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REVIEW

Cdse Quantum Dots Sensitized $K_2Ti_8O_{17}$ Photoanode For Efficient Photoelectrochemical Water Splitting

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Abstract:

Structured $K_2Ti_8O_{17}$ (KTO) compound was synthesized simple hydrothermal route and CdSe quantum dots (QDs) was synthesized by hot injection method. Further, CdSe QDs were sensitized or functionalized over KTO nano rods. The synthesized materials KTO and CdSe KTO were subjected to various characterizations techniques such as XRD, FESEM, TEM, UV-Visible and FTIR analysis to confirm the particles and its behavior. The KTO and CdSe KTO electrodes were prepared and explored as photoanodes in photoelectrochemical water splitting. Photoelectrochemical water splitting activity of KTO and CdSe KTO compounds was analyzed in 1M Na_2S electrolyte. The CdSe KTO photoanode demonstrated enhanced photo-electrochemical water splitting activity.

Keywords: KTO; CdSe QDs sensitized KTO; hydrothermal syntheses; H_2 production.

1. INTRODUCTION

The two main challenges of energy recognized soon are depletion of fossil fuels and an environmental pollution arising from their combustion [1]. At present, the total universal energy supply using exhaustible fossil fuels account for ~80% [2], from which it gives rise to frightening climatic conditions and global warming due to greenhouse effects. To effectively address these issues, modern society has been pointed for a new form of energy that is clean, renewable, cheap, safe, and viable alternative. 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 is about 10000 times larger than the current rate of energy utilization around the globe [3-5]. So far most of the solar energy is converted into electrical energy with the help of photovoltaic effect, but it is still expensive and hard to store for over a long period of time. In this regards, hydrogen (H_2) production from photocatalytic water splitting has provide the way as next-generation of energy carrier by storing solar energy in the form of chemical bonds to satisfy long-term energy needs [6,7]. The field of research in H_2 production was initiated by Honda-Fujishima in 1972, using TiO_2 photoanode and platinum as cathode [8]. Followed by this many researchers started finding many different heterogeneous and homogenous semiconductors for photocatalytic water splitting [9-11].

In recent years, ternary perovskite structured materials (STO, KTO, BTO etc) has been emerged as suitable candidate for 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 region of the electromagnetic solar spectrum and limits in the generation of H_2 production [12]. Therefore, the UV-Visible light driven photocatalytic materials are described as "Holy Grails" of chemistry and it was accepted that no single semiconducting materials will meet the overall requirements of water splitting process [13]. To some extent, it remains still a great challenge to develop highly efficient and stable materials for photocatalytic water splitting applications. Therefore, besides continuous development 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 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) belonging to II-VI semiconductor group has been widely utilized to modify over the semiconductor due to its tunable bandgap and high absorption coefficient favoring the H_2O/H_2 redox reactions. So that several heterostructures based on CdSe had developed and reported emphasizing the role of bandgap in efficient water splitting [18-20].

In this manuscript the preparation of efficient photoelectrode comprising of structured potassium titanate (KTO) sensitized with CdSe QDs was described. KTO a new kind of materials was synthesized via hydrothermal synthesis method; CdSe QDs and CdSe sensitized KTO were synthesized via wet chemical synthesis. hydrothermal synthesis, one of the synthesis methods for ceramic powders, involves hydrothermal synthesis as medium for preparing complex oxides from their constituent materials (oxides and carbonates). Ceramic powders are synthesized from solid, liquid, and gas phases by various methods [21]. For large-scale commercial production, they are mainly fabricated from the solid phase by a conventional powder metallurgical method. hydrothermal synthesis is branch of the powder metallurgical method involving in heating the salts above its melting point, where the hydrothermal synthesis will act as solvent. It has been used as additives to enhance the rates of solid-state reactions over a period.

2. Experimental Section

2.1. Materials and characterization:

Potassium Carbonate (K_2CO_3, Loba-Chemie-Idoaustranal Co. Bombay, India); titanium dioxide (TiO_2, Thermo Fisher Scientific, India Pvt. Ltd); sodium nitrate; potassium nitrate; hydrochloric acid (HCl); cadmium oxide (CdO); oleic acid (OA); HAD; TOPO; toluene; tin doped indium oxide (ITO) conducting glass substrates.

