Asian Journal of Chemistry; Vol. 37, No. 1 (2025), 149-154

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2025.32567

CdSe Quantum Dots Sensitized $K_2Ti_8O_{17}$ Photoanode for Efficient Photoelectrochemical Water Splitting

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Received: 22 August 2024; *Accepted*: 10 December 2024; *Published online*: 31 December 2024; AJC-21862

Structured potassium titanate ($K_2Ti_8O_{17}$, KTO) was synthesized by simple hydrothermal route and CdSe quantum dots (QDs) was synthesized by hot injection method. Further, CdSe QDs were sensitized or modified over synthesized KTO nanorods. The synthesized KTO and CdSe KTO nanorods were subjected to various characterizations techniques such as XRD, FESEM, TEM, UV-visible and FTIR analysis to confirm the particles and its behaviour. The KTO and CdSe KTO electrodes were prepared and investigated as photoanodes in photoelectrochemical water splitting. Photoelectrochemical water splitting action of KTO and CdSe KTO compounds was analyzed in 1 M Na_2S electrolyte. The CdSe KTO photoanode demonstrated advanced photoelectrochemical water splitting activity.

Keywords: Potassium titanate, CdSe QDs sensitized KTO, Hydrothermal synthesis, Hydrogen production.

INTRODUCTION

The two main challenges of energy recognized soon are enhanced light assisted electrochemical energy conversion and an enhanced light assisted electrochemical energy conversion [1]. At present, the total universal energy supply using roughly 80% of energy needs are met by depletable fossil fuels [2], from which it gives rise to frightening climatic conditions and global warming due to greenhouse effects. Fortunately, solar energy an inexhaustible natural resource which is mainly free of pollution and continuous renewable energy supply. The abundance of solar flux striking the earth's surface receives approximately 10,000 times more energy than the current global consumption rate around the globe [3-5]. So far most of the solar energy is transformed into electrical energy with the help of photovoltaic effect, but it remains costly and difficult to store for extended periods. In this regards, hydrogen fabrication from photocatalytic water splitting has provided the way as next-generation of energy carrier by storing solar energy stored in chemical bonds satisfy long-term energy needs [6,7]. The field of research in hydrogen production was initiated by Honda & Fujishima in 1972 [8], using TiO_2 photoanode and platinum as cathode. After this, a plethora of studies aimed at developing photocatalytic water splitting using both homogeneous and heterogeneous semiconductors were conducted and reported [9-11].

In recent years, ternary perovskite structured materials (STO, KTO, BTO, *etc.*) has been emerged as suitable candidate for the energy conversion devices owing to its charge transferring properties and electronic band structure. Most of the perovskite materials will possess wide bandgap structure which results in absorbing UV range of the electromagnetic solar spectrum and constraints in hydrogen production [12]. Therefore, the UV-visible light driven photocatalytic materials are described as "Holy grails" of chemistry and it was recognized that no single semiconducting materials will meet the overall requirements of water splitting process [13]. It is accepted that no single solution is sufficient it remains a significant challenge to develop highly efficient and stable materials for photocatalytic water splitting applications. Therefore, besides continuous advancement of materials it is also more important to enhance activity, selectivity and stability of materials for water splitting [14].

A key to boost the performance of water splitting was to develop materials that can absorb entire visible region of solar spectrum, which holds almost 50% of an entire spectrum [15]. In this study, the quantum dots (QDs) are emerged as promising candidates to absorb wide range of spectrum which possess high absorption coefficient. Thereby the QDs sensitized semiconductor have also introduced for catalytic process in which QDs are bonded either by physical or chemical phenomenon over the surface of host semiconducting materials [16,17]. Cadmium selenide (CdSe), a member of the II-VI semiconductor group has been widely utilized to modify over the semiconductor due to its tunable bandgap and high absorption coefficient favouring the H_2O/H_2 redox reactions. Several heterostructures based on CdSe had developed and reported bandgap plays a pivotal role in achieving efficiency in water splitting processes [18-20].

The present work describes the preparation of an efficient photoelectrode consisting of structured potassium titanate (KTO) sensitized with CdSe QDs for an enhanced water splitting performance. Structured potassium titanate ($K_2Ti_8O_{17}$, KTO), a new kind of materials, was synthesized *via* hydrothermal method, while CdSe QDs and CdSe sensitized KTO were synthesized *via* wet chemical synthesis. The photocatalytic properties of CdSe QDs and CdSe sensitized KTO were achieved by the favourable band-edges positions of KTO and CdSe quantum dots, the broad absorption of solar photons in the UV-to-NIR region, and the separation and transport of charge carriers.

