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Supporting Information

Photoelectrochemical Concurrent Hydrogen Generation and Heavy Metal Recovery from Polluted Acidic Mine Water

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S1. Experimental

S1.a Fabrication of photoanodes

TiO_2 paste preparation: The multistep synthesis of the mesoporous TiO_2 paste used for photoanode fabrication follows. An ethylcellulose solution was prepared by mixing a 50:50 ratio of 30-60mPas ethylcellulose and 5-15mPas ethylcellulose (Sigma Aldrich) for a total of 3g. The ethylcellulose mixture was then dissolved in 30g of ethanol before being left to stir for 12 hours. 3g of titanium (IV) oxide powder (P25 Degussa) grounded with 0.5ml Acetic acid for 5 minutes. It followed that 0.5ml deionised water added and ground for 1 minute. This process was repeated 5 times. Then 0.5ml ethanol added and ground for 1 minute and repeated 15 times. A known amount of ethanol 1.25ml was added and ground for 1 minute and repeated this process 6 times. The mixture was then transferred to a beaker using 50ml of ethanol, before undergoing a sonication process. To avoid the nanoparticle agglomeration, the mixture is sonicated using the "out-gas" pulsing function for 30 seconds and put under magnetic stirred for 1 minute. 10g of α-Terpineol (Sigma Aldrich) was added to the above mixture and stirred for 1 minute. Then sonicate using the "out-gas" pulsing function for 30 seconds and went for 1 minute. Added 15g of the pre-prepared ethylcellulose mixture and stir for 1 minute and repeat the above-said sonication process. Finally, a rotary evaporator was used to remove the solvent

and thicken up the TiO_2 and ethylcellulose mixture until the desired viscosity achieved. The resultant TiO_2 paste was collected and kept in the three milling rolls for a couple of days.

TiO_2 blocking layer coating: Before TiO_2 deposition, fluorine-doped tin oxide (FTO) coated glass substrates (Pilkington NSG TEC, 12 ohms/square) were washed in deionised water and soap, followed by sonication for 30 minutes. The substrates then underwent cleaning with ethanol and a subsequent 30-minute sonication step again. A thin, compact layer of TiO_2 (blocking layer) was deposited onto the FTO substrates at 300^{o}C by pneumatic spray pyrolysis. The blocking layer solution consisted of TiAcAc:Isopropanol (Sigma Aldrich) in a 1:9 ratio with Isopropanol. The mixture was applied using an air gun, with 25 passes at a distance of 20 cm from the substrates. The substrates were then heated from 300^{o}C to 550^{o}C and held at 550^{o}C for 30 minutes to sinter, then left to cool.

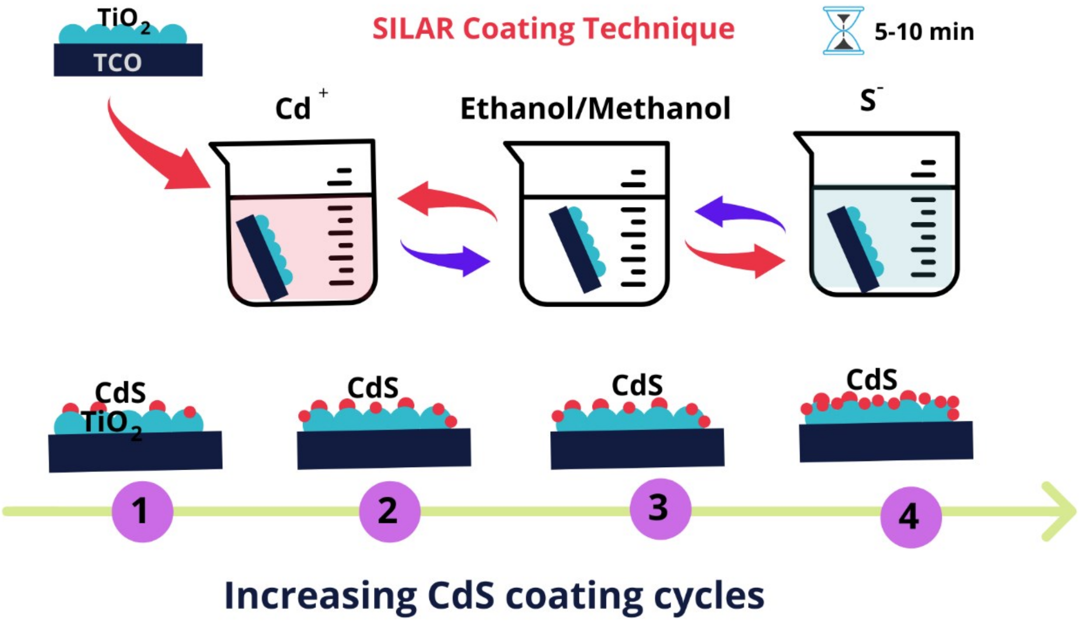
Mesoporous TiO_2 electrode:

