

Photo-Electrochemical Water Splitting Behaviour of CdSe Quantum Dots Sensitized Ferroelectric PbTiO₃ Perovskite Heterostructure

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Received: 14 May 2018;

Accepted: 14 June 2018;

Published online: 31 July 2018;

AJC-19026

Herein, we report the photo-electrochemical water splitting of CdSe quantum dots sensitized PbTiO₃ perovskite in a sacrificial electrolyte. The CdSe quantum dots are synthesized *via* hot injection method and perovskite. The PbTiO₃ is synthesized *via* hydrothermal synthesis procedure. The CdSe quantum dots are sensitized to PbTiO₃ using mercaptopropionic acid as linker to form hetero-structure. The phase purity and crystallinity of CdSe quantum dots and PbTiO₃ are examined using X-ray diffraction analysis and the morphologies are studied using field emission scanning electron microscopy (FESEM) and transition electron microscopy (TEM) techniques. The optical properties are examined using UV-visible spectroscopy and the band gap of quantum dots and perovskite are derived. The XRD analysis of CdSe quantum dots revealed the high crystallinity with a cubic phase and tetragonal phase for PbTiO₃. The surface morphological observations demonstrate that PbTiO₃ size in the range of 80-120 nm in size. The TEM analysis revealed the single crystalline nature for PbTiO₃ nanoparticles. The optical band gap of PbTiO₃ is found to be 3.7 and 2.25 eV for CdSe quantum dots. The CdSe quantum dots sensitized PbTiO₃ hetero-structure's photo-electrochemical water splitting behaviour is examined in 1 M Na₂S electrolyte under 100 mW/cm² light illumination. As photoanode, CdSe quantum dots sensitized PbTiO₃ heterostructure demonstrated 63 mA/cm² under illumination and 51 mA/cm² dark at 0.8 V (*vs.* Ag/AgCl), which implies that photocurrent density of 12 mA/cm² at 0.8 V (*vs.* Ag/AgCl) and also showed 1.2 mmol/g of H₂ evolution during the period of 4 h in chrono-amperometry studies at 0.8 V (*vs.* Ag/AgCl). This work discusses the significance and novelty of the usage of CdSe quantum dots sensitized PbTiO₃ heterostructure as photo-electrocatalyst and paves pathway for newer materials development for enhanced photo-electrochemical water splitting.

Keywords: CdSe Quantum dots, PbTiO₃ perovskites, Nanoparticles, photo-electrochemical water splitting.

INTRODUCTION

The development of stable catalyst for semiconductor based photocatalysis of water, to produce clean futuristic fuel hydrogen, is gaining more importance in the field of material science research and development [1,2]. Since the first report on photo-electrochemical water splitting using TiO₂ semiconductor, reported by Fujishima and Honda in 1972 [3], major efforts have been undertaken by many researchers to develop photo-active semiconductors, which can split water into oxygen and hydrogen with and without bias potentials. Typically, semiconductor based metal oxides, such as TiO₂, WO₃, ZnO and SnO₂ were explored as photocatalyst in the solar water electrolysis [4-7]. Nevertheless, the photo-electrochemical water splitting behaviour of these oxides do have limitations because of inade-

quate visible absorption and also not have negative conduction band (CB) which favours H₂ evolution reaction. Enhanced photo-catalytic water splitting efficiency can be realized with the use of visible light absorbing semiconductors, as the solar spectrum consists of almost 50 % visible light (400 < λ < 800 nm). In this regard, visible light sensitive quantum dots gained more importance, to be as candidate materials in photoelectrochemical water splitting, due to higher band absorption coefficients [8]. However, due to the small band gap, recombination of photo-generated electrons takes part, which is not beneficial for solar water splitting. Hence, the formation of hetero-structures, where narrow band gap quantum dots are sensitized on large band gap semiconductors linked either chemically or physically, is prioritized in photo-electrochemical water splitting [9-14]. To highlight, several heterostructures have been developed using

CdSe quantum dots such as CdSe/TiO₂, CdSe/CdS/TiO₂, CdS/CdSe/ZnO, CdSe/CdS/ZnO, CdSe/ZnS/ZnO, CdSe/SiNWs and CdS/CdSe/ZnO/TiO₂ emphasizing the role of band gap alignment in efficient water splitting [15-21]. Most recent works emphasize that perovskites having ABO₃ formula, are being identified as one of the most suitable materials in energy conversion devices due to its unique electronic band structure and unidirectional charge transfer properties. To highlight, SrTiO₃ perovskite-based oxide with a wide band gap of 3.4 eV, explored as photocatalyst in solar water splitting and in addition to this, the heterostructures, CdSe QDs/SrTiO₃ and NiO/SrTiO₃ structures were also being studied [22,23].