EXPERIMENTAL

All the chemicals and solvents *viz.* potassium carbonate, titanium dioxide, sodium nitrate, potassium nitrate, cadmium oxide, hydrochloric acid, oleic acid, hexyl decylphosphonic acid (HPA), trioctylphosphine oxide (TOPO), toluene were procured from Sigma-Aldrich, USA. Tin doped indium oxide (ITO) coated glass was also purchased from Sigma-Aldrich, USA.

Characterization: The crystal phase of the sample was analyzed using powder X-ray diffraction (XRD) with a PAN Analytical Xpert Pro Model X-ray diffractometer, employing Cu$K\alpha$ radiation (λ = 1.5418 Å) from 10º-80º at 0.02º step size and counting time of 0.25. The XRD pattern was compared with the standard JCPDS database file. The FTIR analysis were conducted using a Perkin Elmer UK Paragon-500 spectrometer in the mid-infrared region (4000-400 cm^{-1}). The chemical composition of the prepared sample was analyzed using a scanning electron microscope (Bruker VEGA3, TESCAN, Germany) equipped with EDAX analysis. The morphology and surface characteristics of potassium titanate ($K_2Ti_8O_{17}$) were further examined using field emission scanning electron microscopy (FESEM) (Carl Zeiss AG Supra 55VP), with an acceleration voltage range of 5-30 kV. The TEM images were captured using a JEOL-3010 transmission electron microscope, operating at an accelerating voltage of 300 kV, with a 400-mesh ultrathin carbon-coated copper grid.

Synthesis of $K_2Ti_8O_{17}$: Titanium oxysulfate ($TiOSO_4{\cdot}H_2O$, 1.92 g) was introduced to 50 mL of KOH solution with 9 M concentration and was continuously stirred for 1 h. Further, the solution was transferred to a Teflon- lined and kept in furnace for 24 h maintained at 180 ºC.

Synthesis of CdSe QDs: CdSe QDs was prepared by wet chemical synthesis by reported method [21]. In a typical synthesis, 0.2 mM of CdO and 0.5 g of oleic acid were taken in a round bottom flask and heated to 180 ºC until the mixture turned clear. After obtaining a clear solution, it was allowed to cool to room temperature. Then, 3 mL of HPA and 6 mL of TOPO were added to the mixture, which was subsequently degassed for an additional 15 min at 100 ºC. After this, the homogeneous mixture was heated to 280 ºC while being stirred vigorously with an injection of 1 mL of 1 M TOPSe to the solution. The obtained CdSe QDs were centrifuged at 3000 rpm and rinsed with a toluene/methanol solvent mixture, then stored in toluene.

CdSe QDs sensitization on KTO: CdSe QDs (10 mg) and 20 mg of KTO powder (1:2 weight ratio) was taken and mixed through continuous stirring for time of 4 h. After the reaction, obtained powder (CdSe sensitized KTO) was washed with ethanol and dried at room temperature. The obtained final powder was then deposited over ITO conducting glass substrates using simple squeegee method [22] and employed as photoelectrodes for photoelectrochemical studies.

RESULTS AND DISCUSSION

XRD studies: The phase identification and crystal structure analysis of as-synthesized $K_2Ti_8O_{17}$ was examined using XRD analysis. XRD spectrum of the synthesized nano powder shows the distinctive peaks of KTO monoclinic crystal structure (Fig. 1a). All the diffraction peaks are matched with standard JCPD file no. (41-1100) and correspond to the crystal planes, specifically the (200), (110), (310), (403), (313) and (020), which confirms the existence of $K_2Ti_8O_{17}$ compound. Some other peaks are also observed which are attributed to the presence of TiO_2. The broadening of the diffraction peaks is linked to the nanoscale structure of the synthesized material. The average crystallite size of the particles is determined to be approximately 19 nm. The phase and crystal structure of CdSe- KTO analyzed using XRD analysis is presented in Fig. 1b. The planes (111), (220), (311) and (420) are corresponds to cubic phase of CdSe quantum dots, while the rest corresponds to KTO. This demonstrates that the existance of both CdSe and KTO phases are present in the compound, which formed by heterojunction.