The pre-prepared TiO_2 paste was deposited onto FTO glass substrates by doctor blade technique. A scotch tape (3mm) size was covered on two sides of each square substrate. The TiO_2 paste was dropped onto the substrate surface in a small area and then quickly drawn across the substrate surface with a small glass implement. The coating was sintering at 450 ^{o}C for 2 hr at air atmosphere. The sintering process carried out at 2 ^{o}C/min ramping rate.

Cadmium Sulphide Quantum Dots (QDs) Deposition:

Successive Ionic Layer Adsorption and Reaction (SILAR) technique was adopted for the cadmium sulphide (CdS) quantum dot deposition. Typically this method has been used for the deposition of CdS and ZnS complimentary semiconductors. The deposition process occurs when the substrate is submerged separately in two precursor solutions, with cleaning baths in between. The cleaning step removes partially bound species and ensures compact, discreet layers of each precursor compound. The first solution facilitates the cation adsorption, while the second is the anion precursor. Discreet layer thickness for each cycle is dependant on the reactivity of the substrate and the precursors, as well as immersion time.

For the CdS QDs deposition four beakers were prepared in the following order: (a) 1.15g cadmium acetate dissolved in 100ml ethanol, (b) 100ml ethanol 0.4g sodium sulphide dissolved in 100ml methanol, and (c) 100ml methanol. An electrode was submerged in each beaker for 4 minutes in the order given above. The first cycle of deposition completed when the electrode reached the fourth bath. The CdS QD deposition was completed on electrodes for cycles of 3, 5 and 7. The above process schematically presented in the **scheme S1**.



Scheme S1. (a) Schematic illustration of SILAR coating for achieving CdS quantum dots onto mesoporous TiO_2.

After the final bath of either the third, fifth or seventh cycle, the electrode a ZnS passivation layer was deposited as follows: (a) 2.9g zinc nitrate dissolved in 100ml deionised water, (b) 100ml deionised water, (c) 0.78g sodium sulphide dissolved in 100ml deionised water and (d) 100ml deionised water. The CdS coated TiO_2 electrode is submerged in each bath for 1 minute, for one cycle. The photos of the final electrodes are presented in inset of Figure 1 in the main text. The colour shift from white to dark yellow is indicative of the CdS QD film formation.

The thickness of the TiO_2 layer is approximately 1 micron and ensured by a cross-section scanning electron microscope image. The post-deposition of CdS QDs (10-15 nm), and ZnS (10 nm) are extremely thin compared to TiO_2 thickness.

Finally, a copper wire with insulator cover was soldered to each electrode, afterwards, the electrodes were sealed with epoxy resin, leaving only the photoactive surface.

S1.b Characterisation

The surface morphology and chemical composition of pristine, and CdS QDs coated TiO_2 electrodes are studied by scanning electron microscope (JEOL 7800F), and energy-dispersive X-ray spectroscopy (EDX). The chemical environment of TiO_2 and CdS QDs-sensitized TiO_2 samples examined by x-ray electron spectroscopy (KRATOS AXIS SUPRA XPS, dual anode (Mg/Al) X-ray source). The optical reflectance was recorded in the range between 300-800 nm using UV Spectrophotometer (JASCO). These values are used to estimate the Kubelka-munk absorbance using the relation

$F (R) = (1-R)^2/R^2$

Where R is the diffuse refection of the film.

The Zn^{2+} ions concentration in the electrolyte has examined using Agilent 4210 MP-AES atomic absorption Spectroscopy (AAS) technique.

