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Photoelectrochemical concurrent hydrogen generation and heavy metal recovery from polluted acidic mine water†

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The feasibility of a solar-driven photoelectrochemical process to generate hydrogen fuel from metal mine polluted water while simultaneously recovering heavy metals has been explored. Electron transport from the photoanode to the cathode plays a key role in generating hydrogen ($37.6 \mu\text{mol h}^{-1} \text{cm}^{-2}$ at 0.2 V RHE, 1 sun illumination), and scavenging Zn^{2+} ions in the form of ZnO.

Hydrogen is a promising future energy carrier for carbon-free transport and electrification due to its high gravimetric energy density (142 MJ kg^{-1}), and non-polluting nature.¹ However, the current hydrogen production from methane steam reforming leaves behind a tremendous carbon footprint. In addition, fossil resources of methane are rapidly depleting, urging the development of green and sustainable alternatives to protect the environment.² In contrast, solar energy is clean and renewable but must be stored as chemical energy (fuel and chemicals) to meet the global energy demand at all times.^{3–5} The solar hydrogen fuel generation from water using semiconductors has received profound attention since the Honda–Fujishima effect was first demonstrated in 1972.⁶ The photoelectrochemical (PEC) technique shows promising performance in converting solar energy into hydrogen fuel by artificial photosynthesis.^{7,8}

The photoanode, the crucial component of a PEC cell is typically a semiconductor that generates photo charge carriers (electrons and holes) under light irradiation.^{8,9} Photoholes

formed at the valence band of the semiconductor oxidize water to O_2 , ($2\text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^-$) and photoelectrons from the conduction band of the semiconductor anode reduces protons to H_2 at the cathode ($4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2(\text{g})$). The overall water splitting process is an uphill reaction and thermodynamically requires 237 kJ mol^{-1} , which equals a standard potential of 1.23 V.¹⁰ The PEC process is recognised to oxidise water at a potential more positive than +1.23 V vs. NHE depending on the photoanode material, electrolyte type, and pH. In contrast, electrochemical water oxidation requires potentials $>1.23 \text{ V vs. NHE}$ for oxygen gas evolution due to high overpotential at the anode compared to the PEC process ($2\text{H}_2\text{O}(\text{l}) + \text{semiconductor} + h\nu \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$). Therefore, the number of protons derived from the anodic water oxidation process, and photoelectrons generated in the photoanode are directly dictating the hydrogen generation rate at the cathode surface. Photoelectron generation from the PEC process relies on the photoanode (light absorption), applied potential in the circuit, charge carrier separation at electrode/electrolyte interfaces (low recombination), and resistance of the electrode and electrolyte solution. All these aspects are well-studied in PEC based solar-to-hydrogen fuel generation.^{11–13} But, less attention has been paid to electrolyte engineering.

Use of fresh water has been one of the primary requirements of PEC water-splitting which when implemented in a large scale would incur additional cost for acquiring fresh water from other means such as desalination of seawater. Recent studies on life-cycle net energy assessment for PEC hydrogen generation showed that approximately $820\,000 \text{ m}^3$ of electrolyte would be required for a 1 GW facility.¹⁴ Furthermore, adding chemicals (acid, base and salts) for enhancing the ionic conductivity of pure water ($0.055 \mu\text{S cm}^{-1}$) in the PEC hydrogen generation process incurs additional cost¹⁵ and creates environmental pollution issues upon discharge after the reaction. Recent demonstrations on PEC hydrogen generation using alternative electrolytes such as seawater abundantly available in oceans showed appreciable performance,^{16–19} but electrode corrosion in highly saline conditions remains a challenge. Another approach

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is to utilize organic water pollutants as electrolyte and feedstock in a PEC cell for yielding hydrogen as a by-product.^{20–23} Therefore, this method also achieves simultaneous low-cost water treatment. However, the pollutant/electrode interfaces in PEC water splitting are yet to be fully understood, and more investigations are needed.

Thousands of metal mine sites worldwide are currently not in operation that have become the major sources for heavy metal leaching and creating acid mine drainage (AMD). This metal mine pollution (so-called mine tailing) which is a potential threat to both humans and grazing animals.^{24,25} AMD pollutant sludge is already widely used in waste management (mineral industry and soil fertiliser), but its potential in water management applications is unrevealed as the heavy metal removal demands a considerable cost. The electrical conductivity of metal mine polluted water depends on heavy metal ions (Fe, Zn, Cd, Cr, Co, Ni, Cu, Pb, *etc.*) present in it and is typically around 1–3 mS cm⁻².²⁶ This is 10³ times higher than that of pure water and hence, it can directly be used in a PEC cell as an electrolyte without adding additional salts or chemicals. However, the acidic nature of AMD-polluted water could affect the photoanode by corrosion. It is still viable for a two-compartment PEC cell where the photoanode and the cathode are separated by a proton-exchange membrane (PEM). Utilizing AMD-polluted water in the cathode compartment, and alkaline or near-neutral pH electrolyte in the photoanode compartment leads to the formation of a pH gradient^{27,28} and expected to form chemical bias that would reduce the thermodynamic potential for water splitting.^{28–31} Recent work on using AMD-contaminated water as an electrolyte in a photovoltaic panel assisted electrolysis cell showed appreciable H₂ generation at 1.48 V applied potential with stainless steel electrodes.³² Unfortunately, uncontrollable bias from the PV panel caused a detrimental heating effect, and corrosion in the reactor and decreased the hydrogen generation efficiency. The direct solar-driven photoelectrochemical cell can avoid this issue, but to the best of our knowledge, this has not been demonstrated.