FTIR spectral studies: The existence of functional groups in the as-synthesized KTO and CdSe sensitized KTO was examined using FTIR analysis and the obtained spectra is displayed in Fig. 2. From the FTIR spectrum of KTO, it is perceived that band appeared at 1700 and 2400 cm^{-1} correspond to the Ti-O stretching vibration mode. The bands observed between 500 and 900 cm^{-1} are attributed to Ti-O-Ti bending vibrations. In higher wavelength region, 3200 to 3500 cm^{-1}, the presence of peaks is mainly due to the hydroxyl group content in synthe-sized compound [23]. In the FTIT spectrum of CdSe-KTO (Fig. 2b), the peak at 1650 cm^{-1} corresponds to C=O (carboxylic group) of KTO is shifted to lower wavenumber for CdSe-KTO and thus confirmed the bonding of CdSe QDs through C=O (carboxylic group) to KTO.

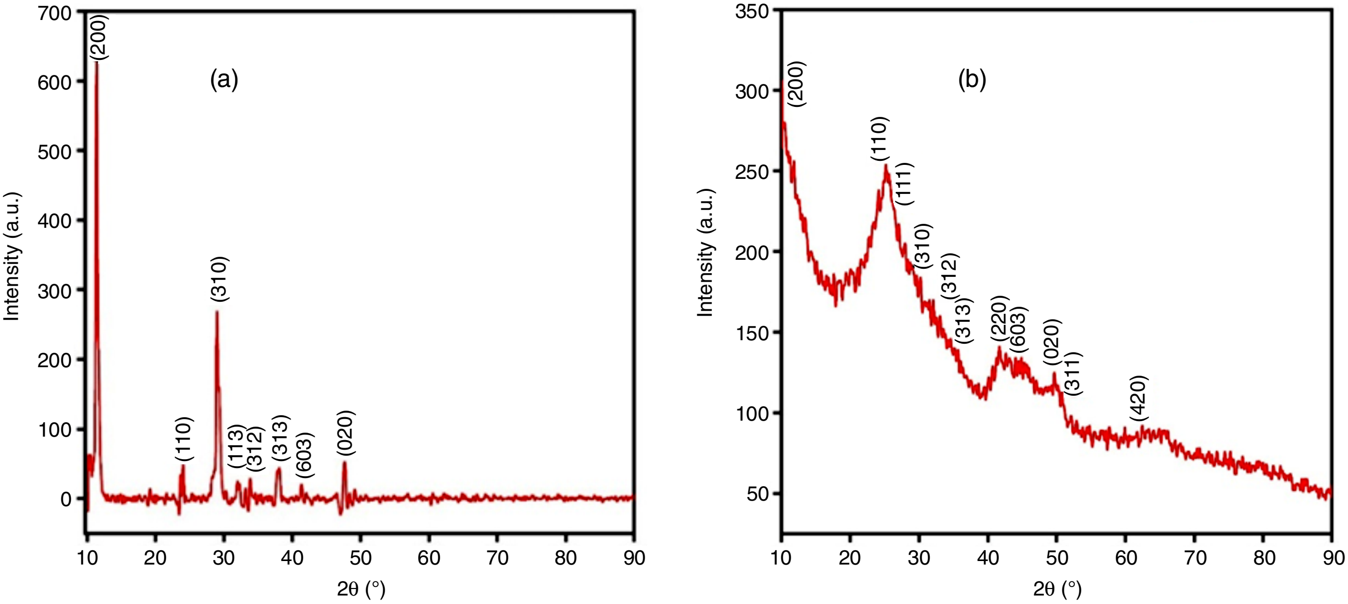

Fig. 1. XRD pattern of (a) synthesized $K_2Ti_8O_{17}$ and (b) CdSe-$K_2Ti_8O_{17}$