S1.c Measurements

Photoelectrochemical measurements:

All the PEC measurements carried out using electrochemical station (Autolab PGSTAT 302N). The NOVA software used to run the electrochemical measurements. A glass made two-electrode chemical cell setup was utilised for electrochemical and photoelectrochemical experiments. The prepared TiO_2 and CdS QDs-sensitized TiO_2 electrodes were used as photoanode in the anode compartment. The Ni mesh (XXX grade, Japan) applied as a counter electrode, and $Hg/HgCl_2$ calomel electrode used as a reference electrode Anode and cathode compartment separated with the Nafion^{TM} membrane. 0.3 M of aqueous Na_2SO_4/Na_2S polysulfide electrolyte used as an electrolyte for PEC studies, mainly it kept in photoanode compartment. Class AAA solar simulator (350-1100nm) with built-in AM1.5G filter was used for PEC experiments (ASAHI SPECTRA, Japan). 1 sun illumination was ensured with ASHAI SPECTRA 1 sun checker (Silicon photodiode and InGaAs PIN diode).

The measured potentials vs. $Hg/HgCl_2$ were converted to the reference hydrogen electrode (RHE) scale according to the Nernst equation:

$$E_{\mathrm{RHE}} = E_{\mathrm{Hg/HgCl2}} + 0.059\ \mathrm{pH} + \mathrm{E^o}_{\mathrm{Hg/HgCl2}} \qquad (1)$$

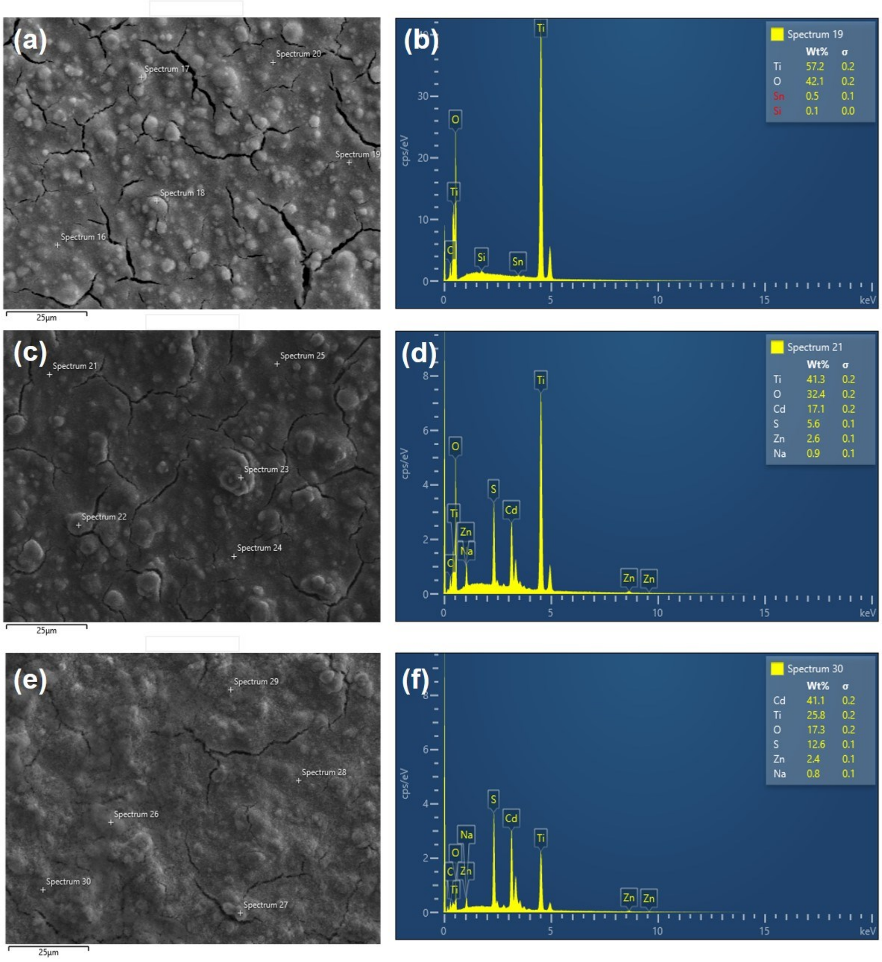
where E_{RHE} is the converted potential vs. RHE, $E^o_{Hg/HgCl2} = 0.1976$ at 25°C, and $E_{Hg/HgCl2}$ is the experimentally measured potential against $Hg/HgCl_2$ reference electrode (Wang, Lee and Schmuki, 2013).