Here, we demonstrate the feasibility of using AMD-polluted water as an electrolyte in direct solar-driven PEC cells for the first time. This work explores artificial photosynthesis for H₂ generation at low overpotential with simultaneous metal recovery. This work thus fosters PEC beyond water-splitting towards a process for water treatment and resource recovery applications.

A mesoporous TiO₂ electrode (1-micron thickness) was prepared on a fluorine-doped tin oxide (FTO) substrate and the same was coated with CdS quantum dots (QDs) using the successive ionic layer adsorption and reaction (SILAR) technique³³ (see the ESI†). A range of different CdS QD-loaded TiO₂ photoanodes were prepared by varying the number of SILAR cycles (3, 5 and 7). These were subsequently employed in a PEC cell filled with a real AMD-contaminated water sample (cathode compartment) and a polysulfide electrolyte as a hole scavenger (photoanode compartment). The CdS quantum dot-sensitised TiO₂ electrode was used as the photoanode and kept separated from the Ni mesh cathode. A Hg/HgCl₂ calomel electrode was used as the reference electrode with a Nafion® membrane.

A detailed description of experimental conditions is given in the ESI.†

Fig. 1(a)–(c) shows the surface morphology of pristine and CdS QD-coated TiO₂ photoanodes. There is a clear trend in surface topography with the number of CdS SILAR coating cycles, as displayed in Fig. 1(b) and (c). The nanoscale CdS particles are notable after seven cycles of SILAR as indicated by the CdS QD growth around nucleation sites. The energy-dispersive X-ray spectroscopy (EDX) analysis further ensured the CdS QD growth on the TiO₂ electrode (Fig. S1†). Consistently, the signals attributed to titanium and oxygen decrease in intensity with the increasing CdS SILAR coating cycles indicating an increase in the CdS film thickness. Chemical composition of the pristine TiO₂, and CdS QD-coated TiO₂ (3 and 7 cycles) was studied using X-ray photoelectron spectroscopy (XPS). Fig. S2† shows wide scan XPS spectra. The core spectra of S 2p, Cd 2p, Ti 2p, O 1s and Zn 2p are presented in Fig. 1(d)–(g). The XPS peaks of Cd 3d are observed at 404.9 eV and 411.9 eV (Fig. 1(d)), which is in line with previous reports.^{34,35} The peaks at 161.9 eV and 163.1 eV are attributed to the characteristics of S 2p_{3/2} and S 2p_{1/2} (Fig. 1(e)).³⁶ Both Cd 2d or S 1s peaks detected on TiO₂ (indexed ii and iii) indicate CdS quantum dots formation on TiO₂ after SILAR coating. The predominant peaks at 458.5 and 464.1 eV (Fig. 1(f)) are attributed to Ti 2p_{1/2} and Ti 2p_{3/2}, respectively. A broader peak at 529.4 eV indicates O 1s, assigned to oxygen species in the TiO₂ lattice.

The Kubelka–Munk analysis (Fig. S3†) revealed the CdS QD coating on TiO₂ with a shift in the band edge from 380 to 488 nm. While increasing the CdS coating cycles from 3 to 7, the band edge gradually shifts further to 514 nm. This indicates that the CdS QD growth on TiO₂ improves absorbance of visible light with the increasing coating cycle. Such an enhanced optical absorbance in the visible region of CdS QD coated TiO₂ demonstrates the suitability of the same as a photoanode in sunlight-driven catalysis. Similar SILAR coating cycles

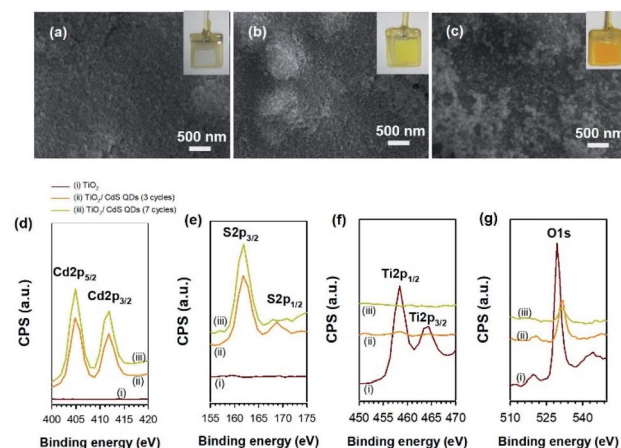


Fig. 1 (a)–(c) Scanning electron images of (a) pristine TiO₂, (b) TiO₂ coated with CdS QDs (3 cycles), (c) TiO₂ coated with CdS QDs (7 cycles) (inset: respective electrode photos); (d)–(g) X-ray photoelectron spectra of pristine TiO₂, and TiO₂ coated with CdS QDs (3 & 7 cycles) (d) Cd2p, (e) S2p, (f) Ti2p and (g) O1s core spectra.

dependence optical density enhancement and absorbance edge shift at CdS QD sensitised TiO₂ was observed by others.^{37,38} The optimized coating cycle is 7 beyond which the properties of CdS QDs dramatically changes and appear to be that of bulk CdS with increasing thickness of the CdS QD layer. On the other hand, the high thick coating led affects the film integrity resulting in peel off.