2.2. Characterization:

The crystal phase of the sample was characterized by powder-ray diffraction (XRD) measurement using a PAN Analytical, Xpert pro model X-ray diffractometer with CuKα radiation (λ= 1.5418Å) from 10° to 80° at 0.02° step and a count time of 0.25. The XRD pattern was compared with the standard JCPDS (41-1100) file. FTIR measurements were performed with a Perklin Elmer UK paragon-500 spectroscope in the mind infrared region (4000-400 cm^{-1}). The chemical composition of the prepared sample was analyzed by employing a (BRUKER VEGA3, TESCAN, Germany) Scanning electron microscope (SEM) equipped with EDAX analysis. The morphology and surface nature of the $K_2Ti_8O_{17}$ compound were characterized by Field emission Scanning Electron microscopy (FESEM) using a Carl Zeiss AG Supra 55VP with an acceleration voltage of 5-30KV. TEM images were recorded using a JEOL-3010 transmission electron microscope using 300 kV accelerating voltage with a 400- mesh ultrathin carbon type copper grid.

2.3. Synthesis of $K_2Ti_8O_{17}$

1.92 g of titanium oxysulfate ($TiOSO_4$ xH_2O,) was introduced to 50 ml of KOH solutions with 9 M concentration and kept stirring for 1 h. Further, the solution was placed in a Teflon-lined autoclave and kept in furnace for 24 h maintained at 180 °C

2.4. Synthesis of CdSe QDs:

CdSe QDs was synthesized by wet chemical synthesis as per earlier report [22]. In a typical synthesis, 0.2 mM of CdO and 0.5 g of OA were taken in a round bottom flask and heated to 180 °C until the mixture became clear. Once clear solution was obtained it is allowed to cool down to room temperature and then 3 mL of HDA and 6 mL of TOPO were added to the mixture and degassed again for period of 15 minutes at 100 °C. After this the homogeneous mixture was heated to 280 °C under vigorous stirring with an injection of 1mL of 1MTOPSe to the solution. The synthesized QDs were centrifuged at 3000 rpm and washed with the toluene/methanol solvent, then stored in toluene. To exchange the OA with MPA, 1 mL of the toluene solution containing 50 mg of OA capped CdSe were mixed with 1 mL of acetone and 1 mL of MPA. The resulting precipitate containing MPA capped CdSe QDs was dissolved and stored in de-ionized water.

2.5. CdSe QDs sensitization on KTO

10 mg of MPA capped CdSe and 20 mg of KTO powder (1: 2 weight ratios) was taken and mixed through continuous stirring for time period of four hours. After the reaction, obtained powder (CdSe sensitized KTO) was washed using ethanol and allowed to dry at room temperature. The obtained final product was then deposited over ITO conducting glass substrates using simple squeegee method and employed as photoelectrodes for photoelectrochemical studies [23]

3. Result and discussions

3.1. XRD analysis

The phase and crystal structure determination of as-synthesized $K_2Ti_8O_{17}$ is examined using XRD analysis and it is presented in Figure 1. XRD patterns of the synthesized nano powder shows characteristic reflections of KTO monoclinic crystal structure. All the diffraction peaks are identified by standard JCPD file no (41-1100) and are observed to correspond to the crystal planes namely (200), (110), (310), (403), (313) and (020). This confirms the presence of $K_2Ti_8O_{17}$ compound. Few peaks appearing in the spectrum can be assigned to the presence anatase TiO_2. The line broadening of the diffraction peak has been ascribed to the fact that the synthesized compounds have nano-structure morphology. The average crystalline size of the particles is found to be in the range of 19 nm. The crystalline size of the compound is determined by using Debye-Scherrer's formula [24]

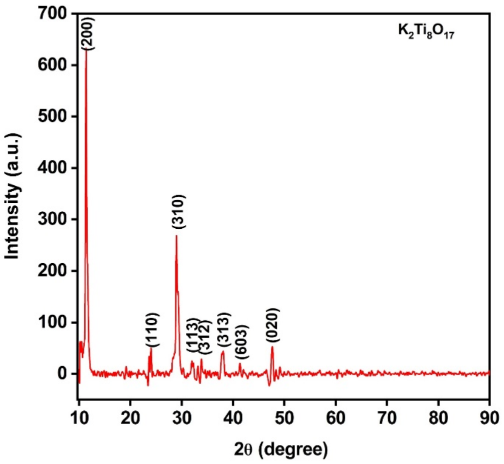

Figure 1: XRD pattern of synthesized $K_2Ti_8O_{17}$

The phase and crystal structure determination of CdSe- KTO is examined using XRD analysis and it is presented in Figure 2.