The acid mine drainage (AMD) water samples obtained from different outlets (pond and lake) at Frongoch metal mine 25 miles south-east of Aberystwyth, Wales, UK. These water samples collected by Nature Resources Wales (NRW), Cardiff, UK and used in our lab experiments with their permission (KESS-II funded project). The AMD water pollutants samples having a high amount of Zn metals concentration (47.1 ppm), with a trace level of other metals level (Cd:0.15 ppm, Cu: 0.02 ppm, Ni (0.04 ppm, Fe: 0.02 ppm). The suspended solid particles present in the AMD water samples were removed by watmann filter (0.45 mm PTFE, 50 mm Dia; 10/Pk). The AMD water sample pH is 4.8 and looks transparent.

Hydrogen gas evolution measurement:

A two-compartment electrochemical cell as described above was used for photoelectrochemical hydrogen gas evolution under illumination with a solar light simulator (Thermo Oriel 92194-1000) equipped with an AM 1.5G filter (Newport) at an intensity of 1 sun.. The cathode compartment headspace was tightly sealed with a rubber stopper and Teflon tape. The sample headspace was subject to a constant purge of N_2 at a rate of 10 mL min^{-1}. H_2 evolution was monitored by gas chromatography (Shimadzu Nexis 2030) using an auto-sampler programmed to periodically inject 2 mL of the headspace stream. Gas chromatography was performed on a Shimadzu Nexis GC-2030 gas chromatograph equipped with a barrier-discharge ionisation detector (BID) and a molecular sieve column. The GC was calibrated using calibration gas (2000 ppm H_2, BOC), diluted with N_2 at different ratios using a set of mass flow controllers (Bronkhorst) to provide known concentrations of H_2. Gas samples were programmed to auto-inject into the GC *via* a multi-port stream selector valve directing the selected sample purge gas stream through a 2 mL sample loop before injection (Restek). H_2 evolution rates were calculated from the measured H_2 concentration in the purge gas and the purge gas flow rate. Cumulative H_2 production was calculated from the H_2 evolution rate and time passed since the previous measurement, assuming a constant H_2 evolution rate between time points.

S2. Elemental mapping analysis



Spectrum 19

	Wt%	σ
Ti	57.2	0.2
O	42.1	0.2
Sn	0.5	0.1
Si	0.1	0.0

Spectrum 21

	Wt%	σ
Ti	41.3	0.2
O	32.4	0.2
Cd	17.1	0.2
S	5.6	0.1
Zn	2.6	0.1
Na	0.9	0.1

Spectrum 30

	Wt%	σ
Cd	41.1	0.2
Ti	25.8	0.2
O	17.3	0.2
S	12.6	0.1
Zn	2.4	0.1
Na	0.8	0.1

Figure S1. Scanning electron images of (a) Pristine TiO_2, (c) TiO_2/CdS QDs (3 cycles)/ ZnS (1 cycle), (e) TiO_2/CdS QDs (3 cycles)/ ZnS (1 cycle) samples, and corresponding EDS results are presented in the right side (b), (d) and (f), respectively.