Before testing these photoanodes with AMD pollutants as an electrolyte, the photoelectrochemical properties of the CdS QD-sensitized TiO₂ photoanode was examined in aqueous polysulfide electrolyte by chopped linear sweep voltammetry (LSV) as shown in Fig. 2 which shows that photocurrent generation at the CdS QD-sensitized photoanode is gradually enhanced with the increasing CdS QD coating cycles. CdS QD coated with seven SILAR cycles exhibits a higher photocurrent density of 3.7 mA cm⁻² at 0.2 V vs. RHE than other photoanodes. The photoelectrochemical process at CdS QD-sensitized TiO₂ can be explained as follows. The photoelectrons (e⁻) and photoholes (h⁺) were generated under light irradiation at the conduction band and valence band of CdS QDs, respectively. Further, the photoelectrons from the CdS conduction band were injected into the TiO₂ conduction band and then reached the charge collector (FTO substrate). Conversely, the photoholes generated at the CdS valence band were scavenged by the polysulfide electrolyte. The polysulfide electrolyte acts as a hole scavenger by the following equation in the photoanode compartment.^{39,40}

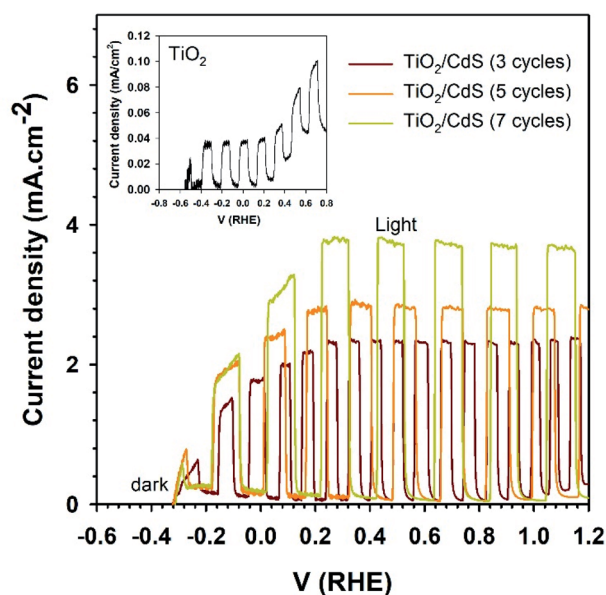
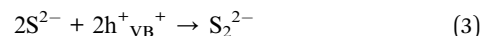


Fig. 2 Chopped linear sweep voltammetry plots of TiO₂ (inset) and the CdS QD sensitised TiO₂ photoanode measured at 100 mV s⁻¹ scan rate. The experiments were carried out under 1 sun illumination conditions using a two-compartment cell. The photoanode and cathode compartments contain 0.3 M of aqueous Na₂SO₄/Na₂S polysulfide electrolyte (pH = 13). The Hg/HgCl₂ calomel electrode was used as a reference electrode in the photoanode compartment.



The protons (H⁺) produced from eqn (1) diffuse through the PEM to the cathode compartment while the photoelectrons from the photoanode are transferred *via* the external circuit to the Ni mesh cathode that reduces protons to H₂ as shown below in eqn (4).



The hydrogen gas generated from the seven cycle CdS QD-sensitized TiO₂ photoanode was quantified to be 27 μmol h⁻¹ cm⁻² at +0.2 V vs. RHE applied potential (Fig. S4†). Importantly, these CdS QD-sensitized photoanodes result in approximately 2.5 mA cm⁻² at 0 V vs. RHE, inferring H₂ generation at a much lower applied potential in the external circuit. Different research groups have studied bias-free photoelectrochemical hydrogen generation in CdS QD-sensitized TiO₂ photoanodes,⁴¹⁻⁴³ suggesting that this PEC cell is suitable to validate photoelectron-driven catalysis reactions in AMD pollutant electrolyte too.

AMD water pollutant samples were collected from an abandoned metal mine site located in Wales (UK) and tested as an electrolyte in a two-compartment photoelectrochemical cell, and the most suitable feedstock was found to have a pH of 4.8 and contain 47.1 ppm (0.72 mmol) of Zn²⁺ ions (ESI†). In the photoanode compartment, aqueous 0.3 M polysulfide solution was used as an electrolyte, and AMD polluted water was placed in the cathode chamber. The chronoamperometry plots (Fig. 3(a)) for different CdS QD-sensitized TiO₂ photoanodes were recorded using a three-electrode configuration as discussed above. Fig. 3(a) shows that CdS QD-sensitized photoanodes result in superior PEC performance than the bare TiO₂ photoanode (inset of Fig. 3(a)). Among the different CdS QD-coated photoanodes, those coated with seven SILAR cycles showed the highest photoelectrochemical activity with an average photocurrent density of 5.5 mA cm⁻². Plausible reasons for the high PEC performance with this electrode are (a) enhanced light absorption and (b) sufficient coverage of CdS QDs on TiO₂ reduces charge recombination loss. The small amount of photocurrent reduction observed in all photoanodes after an hour is likely due to polysulfide scavenger degradation in the photoanode compartment. In the cathode compartment, the observed strong bubble formation indicates hydrogen gas generation (eqn (4)) from AMD electrolyte (see the ESI video†).