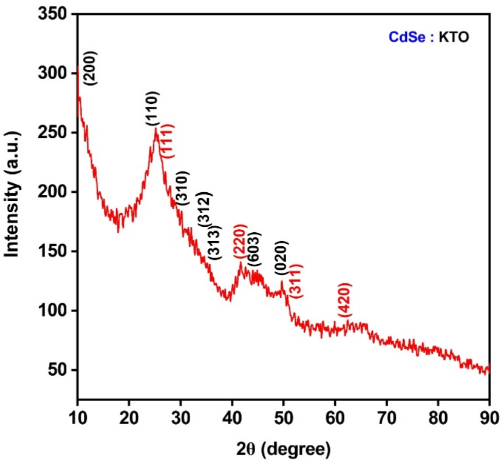

Figure 2: XRD pattern of CdSe-$K_2Ti_8O_{17}$

FTIR spectroscopy

The presence of functional molecules in the as-synthesized KTO and CdSe sensitized KTO is examined

with the help of FTIR analysis and the obtained spectrum is shown in Figure 3.

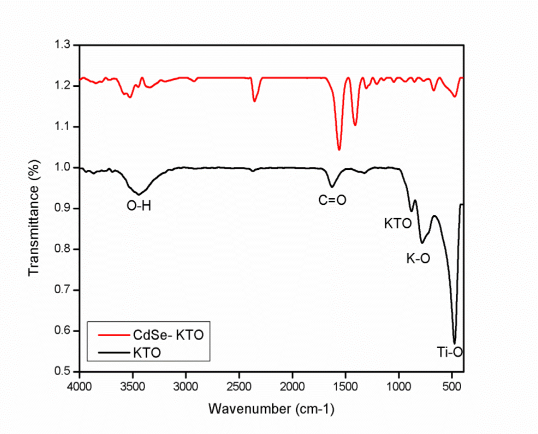

Figure 3: FTIR spectrum of KTO and CdSe - KTO

From the FTIR spectrum, it is perceived that band appeared at 1700 and 2400 cm^{-1} correspond to the Ti-O stretching vibration mode. The bands appearing between 500 and 900 cm^{-1} can be attributed to Ti-O-Ti bending vibrations. At higher wave length region, 3200 to 3500 cm^{-1}, the presence of peaks is mainly due to the hydroxyl group content in synthesized compound [25, 26].

UV-Vis spectroscopy

UV-Vis spectroscopy analysis is used to calculate the bandgap energy of the compound with the help of absorption edge wavelength and cut-off wavelength of the spectrum. From the absorption spectrum, calculate the energy band gab as follows. The bandgap energy iss calculated from the graph and found to be 3.25 eV.

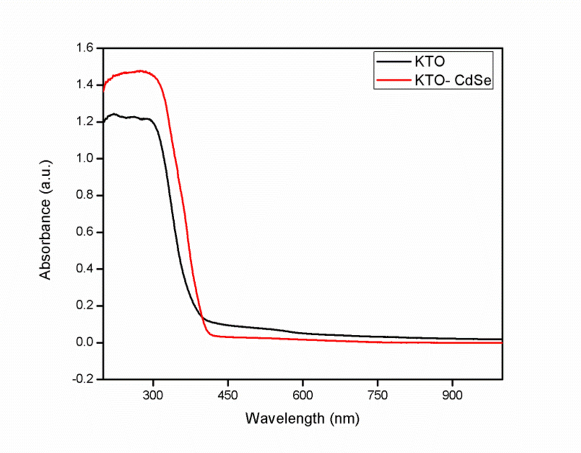

Figure 4: UV-Vis spectra of KTO and CdSe – KTO

The UV-Vis absorption spectra of CdSe/KTO NRs prepared at different growth time. The absorption profiles shifted from blue to red as CdSe growth time increases. it was found that the band gap energy of CdSe/KTO nanorods decrease with growth time and this

smallest band gap value of 2.5eV was obtained at the longest growth time of 120 min, and this indicates quantum confinement effect. This agrees with FESEM analysis in which the sample exhibited the largest nano structured particles. It was found that CdSe/ KTO NRs exhibit better photo electrochemical performance

compare to KTO nano rods. This can be attributed to the light absorption in the visible region by CdSe.

X-Ray photoelectron spectroscopy (XPS) analysis:

The chemical composition, presence of elements and the bonding conditions of the as-synthesized KTO is evaluated using XPS analysis and it is shown in Figure 5. The overall survey spectrum of KTO is shown in Figure 5(a) and it confirms the presence of K, Ti, and O elements. The high-resolution spectrum of K, Ti and O is given in Figure 5(b-d). From the Figure 5(b), the high-resolution spectrum of K shows the signals appeared around ~292.5 and ~295 eV assigned to K $2p_{3/2}$ and K $2p_{1/2}$ electrons of potassium ions on the surface. The signals at ~458.3 and ~464.6 eV is assigned to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ orbital as shown in Figure 5(c). From this it can be predicted that the Ti compounds existed to be in tetravalent (Ti^{4+}) in form [29]. Similarly, Figure 5(d) 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 [30].