S3. Chemical environment analysis: photoanode

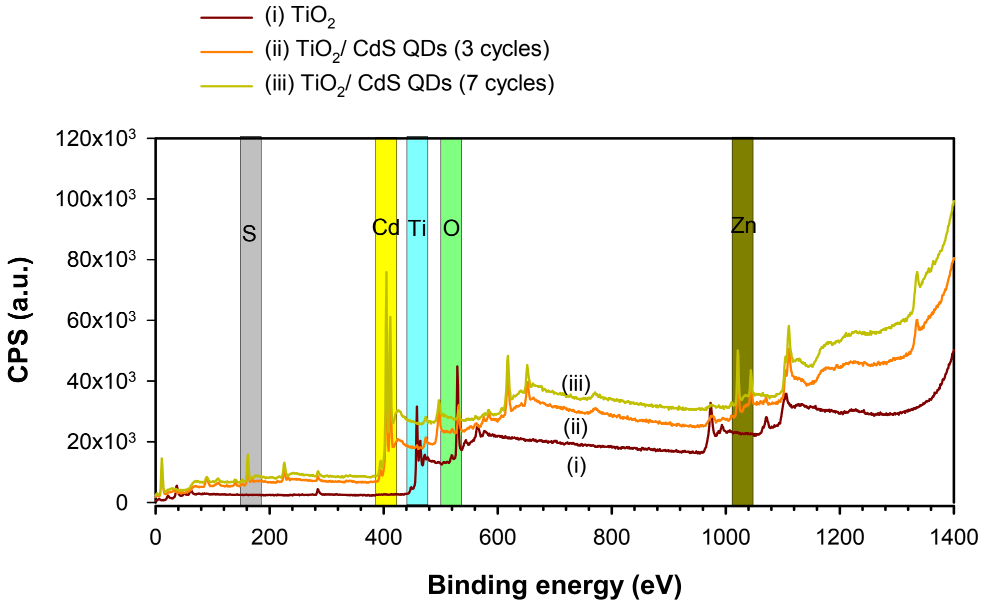


Figure S2. XPS wide scan spectra of pristine TiO$_2$ and CdS QDs-sensitized TiO$_2$ samples. The CdS QDs-sensitized samples passivated with ZnS coating.

S4. Optical absorbance analysis

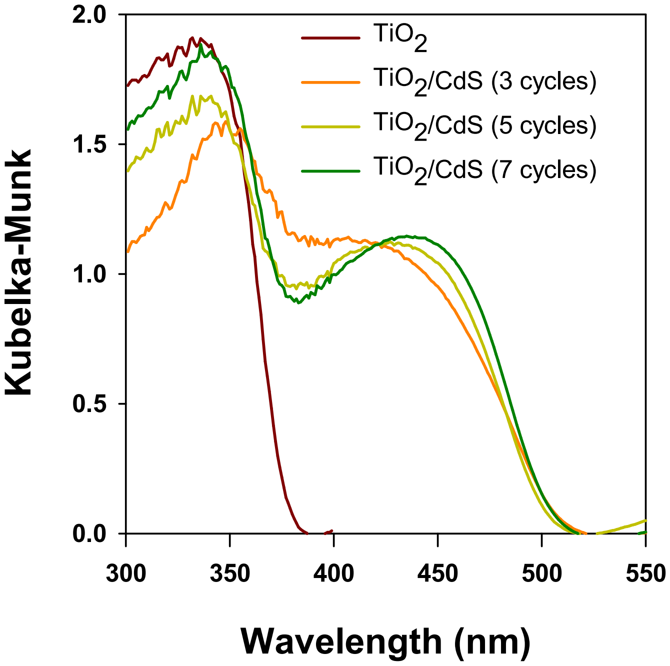


Figure S3. Diffused reflectance spectra of pristine and CdS QDs-sensitized TiO_2 electrodes for different coating cycles (3 and 5).

S5. Hydrogen gas evolution analysis:

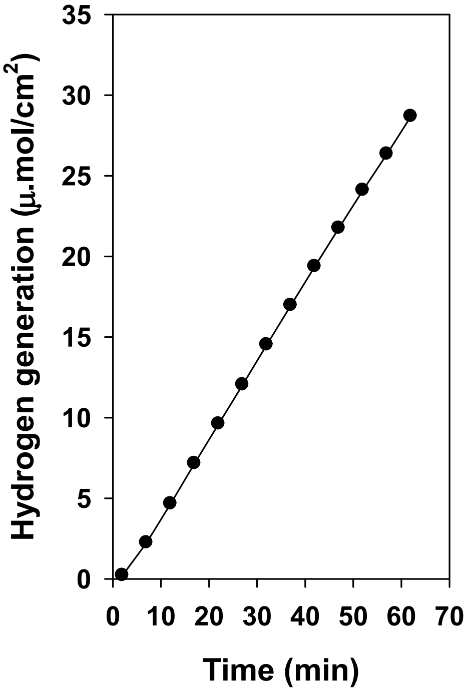


Figure S4. Photoelectrochemical hydrogen evolution at a CdS QD-sensitized TiO_2 photoanode (7 cycles) held at 0.2 V RHE under AM 1.5G irradiation (1 sun) in 0.3 M polysulfide electrolyte in both photoanode and cathode compartment..