Recently, PbTiO₃ perovskite oxide is gaining more importance in the research due to the superior properties like ferroelectricity, piezoelectricity and magnetoresistivity [24-28]. The PbTiO₃ perovskite is d(0) and d(10) metal oxide with ferroelectric polarization and demonstrated as excellent photocatalyst in organic dyes degradation and photocatalytic hydrogen generation [29-31]. The PbTiO₃ perovskite based heterostructure are also being fabricated and explored as photo electrocatalyst in water splitting. To highlight, Won Ahn *et al.* [32] developed Pt nanodot deposited PbTiO₃ and demonstrated effective charge separation with higher photocurrent density in photoelectrochemical water splitting. Jang *et al.* [33] fabricated core-shell PbTiO₃@TiO₂ heterojunction nanotube array and showed excellent photoelectrochemical water splitting. Liu *et al.* [34] constructed TiO₂ islands on ferroelectric PbTiO₃ crystals and demonstrated enhanced photocatalytic hydrogen generation in both UV and visible light irradiation. In spite of the above reported works, surprisingly, photoelectrochemical water splitting activity of CdSe quantum dots sensitized PbTiO₃ heterostructure have not been studied well. In this regard, we have focussed on using CdSe quantum dots sensitized PbTiO₃ heterostructure in photo-electrochemical water splitting behaviour and examined photoelectrochemical hydrogen generation activity in this work.

The present work describes the fabrication of CdSe quantum dots sensitized PbTiO₃ heterostructure and explored as photocatalyst in photo-electrochemical water splitting in 1M Na₂S electrolyte under 100 mW/cm² light illumination. As photoanode, CdSe quantum dots sensitized PbTiO₃ heterostructure demonstrated 63 mA/cm² under illumination and 51 mA/cm² in dark at 0.8 V (*vs.* Ag/AgCl), which implies that photocurrent density of 12 mA/cm² at 0.8 V (*vs.* Ag/AgCl) and also showed 1.2 mmol/g of H₂ evolution during the period of 4 h in chronoamperometry studies at 0.8 V (*vs.* Ag/AgCl). This work discusses the significance and novelty of the usage of CdSe quantum dots sensitized PbTiO₃ heterostructure as photo-electrocatalyst and paves pathway for newer materials development for enhanced photo-electrochemical water splitting.

EXPERIMENTAL

Synthesis of PbTiO₃: PbTiO₃ nanoparticles were synthesized *via* hydrothermal route. Lead nitrate (10 mmol) and TiCl₄ dissolved separately in distilled water and mixed together with constant stirring. Further, 10 mol NaOH solution was added to the above solution and transferred into a 50 mL capacity Teflon-lined stainless-steel autoclave. The reaction temperature was maintained at 170 °C for the period of 8 h and cooled to

room temperature. The resulted product was washed several times using ethanol-water and dried at 120 °C for 15 min.

Synthesis of CdSe quantum dots: The CdSe quantum dots were synthesized according to the reported work [35]. In a typical synthesis using three-neck flask, 0.3 mmol of cadmium oxide mixed with 0.6 g of oleic acid were heated to 180 °C until a clear solution formed and cooled down to room temperature. 1-Hexadecylamine (4 mL) and tri-*n*-octylphosphine oxide (7 mL) were added to the mixture and heated to 100 °C for 10 min. To this solution, tri-*n*-octylphosphine (1 mL) containing selenium was gently injected and allowed for crystal growth at 280 °C. Further, 1 mL of CdSe quantum dots were washed with methanol solvent by centrifugation at 3000 rpm and stored in toluene. In this, 1 mL of solution were mixed with 1 mL of acetone and 1 mL of 3-mercaptopropionic acid (MPA) and the formed 3-mercaptopropionic acid capped CdSe quantum dots was washed and stored in de-ionized water.