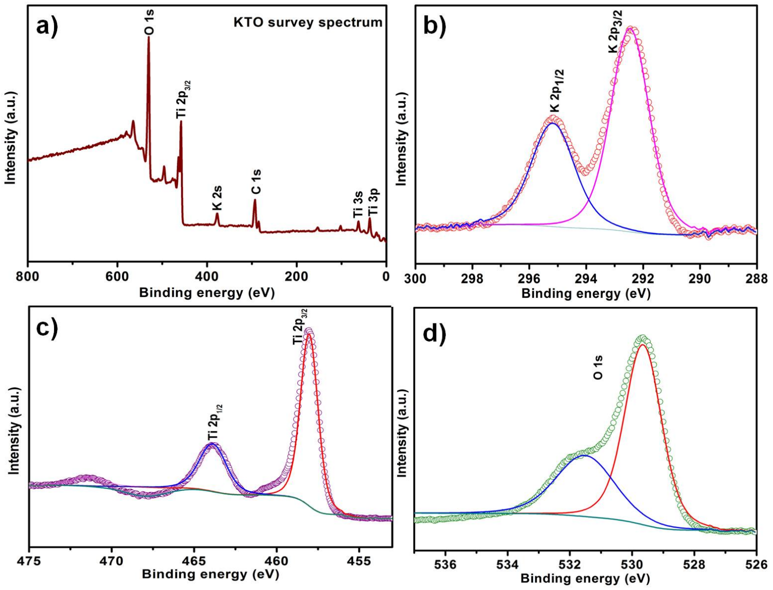

Figure 5: XPS analysis of KTO

Field Emission Scanning Electron Microscopy (FESEM)

The morphology of $K_2Ti_8O_{17}$ and CdSe QDs sensitized $K_2Ti_8O_{17}$b is observed using FESEM analysis. The morphology of the $K_2Ti_8O_{17}$ observed to be one dimensional nano-rods growth like structure as shown in Figure 6(a). The growth of rods is discrete in manner 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 as a function of temperature is reported for similar kind of perovskite structured materials [27].