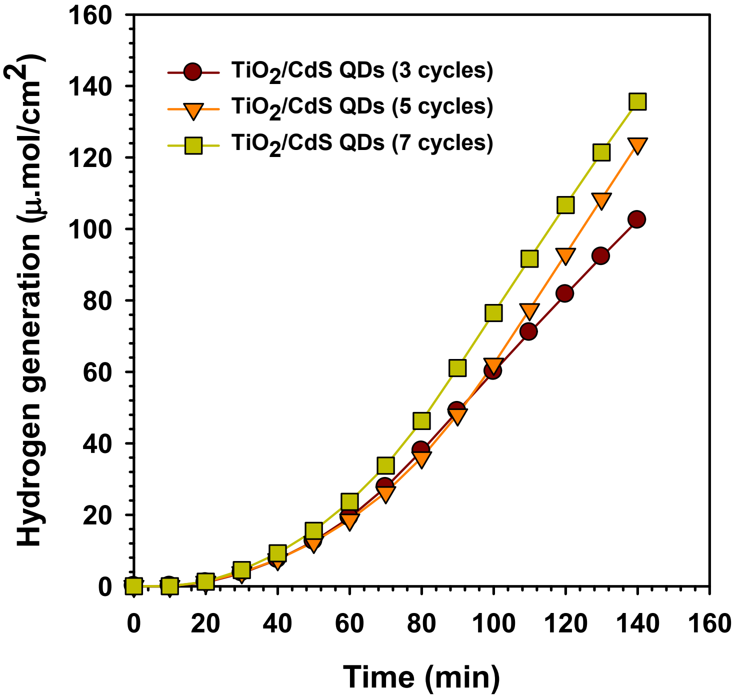


Figure S5. Photoelectrochemical hydrogen evolution from a CdS QD (3,5 and 7)- sensitized TiO_2 photoanode under 2 Sun light irradation. 0.3 M polysulfide electrolyte (pH=14), and AMD pollutant (pH=4.8) were used in the photoanode, and cathode compartment, respectively. The measurements were recorded at 0.2 V RHE using $Hg/HgCl_2$ calomel reference electrode.