The corresponding hydrogen gas generation from these experiments was quantified through gas chromatography (Fig. 3(b)). Hydrogen generation showed a linear tendency against time, and the H₂ generation rate was found to increase with increasing CdS coating cycles, thus proving the role of photoelectron generation at CdS QDs for hydrogen evolution (eqn (4)) at the cathode. Seven SILAR cycles of CdS QDs deposition onto TiO₂ results in a high hydrogen evolution rate of 38 μmol h⁻¹ cm⁻² at 0.2 V vs. RHE applied potential. The AMD-

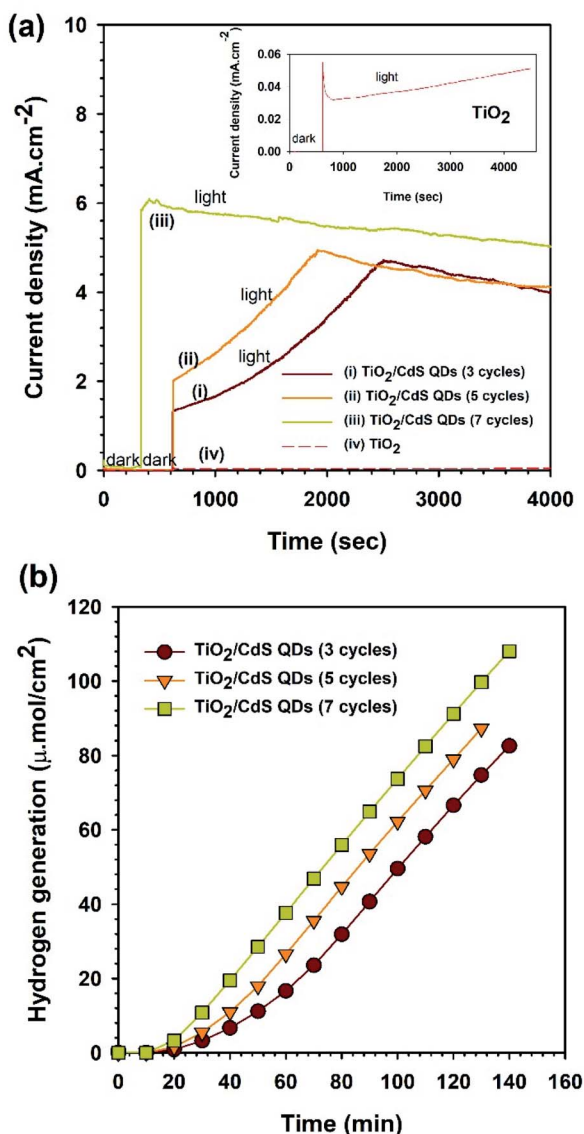


Fig. 3 (a) Chronoamperometry plots of the TiO₂ photoanode (inset) and TiO₂ sensitised with different CdS QDs coating cycles (3, 5 and 7); (b) quantification of H₂ evolved during PEC reactions. Both Fig. 4(a) and (b) experiments measured under 1 sun illumination conditions. Note that 0.3 M of aqueous Na₂SO₄/Na₂S polysulfide electrolyte (pH = 13) and real-time AMD pollutant (pH = 4.8) are used as an electrolyte in the photoanode and cathode compartments, respectively. The measurements were recorded at 0.2 V vs. RHE using a Hg/HgCl₂ calomel reference electrode.

based electrolyte yields slightly higher hydrogen gas evolution than polysulfide electrolyte (27 μmol h⁻¹ cm⁻²) under identical experimental conditions.

It infers that AMD-polluted water can be utilised as an electrolyte feedstock for solar hydrogen fuel generation. A similar PEC experiment was repeated under 2 sun intensity to ensure the potency of photoelectron generation at the photoanode for hydrogen fuel generation. For instance, increasing light intensity is expected to illuminate the entire bandgap energy of CdS QDs and could result in higher hydrogen gas

evolution at the cathode (eqn (4)). After 2 h irradiation, as much as 106 μmol cm⁻² was formed under 2 sun intensity irradiation (Fig. S5†). It is significantly higher than under 1 sun intensity (83 μmol cm⁻²) after an identical period of 2 h. We can conclude that the number of CdS QD coating cycles and the light intensity influences the PEC hydrogen generation by accelerating the photo charge carrier generation at the photoanode.

The CdS QDs has been demonstrated widely on powder-type photocatalysis compared to the wired PEC configuration for solar hydrogen generation. Mostly aqueous polysulfide (S_x⁻/S⁻) is used as electrolyte.⁴⁴ Typically, powder-type CdS QDs exhibits in the order of 0.5–10 mmol g⁻¹ h⁻¹ hydrogen gas generation, and wired PEC configuration results in the order of 10 μmol to 1 mmol cm⁻² h⁻¹. The CdS QDs based photocatalysis and PEC based solar fuel generation depend on the metal oxide support (TiO₂, ZnO, SnO₂),^{45,46} co-catalyst (MoS₂, Ag)^{47–49} and co-sensitizer coating (CdSe, PbS, InP).^{50,51} The present work on the CdS QDs coated TiO₂ photoanode generates 83 μmol cm⁻² hydrogen generation from metal mine polluted water and is comparable with polysulfide electrolyte.

One can raise the question about heavy metals (Zn) present in AMD-polluted water during the PEC reaction. It has been widely reported that photoelectrons generated from the photocatalyst surface could reduce the heavy metals (Cr, Pb, Cd, etc.) in the electrolyte.^{52–55} Mostly, this reaction occurs through chemisorption, reduction, and desorption processes of heavy metal ions on the electrode surface. But Zn²⁺ is one of a few metal ions that cannot be reduced to its metallic state in an electrolyte of pH 4.8 even though we examined the surface of the Ni mesh cathode before and after the PEC reaction.