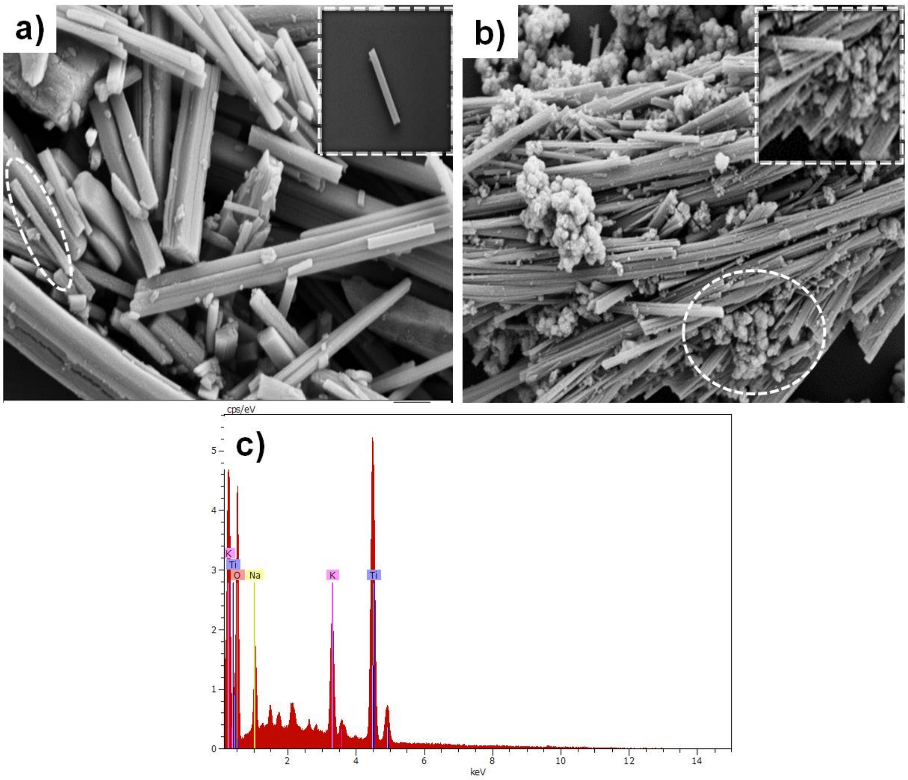

Figure 6: FESEM analysis of KTO and CdSe-KTO

Generally, the shape of particle synthesized via hydrothermal synthesis can be predicted from the crystal structure of the final product, but so far there is no clear report for the statement. Because the chemical species of the salt used during the synthesis will also plays a role in the influence of change in the morphology [28]. Figure 6(b) reveals the morphology of CdSe QDs sensitized KTO compound. The CdSe materials are get anchored and sensitized over the KTO nanorods. The presence of elements in CdSe sensitized KTO compound is analyzed using energy dispersive (EDAX) analysis and it is presented in Figure 6(c).

Transmission Electron Microscope (TEM) analysis:

TEM analysis further revealed the morphology of KTO and CdSe sensitized KTO as shown in Figure 7. The Figure 7(a & b) represents the morphology and SAED pattern obtained for KTO.

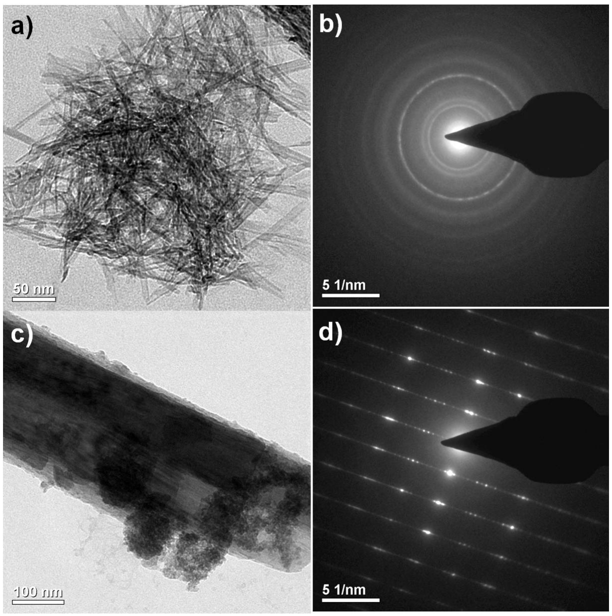

Figure 7: HRTEM analysis of KTO and CdSe sensitized KTO

From the morphological analysis it is confirmed that the particles are in the order of nanoscale and discrete in nature. The SAED pattern states that it is polycrystalline in form. Similarly, the morphology of CdSe sensitized KTO is shown in Figure 6(c) and it is clearly observed

that the particles are CdSe sensitized over the KTO nanorods and its corresponding SAED pattern is given in Figure 6(d).

Photo Electrochemical Water Splitting Studies:

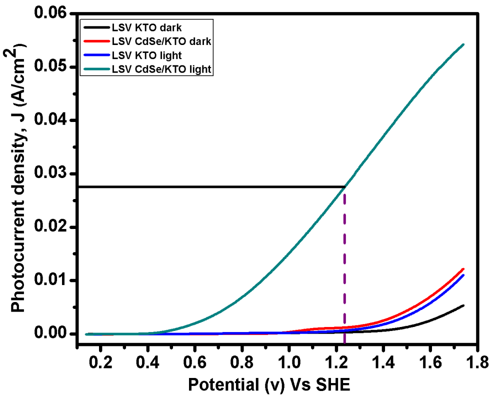

Figure 8: Photo electrochemical Studies of KTO and CdSe sensitized KTO

Figure 8 shows the photoelectrochemical performance of bare $K_2Ti_8O_{17}$ and CdSe functionalized $K_2Ti_8O_{17}$ photo anodes. The current density of both samples are measures in dark and light. The Figure shows $<5\mu A/cm^2$ which is negligible small. The photo current density at 1.23V Vs RHE is $27mA/cm^2$ for the KTO/CdSe photo anode. This result shows the CdSe functionalized KTO is more photoactive and more enhance the current density.

Conclusions:

- Structured $K_2Ti_8O_{17}$ powder was synthesized by hydrothermal method, wherein the KTO powder exhibited nano rods morphology.
- CdSe QDs synthesized via hot injection method, were functionalized over nano rods of KTO
- The PEC water splitting activity of the KTO and CdSe QDs -KTO were studied in 1M Na_2S electrolyte.
- This result shows the CdSe functionalized KTO is more photoactive and demonstrated higher photocurrent density than KTO

Declaration of Funding statement & conflict of interest

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The author declares that there is no conflict of interest

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