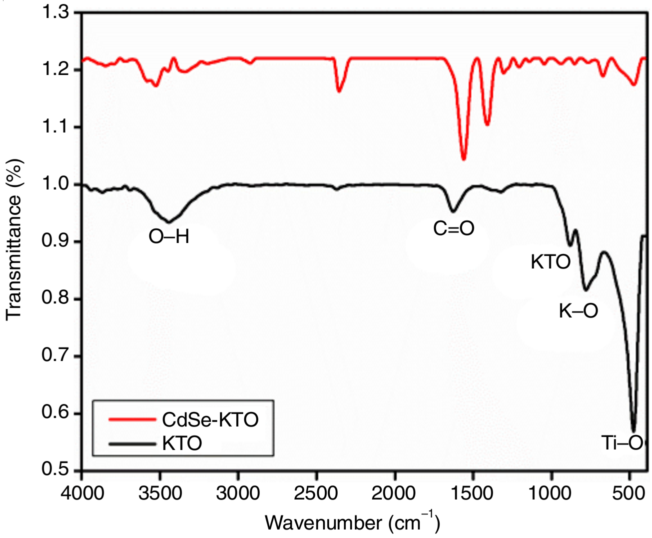

Fig. 2. FTIR spectra of KTO and CdSe-KTO

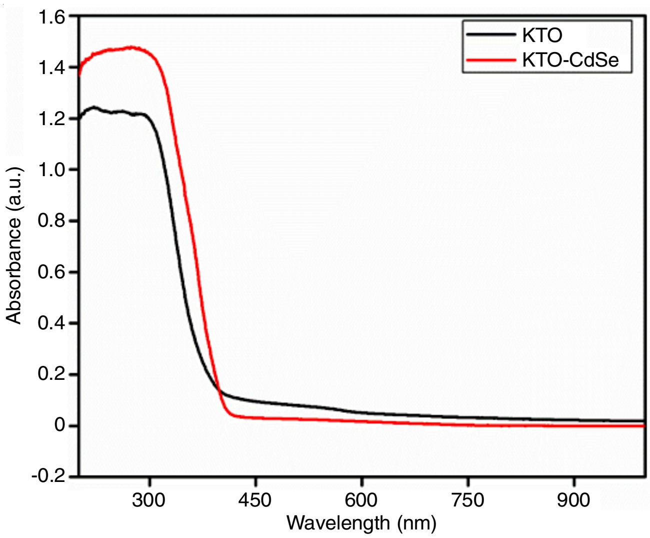

Fig. 3. UV-vis spectra of KTO and CdSe-KTO

UV-vis spectral studies: UV-vis spectroscopy analysis is employed to determine the bandgap energy of the material using absorption edge wavelength and cut-off wavelength of the spectrum. The bandgap energy was calculated from the absorption spectrum and is found to be 3.25 eV. The UV-vis absorption spectra of CdSe/KTO nanorods synthesized revealed a progressive shift from blue to red with increasing CdSe growth duration (Fig. 3). The shift indicates a decrease in the band gap of 2.5 eV observed at the longest growth time of 120 times. This behaviour highlights the quantum confinement effect. Consistent with the FESEM analysis, the sample grown for the longest time exhibited the largest nanostructured particles. Furthermore, the CdSe/KTO nanorods alone, primarily due to the enhanced light absorption in the visible region enabled by the CdSe QDs component.

XPS studies: The chemical composition, presence of elements and the bonding conditions of as-synthesized KTO was evaluated using XPS analysis. The overall survey spectrum of KTO is shown in Fig. 4a and confirms the presence of potassium (K), titanium (Ti) and oxygen (O) elements. The high resolution spectrum of K, Ti and O is shown in Fig. 4b-d. From Fig. 4b, the high-resolution spectrum of K shows the signals appeared around ~ 292.5 and ~ 295 eV values assigned to the $2p_{3/2}$ and $2p_{1/2}$ electrons of potassium ions on the surface. The signals at ~ 458.3 and ~ 464.6 eV are assigned to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ electrons, respectively as shown in Fig 4c. Thus, it can be predicted that the Ti compounds existed to be in tetravalent (Ti^{4+}) form [24]. Similarly, Fig. 4d shows the spectrum observed at ~ 529.2 and ~ 531.6 attributing to O1s. For oxygen the two peaks appeared one as main and the other peak as shoulder peak which may be arised due to an existence of hydroxyl (OH) group.

FESEM studies: The morphology of $K_2Ti_8O_{17}$ and CdSe QDs sensitized $K_2Ti_8O_{17}$ is observed using FESEM analysis.