The SEM images of the Ni cathode before and after the PEC reaction are shown in Fig. 4(a–i). It is challenging to recognise

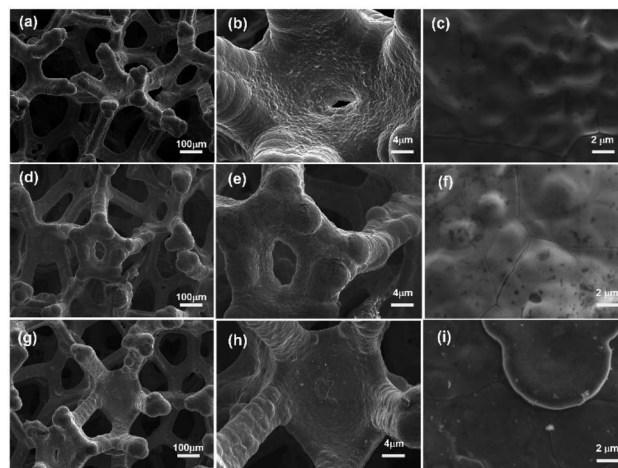


Fig. 4 (a)–(c) FESEM images of Ni mesh before the PEC reaction, measured at different magnification scales (100 μm, 4 μm and 2 μm); (d)–(f) FESEM images of Ni mesh after the PEC reaction, measured at different magnification scales (100 μm, 4 μm and 2 μm) (the photoanode-3 cycles of CdS QDs coated TiO₂); (g)–(i) FESEM images of Ni mesh after the PEC reaction measured at different magnification scales (100 μm, 4 μm and 2 μm) (the photoanode-7 cycles of CdS QD coated TiO₂).

surface modifications from low magnification SEM images (100 and 4 μm scale). High magnification SEM images at 2 μm scale (Fig. 4(c), (f) and (i)) reveal surface changes occurred on the Ni mesh after the PEC reaction. Further analysing the SEM images at 1 μm scale (Fig. S6(b)†), a fish scale-type layer deposition was noticed on the Ni cathode after the PEC experiment with a 7 CdS QDs cycle photoanode. Formation of the fish scale-type layer might be due to electrochemical deposition of Zn^{2+} metal ions present in the AMD electrolyte to form ZnO. A similar approach on arsenic heavy metals leaching from the anode material was recovered at the cathode surface by the electrochemical technique.⁵⁶

Here, photoelectrons generated from the photoanode are transported to the cathode and drive this reaction. The fish scales-type layer is discernible only at the Ni cathode coupled to the 7-cycle photoanode, not at the 3-cycle photoanode, implying that the Ni cathode surface modification varies with photoelectron collection from the photoanode. When the HER is vigorous at the cathode due to such an increased photocurrent, the local pH is expected to sufficiently increase due to H^+ consumption that is just enough to precipitate Zn^{2+} as $\text{Zn}(\text{OH})_2$.

Further examining the surface of these Ni mesh cathodes shed more light on this issue. The wide scan XPS spectra and Zn2p, O1s core spectra of the Ni mesh cathode recorded before and after the PEC reaction clearly explain the origin of surface modification at the Ni cathode. The wide scan XPS (Fig. S7†) showed an additional Zn peak with the native Ni peak of the cathode, and these Zn peaks might be attributed to ZnO formation by Zn^{2+} cations deposition at the Ni cathode due to the sufficient highly localized alkalinity due to vigorous H_2 evolution. Further analysing Zn 2p core spectra (Fig. 5(a)), a distinguished shoulder peak of Zn $2p_{3/2}$ at 1020.5 eV confirms the ZnO formation.^{57,58} Further analysing O 1s peaks (Fig. 5(b)) of the reference Ni mesh sample showed peaks at 532.1, and 533.4 eV, indicating the presence of ZnO and Ni $(\text{OH})_x$, respectively. In Ni mesh after PEC reactions, Zn^{2+} ions deposition results in ZnO as it is catalysed on the $\text{Ni}(\text{OH})_x$ surface instead of the metallic Ni surface (marked as “ii” and “iii” in Fig. 5(b)) as $\text{Ni}(\text{OH})_x$ is inherently present in the commercial Ni mesh product. This is why the ZnO layer is evidenced on Ni mesh used in 7 CdS cycle photoanode assisted the PEC reaction. Similar multi-step reactions were previously reported on the anodic or cathodic electrochemical deposition of ZnO in an acidic environment under the applied potential (−0.8 to −1.3 V).^{59,60} A distinct shift noticed in the O 1s peak from 532.1 to a lower binding energy of 530.5 eV confirms the ZnO formation on Ni mesh (Fig. 5(b)). Therefore, the XPS results strongly suggest that OH groups present on Ni mesh and the localized alkalinity created due to vigorous hydrogen evolution mediate Zn heavy metal recovery in the form of ZnO.

In order to verify the Zn^{2+} ion removal from the electrolyte the Zn concentration was measured before and after PEC experiments using plasma couple atomic absorption spectroscopy (Fig. 5(c)). It is found that the Zn concentration reduced from 7.85 ppm to 2.96 ppm after the PEC treatment.