S6. Surface morphology analysis: cathode

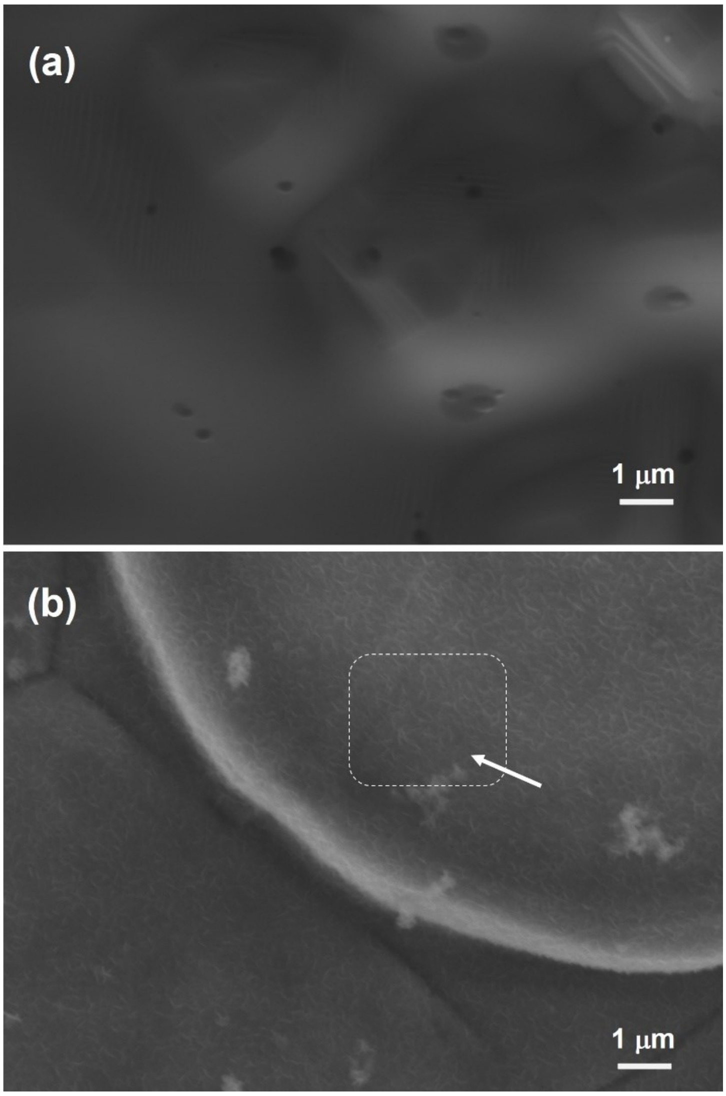


Figure S6. FESEM images of Ni mesh **(a)** before involved in PEC reaction and **(b)** after involved in PEC reaction as a cathode (photoanode: 7 cycles of CdS QDs coated TiO_2).

S7. Chemical environment analysis: cathode

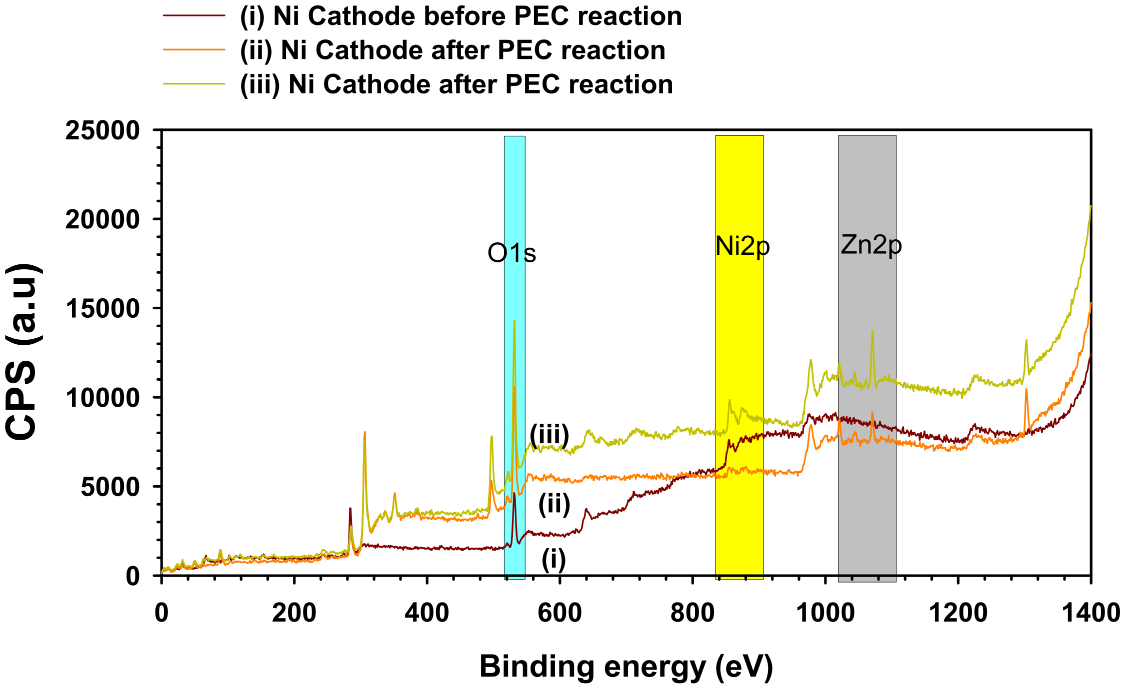


Figure S7. The XPS wide scan spectra results of Ni mesh (cathode) before and after PEC experiments. The reference Ni mesh sample before the PEC process marked as “i”. Note that the Ni mesh cathode kept at cathode compartment of PEC cells and expose with AMD pollutant. The Ni mesh collected after PEC experiments involved 3 and 7 cycles of CdS QDs-sensitized TiO_2 photoanode marked as “ii” and “iii”, respectively.