Sensitization of CdSe quantum dots on PbTiO₃: The 3-mercaptopropionic acid capped CdSe quantum dots (10 mg) was mixed with 20 mg of PbTiO₃ powder and stirred for 4 h to form CdSe quantum dots sensitized PbTiO₃ heterostructure. The resulted powder applied as paste on conducting glass and dried at 60 °C and explored as photoanodes in photoelectro-chemical studies.

RESULTS AND DISCUSSION

X-ray diffraction analysis: The phase purity and crystallinity of CdSe sensitized PbTiO₃ perovskite are examined using X-Ray diffraction (Bruker-Advanced D8) analysis. Fig. 1 shows high crystallinity for CdSe sensitized PbTiO₃ perovskite. The peaks for CdSe quantum dots are well matched with standard JCPDS file no. # 19-0191 and demonstrate the cubic phase, where $a = b = c = 6.07 \text{ \AA}$ and belongs to F-43m space group [15-21]. The broadened peaks at 24.9° corresponds to (111) plane of CdSe quantum dots and rest of the peaks at 42° and 49.7° correspond to (220) and (311) planes, respectively.

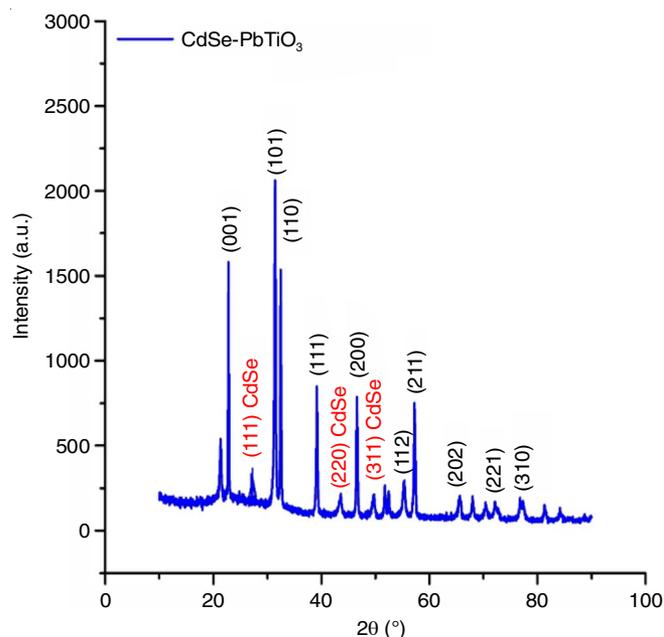


Fig. 1. X-ray diffraction pattern for CdSe sensitized PbTiO₃ perovskite

The major peak 31.4° corresponds to (101) plane with interplanar distance (*d*) of 0.28 nm and other major peaks at 24.6° and 32.4° corresponds to (001) and (110) planes respectively, demonstrates the high crystallinity with tetragonal phase for PbTiO₃ perovskite. All the obtained peaks are well matched with standard JCPDS file no. # 78-0298. The XRD result revealed that the CdSe quantum dots are functionalized with PbTiO₃ perovskite and formed as heterostructure.

UV-visible spectra: The UV-visible spectra recorded using (Speccord 200 Plus, 200-800 nm). UV-visible spectra of PbTiO₃ perovskite and CdSe sensitised PbTiO₃ perovskite are shown in Fig. 2. The UV-visible spectrum of PbTiO₃ perovskite shows the absorption at 335 nm wavelength indicating the band gap of 3.7 eV. The CdSe sensitised CdSe sensitised PbTiO₃ perovskite demonstrated the absorbance at 550 nm wavelength, which indicate the band gap 2.25 eV attributed to the presence of CdSe quantum dots. This behaviour clearly indicates that the formation of heterostructure.

Surface morphological analysis: The surface morphologies of CdSe sensitised PbTiO₃ and are shown in Fig. 3a-b. The FESEM images of CdSe sensitised PbTiO₃ perovskite is shown in Fig. 3c-d. It is seen that irregular shaped nanoparticles for CdSe sensitised PbTiO₃ and CdSe sensitised PbTiO₃ perovskite is shown that CdSe quantum dots presence over PbTiO₃ nanoparticles.