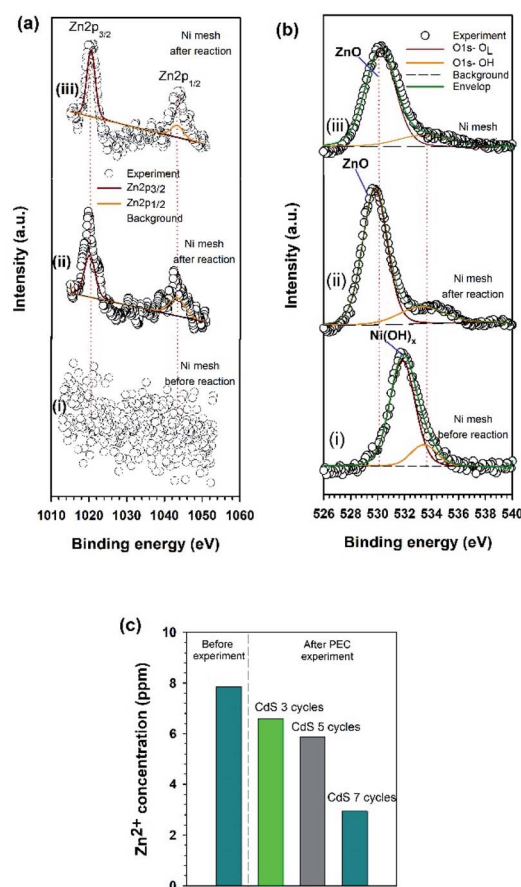


Fig. 5 The XPS core spectra results of (a) Zn 2p and (b) O1s core spectra recorded from Ni mesh before and after PEC experiments. Note that the Ni mesh cathode was kept in the cathode compartment of PEC cells. The reference Ni mesh sample before the PEC process is marked as “i”. The Ni mesh after PEC experiments – with 3 CdS QD cycles coated TiO_2 marked as “ii”, and 7 CdS QD cycles coated TiO_2 mentioned as “iii”. OL-lattice oxygen, the OH- hydroxyl group. (c) The Zn^{2+} ions concentration (ppm) before and after PEC treatment using different photoanodes.

The high removal rate at 7 cycle coated CdS QD TiO_2 photoanode might be due to higher amount of photoelectrons generation which facilitate the electrochemical reaction at the cathode.

Based on the above results, we propose a possible photoelectrochemical hydrogen generation mechanism and metal recovery from AMD polluted water, as illustrated in Fig. 6. The CdS QD-sensitized TiO_2 photoanode generates photo charge carriers (electrons and holes) under simulated solar light illumination. The photo holes scavenged by polysulfide ions undergo redox reactions and produce protons (H^+). Meanwhile, photoelectrons transported to the cathode reduce the protons/water molecules to hydrogen gas. Concurrently, a heavy metal (Zn^{2+}) present in the AMD is deposited on the cathode catalysed by surface OH and localized alkalinity created by vigorous hydrogen evolution is recovered in the form of ZnO after the reaction. The current work majorly focuses on hydrogen fuel generation, but

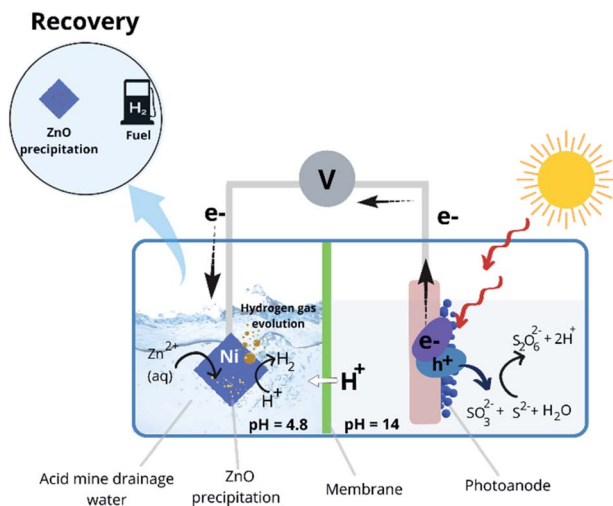


Fig. 6 Schematic illustration of AMD polluted water feedstock-based PEC cells, proposed mechanism for hydrogen generation, and heavy metal recovery. Real AMD water samples collected from an abandoned metal mine site at Frongoch, mid Wales region in the UK was used as an electrolyte in the cathode compartment (AMD samples were kindly supplied by Natural Resources Wales, Cardiff, UK).

further experiments of quantifying Zn^{2+} metal ions in the cathode compartment, before and after PEC reaction, will explain the heavy metal recovery pathways. We have tested different cathodes such as Pt, stainless steel, and Ti, in addition to Ni mesh. In comparison, Ni mesh showed the highest stability. Still, high surface area-based two-dimensional materials (graphene composite, MoS_2 , MXenes, *etc.*), chalcogenide semiconductors, or carbon-based cathodes that may be used in these experiments are expected to reduce the cost.

Overall, the proton reduction to hydrogen gas showed high priority compared to the metal recovery reaction. According to Brooks *et al.*,¹¹ the photoelectron-driven reduction of the Zn^{2+} cation is slower than hydrogen generation when the electrolyte is diluted with a high amount of water. This infers that the absence of electron scavengers or metal-binding agents in the aqueous electrolyte results in the weak metal reduction reaction. Therefore, modifying the AMD polluted electrolyte with an appropriate organic solvent may result in high metal recovery rather than hydrogen gas evolution. However, recovery of Zn as ZnO even in smaller quantity is complementary to solar hydrogen fuel generation. This present work is first-of-its-kind in PEC process-based simultaneous hydrogen generation with heavy metal recovery from real-world AMD water.

Conclusions

We demonstrated real-world acid mine drainage (AMD) polluted water collected from an abandoned metal mine site as a potential electrolyte in solar hydrogen fuel generation, and heavy metal recovery using a CdS QD-sensitized TiO_2 photoanode and a Ni mesh cathode. Photoelectrons generated at the

CdS QD-sensitized TiO_2 photoanode was modulated by varying the number of QD coating cycles and light intensity. We observed as high as ~ 85 and $106 \mu\text{mol cm}^{-2}$ of hydrogen gas evolution at the 2 h reaction under 1 and 2 sun illumination, respectively. Single metal (Zn) AMD polluted water was tested in the current work. Multi metal-based real-world AMD pollutants are tried for validating their potential in PEC reactions. Poly-sulfide sacrificial electrolyte in the photoanode compartment can be replaced with non-corrosive organic water pollutants, or biomass substances to oxidise and convert them into toxic-free mineral by-products. A simultaneous water pollutant treatment at a photoanode and solar fuel generation at the cathode along with a heavy metal recovery open new pathways beyond the water-splitting process. Further understanding of AMD pollutants/electrode interfaces through in-operando tools are appreciable compared to conventional post-processing analysis.

