, B. Zou, H. Shi, Enhanced photoelectrochemical water splitting with TiO₂@Ag₂O nanowire arrays via p-n heterojunction formation, *Sol. Energy Mater. Sol. Cells* 174 (2018) 132–139, <https://doi.org/10.1016/j.solmat.2017.08.033>.
- [63] C. Chen, N. Wang, P. Zhou, H. San, K. Wang, X. Chen, Electrochemically reduced graphene oxide on well-aligned titanium dioxide nanotube arrays for betavoltaic enhancement, *ACS Appl. Mater. Interfaces* 8 (2016) 24638–24644, <https://doi.org/10.1021/acsami.6b08112>.
- [64] N. Liu, S. Chen, Y. Li, H. Dai, Y. Lin, Self-enhanced photocathodic matrix based on poly-dopamine sensitized TiO₂ mesocrystals for mycotoxin detection assisted by a dual amplification nanotag, *New J. Chem.* 41 (2017) 3380–3386, <https://doi.org/10.1039/C6NJ03157A>.
- [65] S. Hernández, D. Hidalgo, A. Sacco, A. Chiodoni, A. Lamberti, V. Cauda, E. Tresso, G. Saracco, Comparison of photocatalytic and transport properties of TiO₂ and ZnO nanostructures for solar-driven water splitting, *Phys. Chem. Chem. Phys.* 17 (2015) 7775–7786, <https://doi.org/10.1039/C4CP05857G>.
- [66] Y. Rambabu, M. Jaiswal, S.C. Roy, Probing the charge recombination in rGO decorated mixed phase (anatase-rutile) TiO₂ multi-leg nanotubes, *AIP Adv.* 6 (11) (2016) 115010.
- [67] M. Hannula, H. Ali-Löytty, K. Lahtonen, E. Sarlin, J. Saari, M. Valden, Improved stability of atomic layer deposited amorphous TiO₂ photoelectrode coatings by thermally induced oxygen defects, *Chem. Mater.* 30 (2018) 1199–1208, <https://doi.org/10.1021/acs.chemmater.7b02938>.
- [68] G. Greczynski, L. Hultman, X-ray photoelectron spectroscopy: Towards reliable binding energy referencing, *Prog. Mater. Sci.* 107 (2020), 100591, <https://doi.org/10.1016/j.pmatsci.2019.100591>.
- [69] Z. Dong, D. Ding, T. Li, C. Ning, Black Si-doped TiO₂ nanotube photoanode for high-efficiency photoelectrochemical water splitting, *RSC Adv.* 8 (2018) 5652–5660, <https://doi.org/10.1039/C8RA00021B>.
- [70] Z. Jiang, C. Zhu, W. Wan, K. Qian, J. Xie, Constructing graphite-like carbon nitride modified hierarchical yolk-shell TiO₂ spheres for water pollution treatment and hydrogen production, *J. Mater. Chem. A* 4 (2016) 1806–1818, <https://doi.org/10.1039/C5TA09919F>.
- [71] I.H. Yoo, S.S. Kalanur, H. Seo, A nanoscale p-n junction photoelectrode consisting of an NiO_x layer on a TiO₂/CdS nanorod core-shell structure for highly efficient solar water splitting, *Appl. Catal. B: Environ.* 250 (2019) 200–212, <https://doi.org/10.1016/j.apcatb.2019.02.063>.
- [72] Y. Tong, T. Jiang, A. Bendounan, F. Nicolas, S. Kubsy, V.A. Esaulov, Selenium, benzeneselenol, and selenophene interaction with Cu(100), *J. Phys. Chem. C* 120 (2016) 21486–21495, <https://doi.org/10.1021/acs.jpcc.6b06217>.
- [73] G.S. Selopal, I. Concina, R. Milan, M.M. Natile, G. Sberveglieri, A. Vomiero, Hierarchical self-assembled Cu₂S nanostructures: Fast and reproducible spray deposition of effective counter electrodes for high efficiency quantum dot solar cells, *Nano Energy* 6 (2014) 200–210, <https://doi.org/10.1016/j.nanoen.2014.04.003>.
- [74] C. Zhao, K. Fezzaa, R.W. Cunningham, H. Wen, F. De Carlo, L. Chen, A.D. Rollett, T. Sun, Real-time monitoring of laser powder bed fusion process using high-speed X-ray imaging and diffraction, *Sci. Rep.* 7 (1) (2017), <https://doi.org/10.1038/s41598-017-03761-2>.
- [75] S.Y. Zhang, C.X. Fang, Y.P. Tian, K.R. Zhu, B.K. Jin, Y.H. Shen, J.X. Yang, Synthesis and characterization of hexagonal cuse nanotubes by templating against trigonal Se nanotubes, *Cryst. Growth Des.* 6 (2006) 2809–2813, <https://doi.org/10.1021/cg0604430>.
- [76] X. Du, Q. Wang, T. Feng, X. Chen, L. Li, L. Li, X. Meng, L. Xiong, X. Sun, L. Lu, Y. Xu, One-step preparation of nanoarchitected TiO₂ on porous Al as integrated anode for high-performance lithium-ion batteries, *Sci. Rep.* 6 (2016) 1–8, <https://doi.org/10.1038/srep20138>.
- [77] Y.Q. Liu, F.X. Wang, Y. Xiao, H.D. Peng, H.J. Zhong, Z.H. Liu, G.B. Pan, Effect of aspect ratio and surface defects on the photocatalytic activity of ZnO nanorods, *Sci. Rep.* 4 (2014) 1–8, <https://doi.org/10.1038/srep04596>.
- [78] F. Vaquero, R.M. Navarro, J.L.G. Fierro, Influence of the solvent on the structure, morphology and performance for H₂ evolution of CdS photocatalysts prepared by solvothermal method, *Appl. Catal. B: Environ.* 203 (2017) 753–767, <https://doi.org/10.1016/j.apcatb.2016.10.073>.
- [79] G. Liu, R. Mazzaro, Y. Wang, H. Zhao, A. Vomiero, High efficiency sandwich structure luminescent solar concentrators based on colloidal quantum dots, *Nano Energy* 60 (2019) 119–126, <https://doi.org/10.1016/j.nanoen.2019.03.038>.
- [80] X. Wang, Z. Liang, X. Xu, N. Wang, J. Fang, J. Wang, G. Xu, A high efficient photoluminescence Zn–Cu–In–S/ZnS quantum dots with long lifetime, *J. Alloys Comp.* 640 (2015) 134–140, <https://doi.org/10.1016/j.jallcom.2015.03.249>.
- [81] G.S. Selopal, M. Mohammadnezhad, L.V. Besteiro, O. Cavuslar, J. Liu, H. Zhang, F. Navarro-Pardo, G. Liu, M. Wang, E.G. Durmusoglu, H.Y. Acar, S. Sun, M. Zhao, Z.M. Wang, F. Rosei, Synergistic effect of plasmonic gold nanoparticles decorated carbon nanotubes in quantum dots/TiO₂ for optoelectronic devices, *Adv. Sci.* 7 (2020) 2001864, <https://doi.org/10.1002/adv.202001864>.
- [82] M.G. Stanford, P.R. Pudasaini, A. Belianinov, N. Cross, J.H. Noh, M.R. Koehler, D. G. Mandrus, G. Duscher, A.J. Rondinone, I.N. Ivanov, P.D. Rack, Focused helium-ion beam irradiation effects on electrical transport properties of few-layer WSe₂: enabling nanoscale direct write homo-junctions, *Sci. Rep.* 6 (2016) 1–10, <https://doi.org/10.1038/srep27276>.