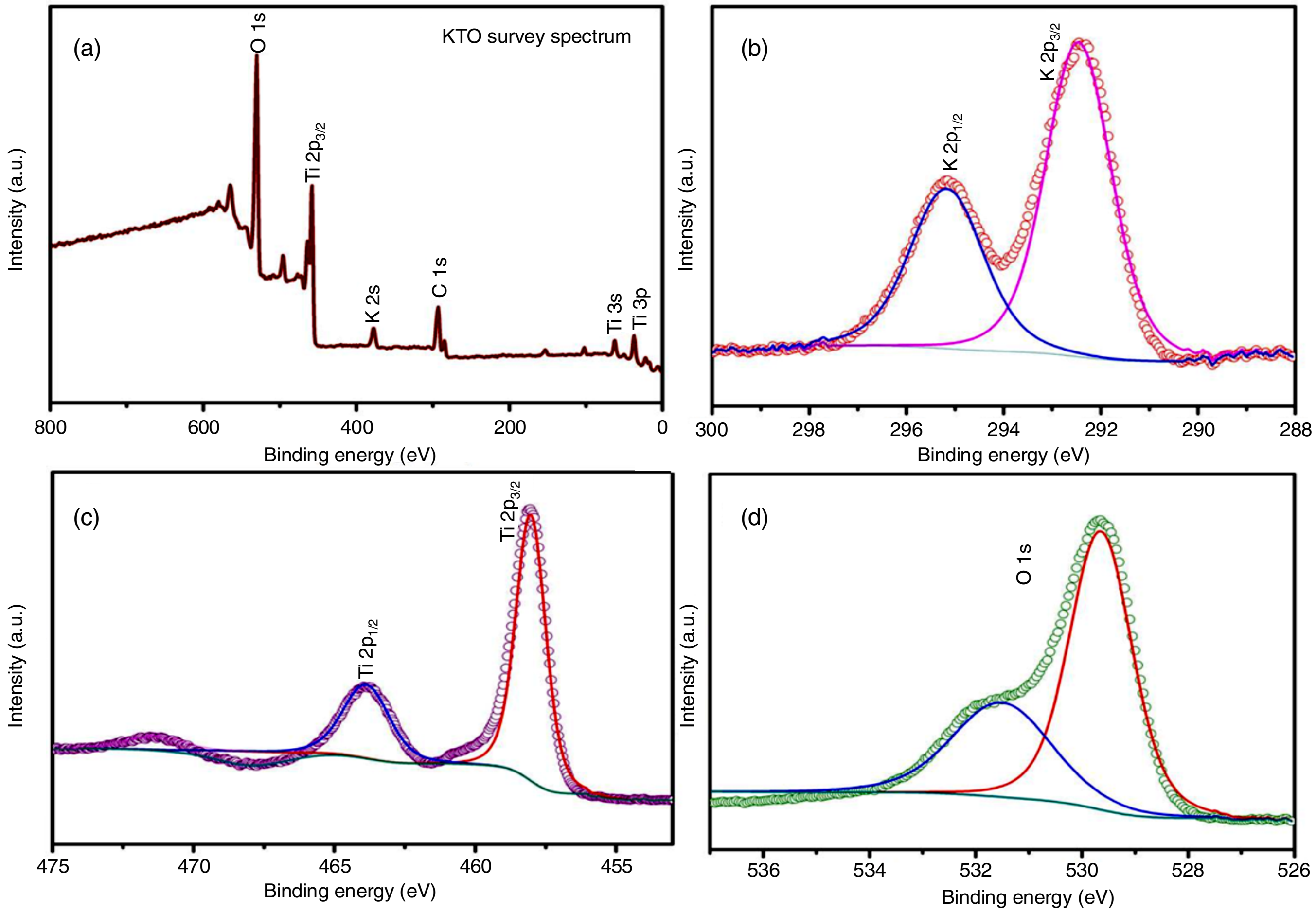

Fig. 4. XPS analysis of potassium titanate (KTO)

The morphology of $K_2Ti_8O_{17}$ observed to be one dimensional nano-rods growth like structure as shown in Fig. 5a. The growth of rods is discrete due to function of temperature while synthesizing the KTO powders. During the hydrothermal synthesis high temperature and pressure applied which tends to cause a breakage in the growth of rods and making the growth in a discrete manner. The change in shape of the particle's properties as a function of temperature are presented similar kind of perovskite structured materials [25]. Fig. 5b reveals the morphology of CdSe QDs sensitized KTO compound, where CdSe get anchored and sensitized over the KTO nanorods. The presence of elements in CdSe sensitized KTO compound was analyzed using energy dispersive (EDAX) analysis and confirmed the presence of Cd, Se, K, Ti, O and demonstrated that CdSe nanoparticles are functionalized over KTP rods.

