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Photoelectrochemical performance of ZnCdSe-sensitized WO_3 thin films

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ABSTRACT

Due to its wide gap, WO_3 mostly absorbs only the ultraviolet radiation, resulting into lower charge collection and thus necessitating the coupling (doping or sensitization) of WO_3 with low band gap materials so as to achieve the photoexcitation and charge separation. This study reports the sensitization of WO_3 films with ternary quantum dots (ZnCdSe) using SILAR technique for the first time. The porous WO_3 layer was spray deposited using ammonium metatungstate as precursor. The structural, surface morphological and optical properties of the sensitized WO_3 thin films were studied. Photoelectrochemical (PEC) studies of the sensitized films showed superior performance to that of unmodified WO_3 films. Photocurrent density of 8.53 mA/cm^2 (at 0 V vs Ag/AgCl) was observed for film sensitized with 9 cycles of SILAR deposition annealed at 400 °C under nitrogen atmosphere, which is a 120-fold and 14-fold increase in photocurrent density when compared to unsensitized WO_3 film and WO_3/TiO_2 film, respectively. Sensitization with ternary quantum dots as ZnCdSe thus offers two advantages: (i) the lower band gap of ZnCdSe allows it to absorb more energy and in turn produce more charge carriers and (ii) the conduction band of ZnCdSe, which lies above the conduction band of TiO_2, results in a better charge transfer from sensitizer to the substrate material.

1. Introduction

Tungsten oxide (WO_3), an indirect band gap semiconductor, has been extensively investigated as a photoelectrode due to its chemical stability and non-toxicity. With a bandgap of 2.6–3.0 eV, WO_3 has potential to be used in electrochromic devices [1–3], solar cells [4,5], photocatalysis [6], fuel cells [7], batteries [8], and gas/chemical sensors [9]. However, its activity has so far been restricted by the relatively short hole diffusion length ~150 nm and low carrier mobility [10,11].

As suggested by Scaife [12], metal oxides with partly filled d-orbitals, having a valence band (VB) composed of O2p and the VB top potential located at about +3 eV or higher (vs NHE), are expected to form photogenerated holes with strong oxidative power. TiO_2 and WO_3 are two such candidates with VB top potentials at 3.04 V and 3.1–3.2 V (vs NHE at pH 0), respectively. Although WO_3 has lower photoconversion efficiency than the widely used TiO_2, this material intrigued us due to its shorter band gap, better light absorption in the near UV and visible regions, the ease of preparation of high purity material and its long-term stability during irradiation.

However, the bandgap of WO_3 is still large to realize a sufficient absorption of the solar spectrum, which imposes a fundamental limitation on overall photo-to hydrogen efficiency. This limitation may be addressed by doping and sensitization, two possible ways by which the electronic structure and PEC properties of semiconducting oxides can be tailored. There have been reports in literature on the use of various dopants to enhance the PEC activity of WO_3 [13–16]. However, there are very few reports on the sensitization of WO_3. In 2014, Liu et al. [17] have a investigated CdS-sensitized WO_3 system with TiO_2 buffer layer and found an enhancement in photocurrent density which reached 0.92 mA cm^{-2} for CdS sensitized films. The same group has recently reported the sensitization of WO_3 with $Zn_xBi_2S_{3+x}$ which led to a photocurrent density of 7 mA cm^{-2} [18]. The photocurrent density obtained for various doped and sensitized WO_3 systems is tabulated in Table 1.

To the best of our knowledge, there have been no reports on sensitization of WO_3 with ZnCdSe quantum dots. In the present study, synthesis of a visible light-sensitive heterostructure by sensitization of WO_3 with ternary ZnCdSe quantum dots (QDs) has been reported for the first time. The WO_3 films were sensitized with ZnCdSe QDs using SILAR (Successive Ionic Adsorption and Reaction) technique. The SILAR technique presents a simple and inexpensive method of sensitization that does not require harsh pressure or temperature conditions and is time efficient.

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Table 1
Peak-fitting parameters for core-level scans of W 4f, Zn 2p, Cd 3d and Se 3d.

Peak	Species	BE (eV)	FWHM
W 4f	$W4f_{7/2}$	35.6	1.2
	$W4f_{5/2}$	37.7	1.2
Zn 2p	$Zn2p_{3/2}$	1021.5	1.8
	$Zn2p_{1/2}$	1044.6	2.1
Cd 3d	$Cd3d_{3/2}$	411.7	1.2
	$Cd3d_{5/2}$	405.0	1.2
Se 3d	Se (-II) main contribution	53.8	1.1
	Se (-II) second contribution	54.6	1.5

Furthermore, the effect of number of SILAR cycles on the PEC properties of sensitized films has not been previously reported for the WO_3 based system.

2. Experimental

Neat WO_3 thin films were synthesized by spray deposition onto SnO_2:F coated glass. The precursor solution (10 mM Ammonium metatungstate) was sprayed onto pre-heated, ultrasonically cleaned rectangular glass slides through a carrier gas. Films were maintained at a distance of 25 cm from the nozzle. The films were sprayed (at a pressure of 5 psi) for 5 s and dried for 55 s to ensure complete evaporation of solvent and pyrolysis of sprayed material on the film. The substrate temperature was maintained at 250 °C throughout the entire process. At this temperature, ammonium metatungstate was pyrolytically decomposed into tungsten oxide and was deposited as thin films on the substrates according to the following reaction [19]–

$$2W_{12}O_{41}N_6H_{26} \xrightarrow[250^{\circ}C]{} 24WO_3 + 12NH_3\uparrow + 8H_2O\uparrow + O_2\uparrow$$

The deposited films were observed to be uniform and well adherent to the substrate. These films were annealed at 550 °C for 2 h under oxygen atmosphere. After annealing, films acquired characteristic yellow color of stoichiometric WO_3. The films were sprayed for various number of WO_3 cycles; however, the films with 150 spray cycles were found to be optimum. Therefore, the WO_3(150) films were used further for sensitization.