TEM images of PbTiO₃ nanoparticles and CdSe sensitised PbTiO₃ perovskites are shown in Fig. 4 (using TEM, Technai

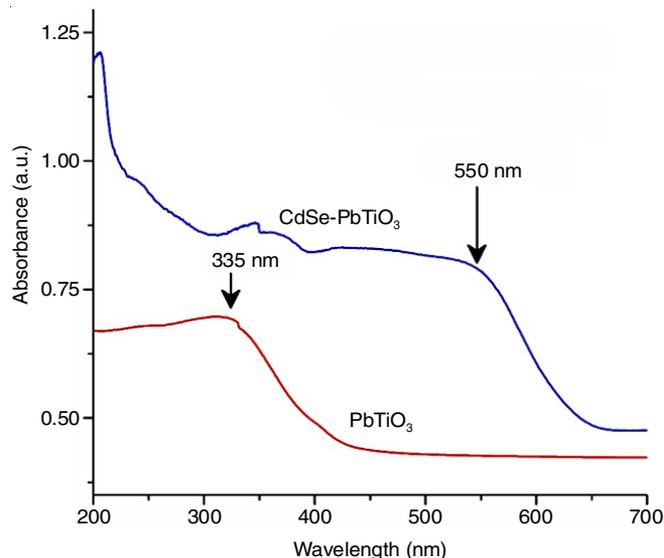


Fig. 2. UV-visible absorbance spectra of PbTiO₃ and CdSe sensitised PbTiO₃ perovskite

G2 20). The TEM images of PbTiO₃ perovskite nanoparticles are shown in Fig. 4a-b indicate the irregular shaped nanoparticles. Fig. 4c shows the morphology of CdSe sensitised PbTiO₃ perovskite and it can be seen that the smallest nanoparticles (CdSe quantum dots) covered over larger nanoparticles of PbTiO₃. Fig. 4c revealed that polycrystalline CdSe quantum dots are mixed with single crystalline PbTiO₃ nanoparticles.