Author contributions

SP conceived the concept, designed the research work, and wrote the manuscript with all the authors' inputs and comments. The photoanode sample preparation and photoelectrochemical experiments were performed by BJ with assistance from KD. MGA carried out the hydrogen gas evolution experiment. SA interpreted the deposition of ZnO and correlated with other experimental studies and also involved in manuscript preparation. MFK contributed technical input, manuscript preparation, designed the hydrogen gas measurement setup and supervised the hydrogen evolution studies. JRD act as an advisor for the project and provided technical inputs. IM and TW facilitated necessary support for XPS and optical measurements.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

- 1 A. Züttel, A. Remhof, A. Borgschulte and O. Friedrichs, *Philos. Trans. R. Soc., A*, 2010, **368**, 3329–3342.
- 2 J. A. Turner, *Science*, 2004, **305**, 972–974.

- 3 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729–15735.
- 4 Y. Tachibana, L. Vayssieres and J. R. Durrant, *Nat. Photonics*, 2012, **6**, 511–518.
- 5 N. S. Lewis, *Science*, 2016, **351**, aad1920.
- 6 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37–38.
- 7 A. Harriman, *Nature*, 1978, **276**, 15–16.
- 8 G. Hodes, J. Manassen and D. Cahen, *Nature*, 1976, **261**, 403–404.
- 9 G. Hodes, *J. Phys. Chem. Lett.*, 2012, **3**, 1208–1213.
- 10 M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.*, 2010, **110**, 6446–6473.
- 11 A. C. Brooks, K. Basore and S. Bernhard, *Inorg. Chem.*, 2013, **52**, 5794–5800.
- 12 J. H. Kim, D. Hansora, P. Sharma, J.-W. Jang and J. S. Lee, *Chem. Soc. Rev.*, 2019, **48**, 1908–1971.
- 13 C. Ros, T. Andreu and J. R. Morante, *J. Mater. Chem. A*, 2020, **8**, 10625–10669.
- 14 R. Sathre, C. D. Scown, W. R. Morrow, J. C. Stevens, I. D. Sharp, J. W. Ager, K. Walczak, F. A. Houle and J. B. Greenblatt, *Energy Environ. Sci.*, 2014, **7**, 3264–3278.
- 15 S. Crawford, E. Thimsen and P. Biswas, *J. Electrochem. Soc.*, 2009, **156**, H346.
- 16 S. Ichikawa, *Int. J. Hydrogen Energy*, 1997, **22**, 675–678.
- 17 Y. Li, J. Feng, H. Li, X. Wei, R. Wang and A. Zhou, *Int. J. Hydrogen Energy*, 2016, **41**, 4096–4105.
- 18 M. Jadwiszczak, K. Jakubow-Piotrowska, P. Kedzierzawski, K. Bienkowski and J. Augustynski, *Adv. Energy Mater.*, 2020, **10**, 1903213.
- 19 M. M. Ayyub, M. Chhetri, U. Gupta, A. Roy and C. N. R. Rao, *Chem. – Eur. J.*, 2018, **24**, 18455–18462.
- 20 M. S. Koo, K. Cho, J. Yoon and W. Choi, *Environ. Sci. Technol.*, 2017, **51**, 6590–6598.
- 21 D. Pan, S. Xiao, X. Chen, R. Li, Y. Cao, D. Zhang, S. Pu, Z. Li, G. Li and H. Li, *Environ. Sci. Technol.*, 2019, **53**, 3697–3706.
- 22 L. Sun, Y. Wang, F. Raziq, Y. Qu, L. Bai and L. Jing, *Sci. Rep.*, 2017, **7**, 1303.
- 23 C. Wu, Z. Gao, S. Gao, Q. Wang, H. Xu, Z. Wang, B. Huang and Y. Dai, *J. Energy Chem.*, 2016, **25**, 726–733.
- 24 A. Roychowdhury, D. Sarkar and R. Datta, *Curr. Pollut. Rep.*, 2015, **1**, 131–141.
- 25 W. Salomons, *J. Geochem. Explor.*, 1995, **52**, 5–23.
- 26 C. N. Kien, N. V. Noi, L. T. Son, H. M. Ngoc, S. Tanaka, T. Nishina and K. Iwasaki, *Soil Sci. Plant Nutr.*, 2010, **56**, 344–356.
- 27 D. A. Vermaas, S. Wiegman, T. Nagaki and W. A. Smith, *Sustainable Energy Fuels*, 2018, **2**, 2006–2015.
- 28 K. Sun, R. Liu, Y. Chen, E. Verlage, N. S. Lewis and C. Xiang, *Adv. Energy Mater.*, 2016, **6**, 1600379.
- 29 S. Anantharaj, K. Karthik, T. S. Amarnath, S. Chatterjee, E. Subhashini, K. C. Swaathini, P. E. Karthick and S. Kundu, *Appl. Surf. Sci.*, 2019, **478**, 784–792.
- 30 L. Chen, X. Dong, F. Wang, Y. Wang and Y. Xia, *Chem. Commun.*, 2016, **52**, 3147–3150.
- 31 W. Zhu, W. Zhang, Y. Li, Z. Yue, M. Ren, Y. Zhang, N. M. Saleh and J. Wang, *J. Mater. Chem. A*, 2018, **6**, 24277–24284.
- 32 F. Castelan Marques, G. Mendonça Valane and V. Mezadre Buzato, *Int. J. Energy Res.*, 2020, **44**, 12188–12196.
- 33 P. Sudhagar, J. H. Jung, S. Park, R. Sathyamoorthy, H. Ahn and Y. S. Kang, *Electrochim. Acta*, 2009, **55**, 113–117.
- 34 A. Subramanian, D. Punnoose, S. S. Rao, C. Venkata Thulasi Varma, B. Naresh, V. Raman and H.-J. Kim, *New J. Chem.*, 2017, **41**, 5942–5949.
- 35 Y. Liu, F. Dai, R. Zhao, X. Huai, J. Han and L. Wang, *J. Mater. Sci.*, 2019, **54**, 8571–8580.
- 36 M. J. Jackman, A. G. Thomas and C. Muryn, *J. Phys. Chem. C*, 2015, **119**, 13682–13690.
- 37 A. G. Aragon, W. Kierulf-Vieira, T. Łęcki, K. Zarębska, J. Widera-Kalinowska and M. Skompska, *Electrochim. Acta*, 2019, **314**, 73–80.
- 38 E. Rabinovich and G. Hodes, *J. Phys. Chem. C*, 2013, **117**, 1611–1620.
- 39 V. N. Rao, S. Pitchaimuthu, P. Ravi, M. Sathish, H. Han and S. M. Venkatakrishnan, *ChemCatChem*, 2020, **12**, 3139–3152.
- 40 N. Buehler, K. Meier and J. F. Reber, *J. Phys. Chem.*, 1984, **88**, 3261–3268.
- 41 R. Raja, P. Sudhagar, A. Devadoss, C. Terashima, L. K. Shrestha, K. Nakata, R. Jayavel, K. Ariga and A. Fujishima, *Chem. Commun.*, 2015, **51**, 522–525.
- 42 P. Rodenas, T. Song, P. Sudhagar, G. Marzari, H. Han, L. Badia-Bou, S. Gimenez, F. Fabregat-Santiago, I. Mora-Sero, J. Bisquert, U. Paik and Y. S. Kang, *Adv. Energy Mater.*, 2013, **3**, 176–182.
- 43 R. Trevisan, P. Rodenas, V. Gonzalez-Pedro, C. Sima, R. S. Sanchez, E. M. Barea, I. Mora-Sero, F. Fabregat-Santiago and S. Gimenez, *J. Phys. Chem. Lett.*, 2013, **4**, 141–146.
- 44 L. Jin, H. Zhao, Z. M. Wang and F. Rosei, *Adv. Energy Mater.*, 2021, **11**, 2003233.
- 45 P. S. Shinde, J. W. Park, M. A. Mahadik, J. Ryu, J. H. Park, Y.-J. Yi and J. S. Jang, *Int. J. Hydrogen Energy*, 2016, **41**, 21078–21087.
- 46 W. Wang, C. Jin and L. Qi, *Small*, 2018, **14**, 1801352.
- 47 B. Han and Y. H. Hu, *Energy Sci. Eng.*, 2016, **4**, 285–304.
- 48 Y. Zhang, C. Yuan, Q. Wang, M. R. Hoffmann, X. Zhang, J. Nie, C. Hu, S. Chen, J. Qiao, Q. Wang and Y. Cong, *Electrochim. Acta*, 2019, **328**, 135124.
- 49 S. R. Kadam, S. W. Gosavi, B. B. Kale, N. Suzuki, C. Terashima and A. Fujishima, *Journal*, 2019, **9**, 12036.
- 50 Z.-J. Li, X.-B. Fan, X.-B. Li, J.-X. Li, F. Zhan, Y. Tao, X. Zhang, Q.-Y. Kong, N.-J. Zhao, J.-P. Zhang, C. Ye, Y.-J. Gao, X.-Z. Wang, Q.-Y. Meng, K. Feng, B. Chen, C.-H. Tung and L.-Z. Wu, *J. Mater. Chem. A*, 2017, **5**, 10365–10373.
- 51 D. W. Su, J. Ran, Z. W. Zhuang, C. Chen, S. Z. Qiao, Y. D. Li and G. X. Wang, *Sci. Adv.*, 2020, **6**, eaaz8447.
- 52 D. Chen and A. K. Ray, *Chem. Eng. Sci.*, 2001, **56**, 1561–1570.
- 53 C. Singh and R. Chaudhary, *J. Renewable Sustainable Energy*, 2013, **5**, 053102.