Transmission electron microscope (TEM) analysis: TEM analysis further revealed the morphology of KTO and CdSe sensitized KTO as shown in Fig. 6. Fig. 6a-b represents the morphology, which confirmed that the particles are in the order of nanoscale and discrete in nature. The SAED pattern indicates that it exhibits a polycrystalline structure. It is clearly observed that the CdSe particles are sensitized over the KTO nanorods and its corresponding SAED pattern is shown in Fig. 6d.

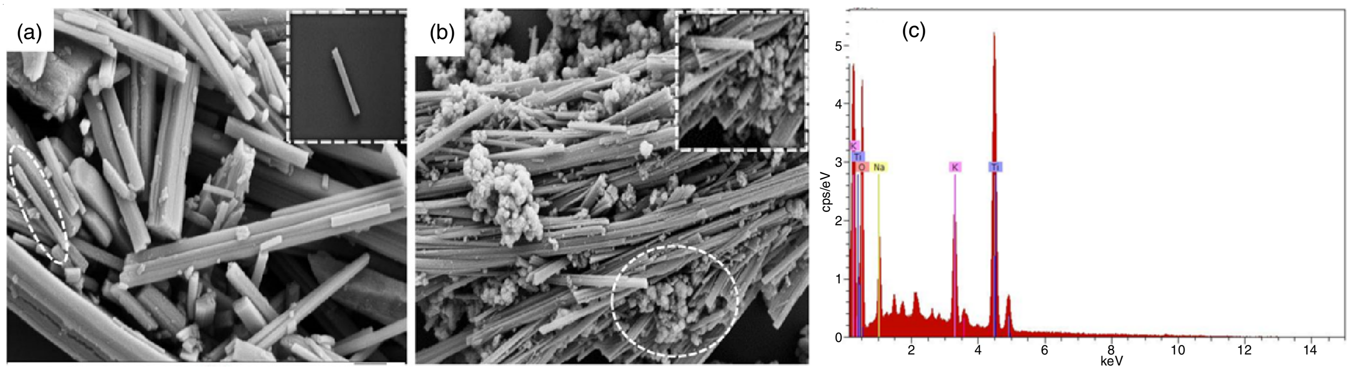

Fig. 5. FESEM analysis of KTO and CdSe-KTO

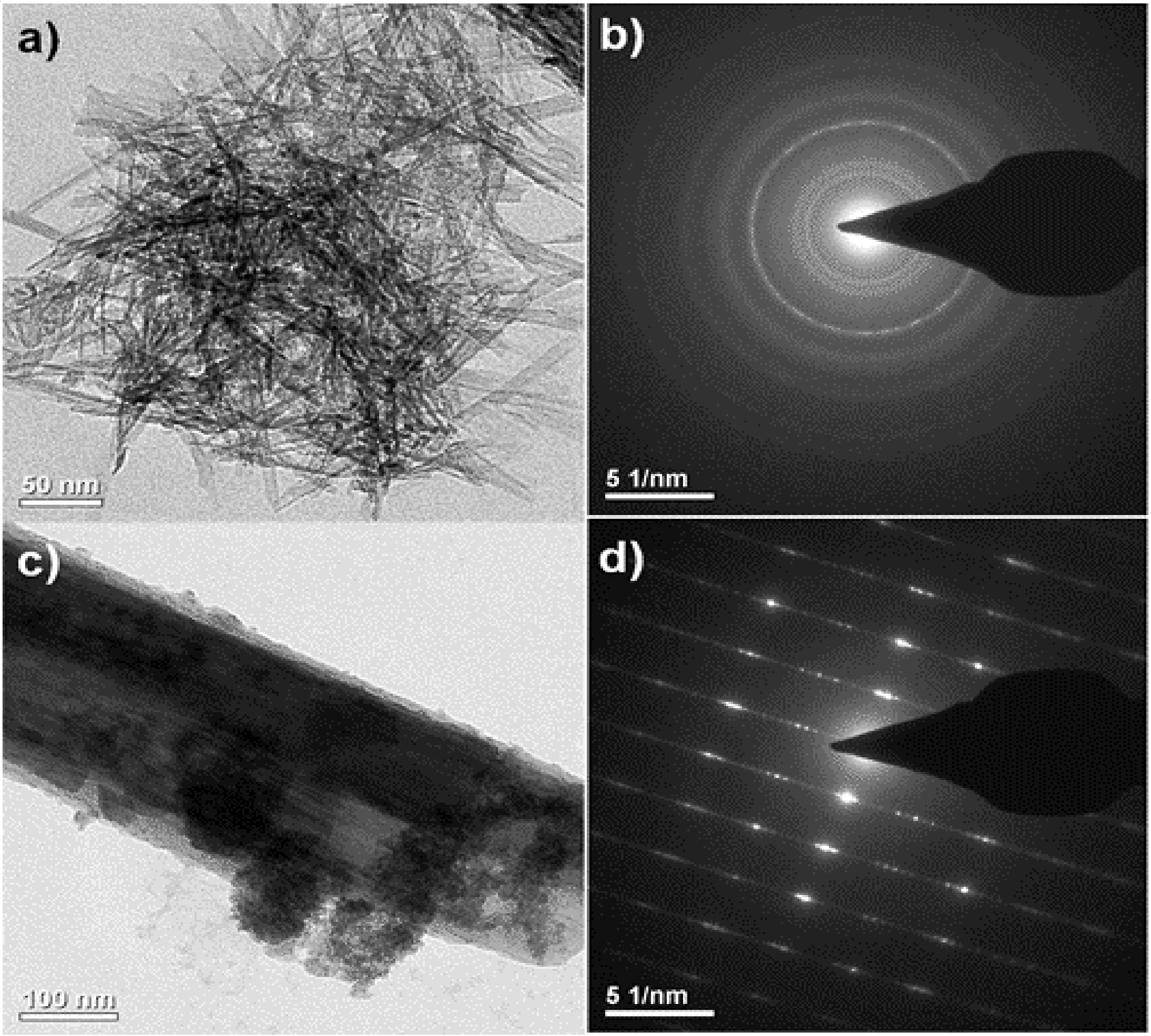

Fig. 6. HRTEM analysis of KTO and CdSe sensitized KTO

Photoelectrochemical water splitting studies: Fig. 7 shows the photoelectrochemical performance of bare KTO and CdSe functionalized KTO photoanodes. The current density of both samples were measured in dark and light. The potentials required for the current density was found to be < 5 μA/cm^2 which is negligible small in case of KTO photoanode. The photocurrent density at 1.23 V *vs.