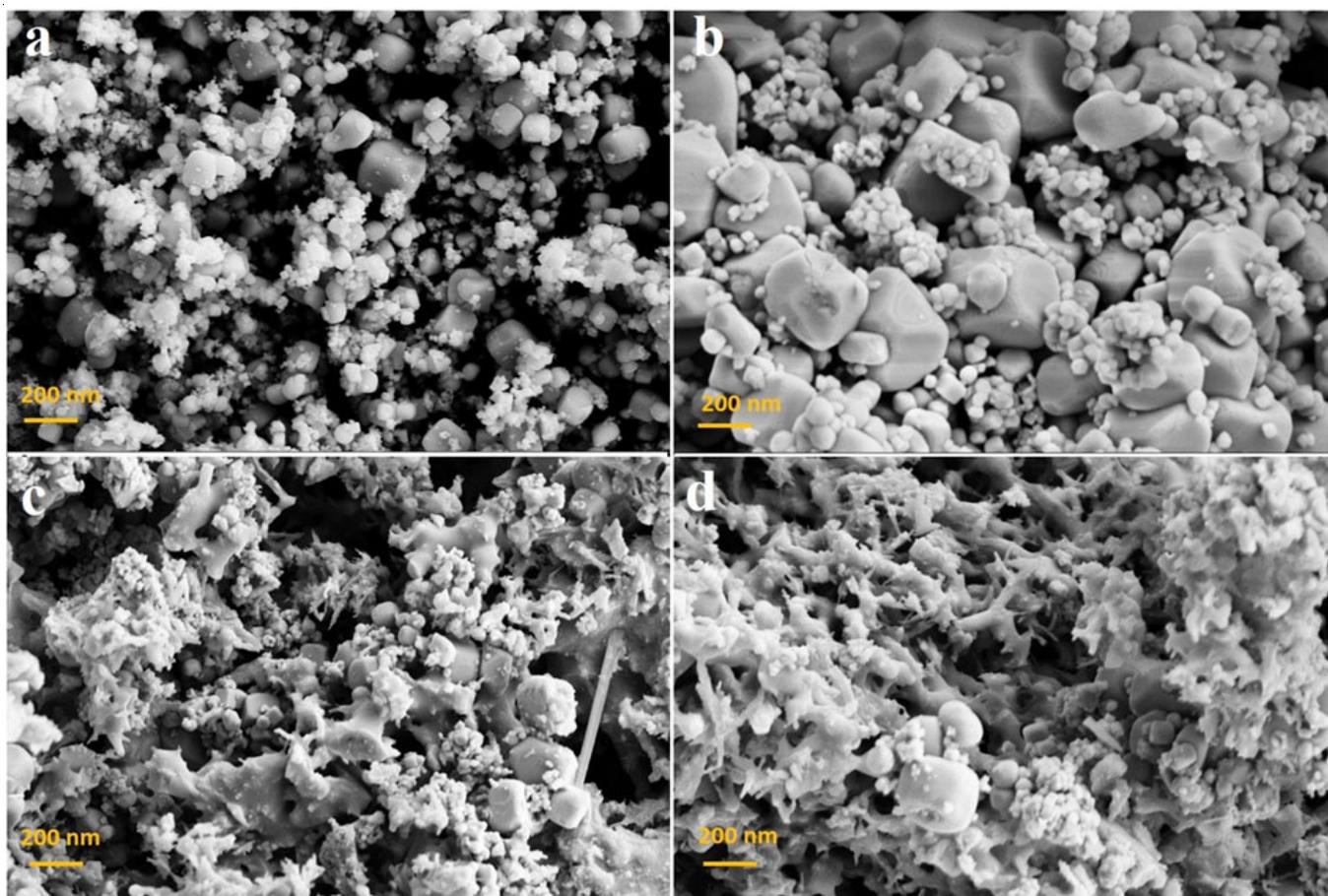


Fig. 3. FESEM images of (a & b) PbTiO₃ and (c & d) CdSe sensitised PbTiO₃ perovskite