- 54 L. X. Chen, T. Rajh, O. Mićić, Z. Wang, D. M. Tiede and M. Thurnauer, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 1997, **133**, 8–14.
- 55 F. Hosseini and S. Mohebbi, *J. Ind. Eng. Chem.*, 2020, **85**, 190–195.
- 56 R. Beltrán-Suito, V. Forstner, J. N. Hausmann, S. Mebs, J. Schmidt, I. Zaharieva, K. Laun, I. Zebger, H. Dau, P. W. Menezes and M. Driess, *Chem. Sci.*, 2020, **11**, 11834–11842.
- 57 L. S. Dake, D. R. Baer and J. M. Zachara, *Surf. Interface Anal.*, 1989, **14**, 71–75.
- 58 C. D. Wagner and G. E. Muilenberg, *Handbook of X-ray photoelectron spectroscopy: a reference book of standard data for use in X-ray photoelectron spectroscopy*, Physical Electronics Division, PerkinElmer Corp., Eden Prairie, Minn., 1979.
- 59 J. S. Wellings, N. B. Chaure, S. N. Heavens and I. M. Dharmadasa, *Thin Solid Films*, 2008, **516**, 3893–3898.
- 60 M. Skompska and K. Zarębska, *Electrochim. Acta*, 2014, **127**, 467–488.