* RHE is 27 mA/cm^2 for KTO/CdSe photoanode. This result shows the CdSe functionalized KTO is more photoactive and more enhance the current density.

Conclusion

The structured $K_2Ti_8O_{17}$ powder was synthesized by hydrothermal method, wherein the KTO powder exhibited nanorods morphology with high crystallinity. The CdSe QDs synthesized *via* hot injection method, were functionalized over nanorods of KTO. The PEC water splitting activity of the KTO and CdSe QDs-KTO were studied in 1 M Na_2S electrolyte.

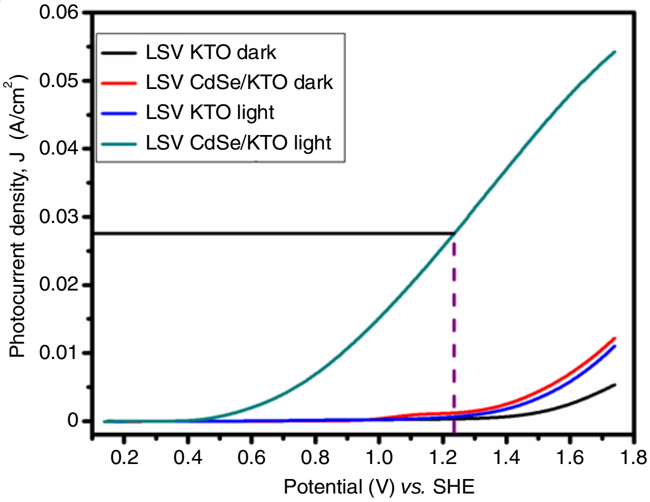

Fig. 7. Photo electrochemical studies of KTO and CdSe sensitized KTO

This result shows that the CdSe-KTO is more photoactive and higher photocurrent density than KTO.

CONFLICT OF INTEREST

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

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