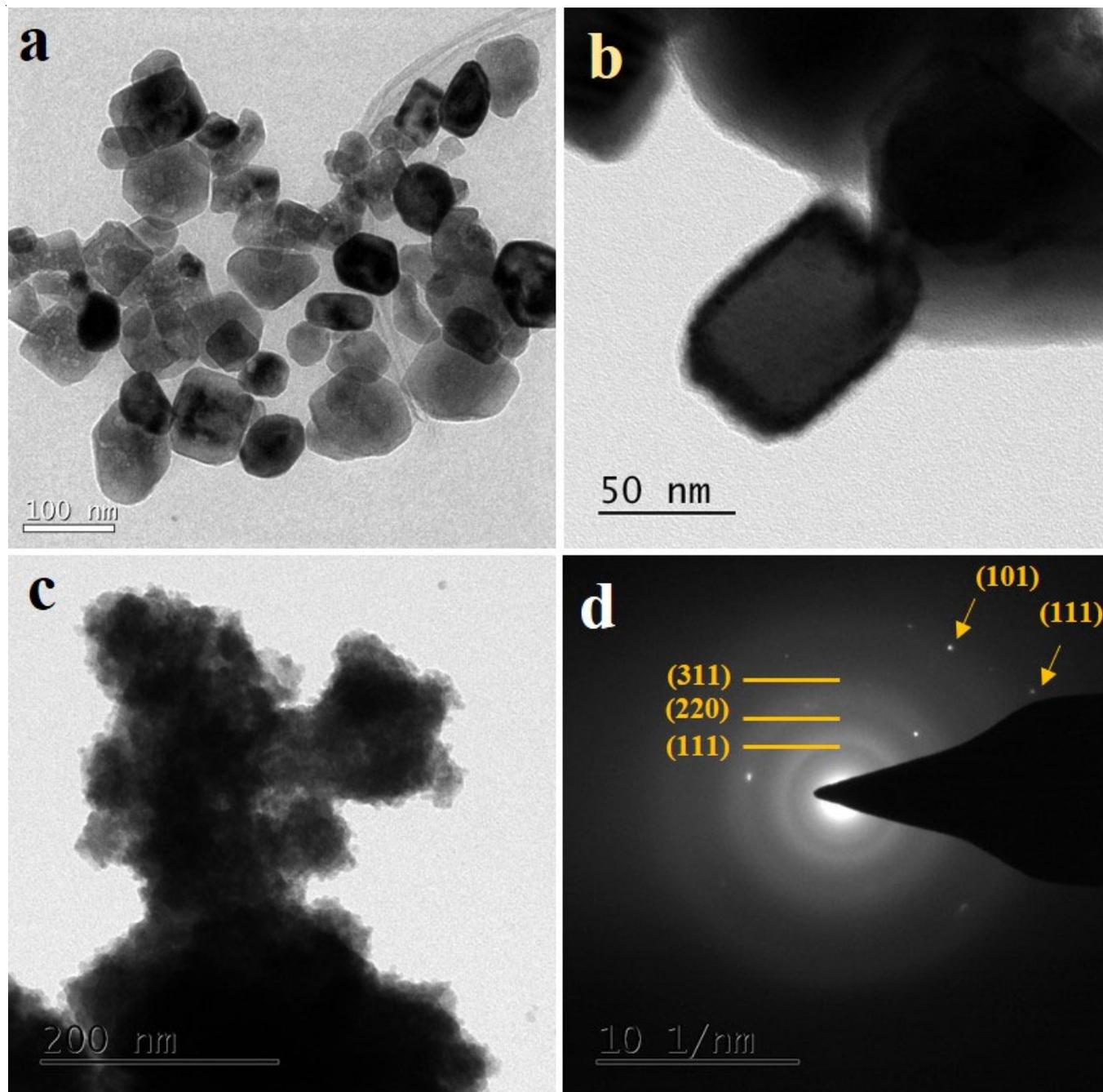


Fig. 4. TEM images of (a & b) PbTiO_3 , (c) CdSe sensitized PbTiO_3 perovskite and (d) SEAD pattern for CdSe sensitized PbTiO_3 perovskites

Photo-electrochemical water splitting: The CdSe quantum dots sensitized PbTiO_3 perovskite photoanode generate electrons under UV-visible light illumination. The PbTiO_3 showed large band gap of 3.7 eV, where incident photon energy to excite the electrons from valance band to conduction band of PbTiO_3 , requires more energy and also a limited UV region absorption of PbTiO_3 perovskite makes inefficient to act as photocatalyst in solar water splitting. However, use of narrow band gap co-catalyst, sensitized over large band gap, makes the heterostructure, which may have expected to perform the superior solar water splitting activity. In this regard, CdSe quantum dots sensitized PbTiO_3 heterostructure is fabricated and the electron transfer mechanism with band structure analysis is shown in Fig. 5. The photogenerated electrons in CdSe quantum dots are transferred

to the charge band of PbTiO_3 , then further transferred to the platinum foil (counter electrode) where protons are reduced and favours the H_2 generation. Simultaneously, the holes move to the photoanode/electrolyte interface and are collected by hole scavengers (S_2^{2-}).

Photoelectrochemical water splitting behaviour analyzed in three electrode systems using Bio-Logic, Model: VMP3 and EC-Lab software, version 10.31, the exposure area of working electrode was illuminated with a solar-simulated light source (power intensity of 100 mW/cm^2 from 300 W Xe lamp passing through an AM 1.5G filter Model-SS80AA).

The prepared photoanodes of CdSe quantum dots sensitized PbTiO_3 perovskite heterostructure were used as working electrodes in an aqueous solution of 1 M Na_2S , 0.1 M Na_2SO_3

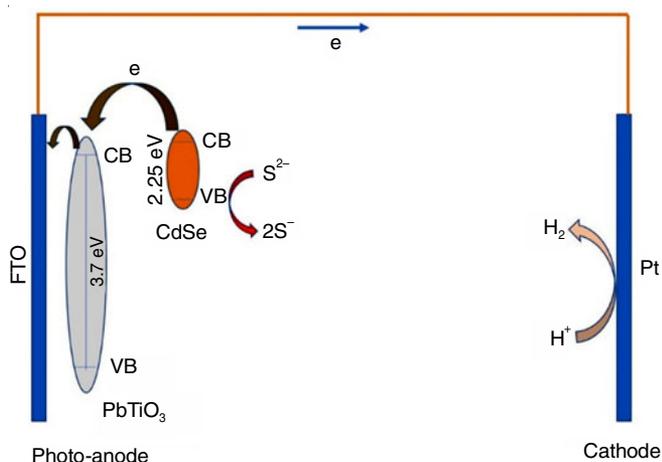


Fig. 5. Band gap structure of CdSe sensitized PbTiO₃ perovskite heterostructure

and 1 M KOH electrolytes. Fig. 6a illustrates linear sweep voltammograms of CdSe sensitized PbTiO₃ perovskite heterostructure in 1 M Na₂S electrolyte under light and dark conditions. The onset potential of oxygen evolution reaction starts at -0.4 V in dark and shifted to -0.5 V in light condition. The current density obtained is 51 and 63 mA/cm² in dark and light condition at 0.8 V (vs. Ag/AgCl), indicates that the photocurrent density is about 12 mA/cm².

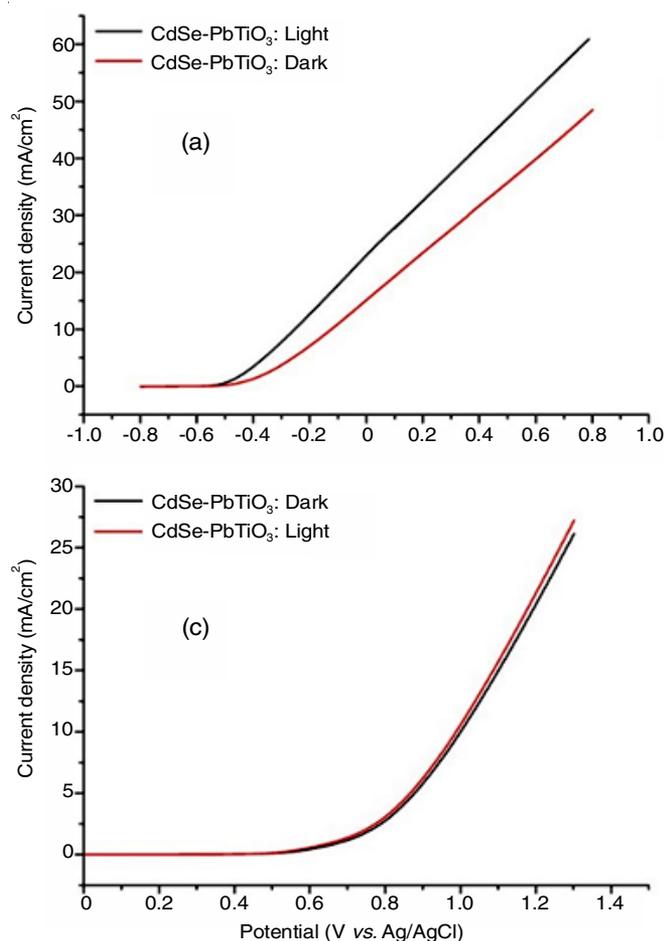


Fig. 6b illustrates linear sweep voltammograms of CdSe sensitized PbTiO₃ perovskite heterostructure in 1 M KOH electrolyte under light and dark conditions. The current density obtained is 6.7 and 9 mA/cm² in dark and light condition at 0.8 V (vs. Ag/AgCl), indicates that the photocurrent density is about 2.3 mA/cm². Fig. 6c illustrates linear sweep voltammograms of CdSe sensitized PbTiO₃ perovskite heterostructure in 0.1 M Na₂SO₃ electrolyte under light and dark conditions. The current density obtained is 26.5 and 28 mA/cm² in dark and light condition at 0.8 V (vs. Ag/AgCl), indicates that the photocurrent density is about 1.5 mA/cm². Fig. 6d shows the amount of hydrogen evolved during 4 h chrono-amperometric studies on CdSe quantum dots sensitized PbTiO₃ perovskite at 0.8 V (vs. Ag/AgCl) in 1M Na₂S electrolyte under dark and illumination condition. In dark, nearly 0.6 mmol of H₂ is evolved, while in light, 1.3 mmol is generated per gram of CdSe quantum dots sensitized PbTiO₃ perovskite. The LSV curves of CdSe quantum dots sensitized PbTiO₃ perovskite in all the three electrolytes demonstrated appreciable photoactivity. It is worth to compare the current work results with the reported catalysts. Sreedhar *et al.* [36] fabricated CdSe quantum dots sensitized SrTiO₃ perovskite and explored as photocatalyst in 1M Na₂S electrolyte. The authors demonstrate 2 mA/cm² photocurrent density at 0.8 V (vs. Ag/AgCl). Similarly, Wang *et al.* [37] fabricated carbon quantum dots sensitized SrTiO₃ and showed 0.5 mA/

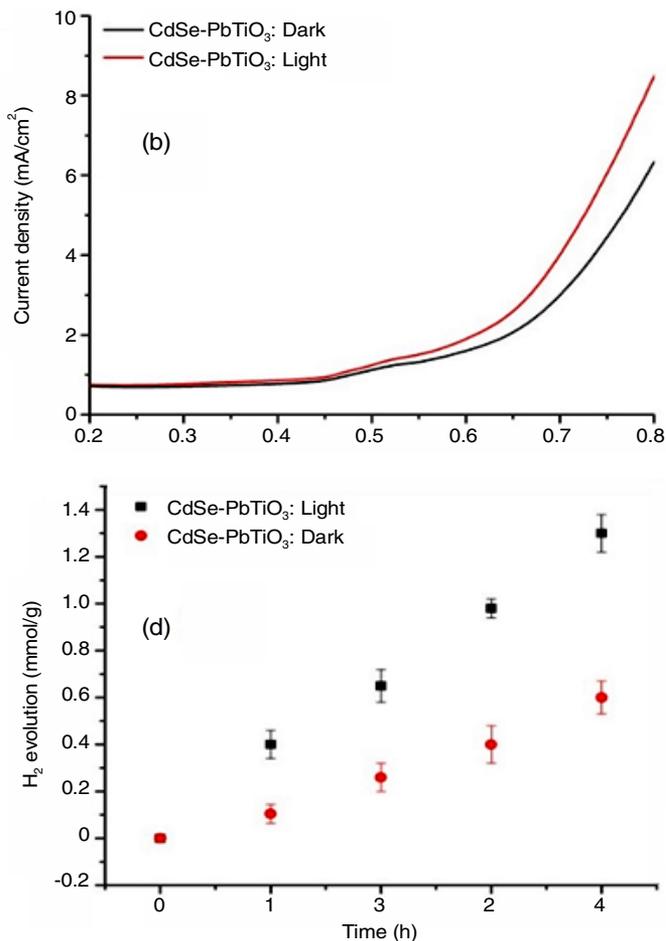


Fig. 6. Linear sweep voltammograms of CdSe QDs sensitized PbTiO₃ perovskite in (a) 1 M Na₂S electrolyte (b) 1 M KOH electrolyte (c) 0.1 M Na₂SO₃ electrolyte and (d) amount of hydrogen evolution using CdSe QDs sensitized PbTiO₃ in 1 M Na₂S electrolyte for the period of 4 h at 0.8 V (vs. Ag/AgCl)

cm² photocurrent density in 0.1 M Na₂SO₄ electrolyte. Yang *et al.* [38] fabricated TiO₂/BaTiO₃ core-shell heterostructure and demonstrated 0.6 mA/cm² in 1M NaOH electrolyte. The photocurrents obtained in the current work is higher than the reported results. This could be achieved *via* strong absorption band edge of CdSe quantum dots and effective utilization of photogenerated electrons using PbTiO₃ perovskite heterostructure. Won-Ahn *et al.* [32] developed platinum nanodot deposited PbTiO₃ heterostructure for effective charge separation for enhanced photoelectrochemical water splitting and showed 60 μA/cm² photocurrent density in 1 M KOH solution, which is lower than that in comparison with CdSe quantum dots sensitized PbTiO₃ photocatalyst in 1 M KOH electrolyte, where we demonstrated 1.5 mA/cm² at 0.8 V (*vs.* Ag/AgCl).

Conclusion

We have synthesized and fabricated CdSe quantum dots sensitized PbTiO₃ perovskite-heterostructure and explored as photoelectrocatalyst in Na₂S, Na₂SO₃ and KOH electrolytes. Higher photo current density of ~12 mA/cm² was drawn CdSe quantum dots sensitized PbTiO₃ perovskite-heterostructure in a sacrificial 1 M Na₂S aqueous solution at 0.8 V (*vs.* Ag/AgCl), whereas 2.3 and 1.5 mA/cm² obtained in 1M KOH and 0.1M Na₂SO₃ electrolytes, respectively. It is anticipated that this new approach for the fabrication of CdSe quantum dots sensitized PbTiO₃ perovskite-heterostructure for high efficiency perovskite solar energy conversion and hydrogen generation devices.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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