WO_3 films were coated with TiO_2 buffer layer prior to ZnCdSe sensitization. This step is expected to result in better charge separation and reduced charge recombination in the hybrid system, as the conduction band (CB) edge of TiO_2 lies above than that of WO_3 [17,20]. The procedure involved immersion of annealed WO_3 films into 40 mM aqueous $TiCl_4$ solution in a closed vessel at 70 °C for 2 h. Then, the films were rinsed thoroughly with ethanol and then annealed in air at 450 °C for 2 h [17].

ZnCdSe nanocrystals were deposited onto TiO_2 coated WO_3 thin film using the SILAR technique. Sensitization with ZnCdSe quantum dots offers two-fold advantage, the lower band gap of ZnCdSe allows it to absorb more energy and the higher energy conduction band edge of ZnCdSe (compared to TiO_2) results in a better charge transfer from sensitizer to the substrate. The solvent used for precursor solution was 50/50 vol% ethanol/H_2O and deposition time was 1 min. The deposition was carried out under ambient temperature and pressure conditions. The samples were prepared with 6, 9, 12 and 15 cycles of deposition, where one SILAR cycle comprised of immersion of annealed WO_3 film in 0.02 M $Zn(NO_3)_2$ solution for one minute, followed by rinsing in ethanol/H_2O solvent and subsequent immersion in 0.02 M $Cd(CH_3CO_2)_2$ solution, and finally in a Na_2Se solution (generated in-situ by the reduction of Se metal with 0.04 M $NaBH_4$). The films were then annealed at 400 °C under N_2 atmosphere for 1 h. The prepared films were then used as working electrodes for the PEC measurements.

3. Characterization

UV–visible absorption spectra of prepared photoelectrodes were obtained with a Shimadzu UV-2401PC UV–vis diffuse reflectance spectrophotometer and $BaSO_4$ was used as the reflectance standard. X-ray diffraction patterns of the electrodes were recorded using a Rigaku Smartlab 3 kW X-ray diffractometer using Cu Kα wavelength (λ=1.541 Å; 40 kV, and 44 mA). The measurements were recorded in the 2θ range from 20° to 60° in Parallel Beam (PB) mode, with a scan speed of 1°/min and step width of 0.06°. Surface of the films was analyzed using a PHI 5600 model X-ray photoelectron spectrometer (XPS) with a monochromatic AlKα (1486.6 eV) excitation source. The spectrometer was calibrated to the Ag $3d_{5/2}$ line at 368.27 ± 0.05 eV. The XPS spectra were recorded at 14 kV and 300 W, with an analysis area of 800 μm^2. The survey spectra were acquired at pass energy of 29.35 eV and narrow scans at 23.95 eV. Charging effects were corrected using the adventitious C 1 s line at 284.6 eV. The peaks were fitted using SDP v4.6 Gaussian fitting software from XPS International. The photoelectrochemical (PEC) responses of the samples were measured in a conventional three-electrode system with ZnCdSe-sensitized WO_3 films (surface area of 1 cm^2) as the working electrodes, coiled platinum wire as counterelectrode, Ag/AgCl as reference electrode and an aqueous solution containing 0.35 M Na_2SO_3 and 0.25 M Na_2S as electrolyte. The measurements were conducted under ambient conditions in a custom-made quartz window cell with a Gamry® Reference 600 potentiostat. A 300 W Xe lamp solar simulator supplied by Newport served as incident light source. The visible light intensity through standard AM 1.5G filter was tuned to 100 mW/cm^2 measured using a Newport Thermopile Sensor 919P-003-10.

4. Results and discussions

Light absorption properties of the ZnCdSe QDs-sensitized WO_3 electrodes, as determined using a UV–vis spectrometer, are depicted in Fig. 1. The effect of number of SILAR layers on the performance of the QD-modified electrodes was investigated, and the optimal thickness for the ZnCdSe-sensitized WO_3 electrodes was found to be 9 layers. The spectra for WO_3/TiO_2 film show an absorption edge at 550 nm with main absorption peak around 370 nm, indicating light absorption significantly in UV region. With ZnCdSe sensitization, the absorption spectrum extended to longer wavelengths (~750 nm), exhibiting strong light absorption in almost the entire visible region. This suggests complementary

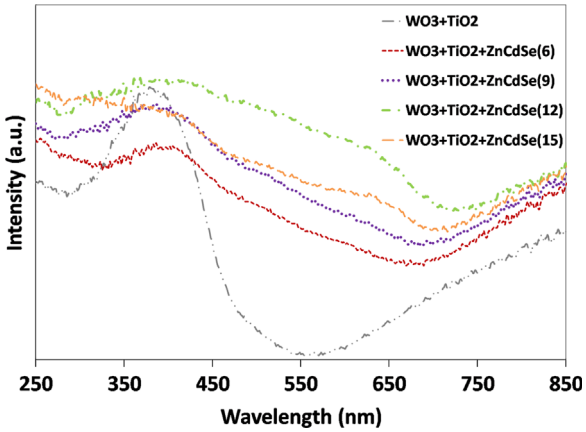

Fig. 1. Absorption spectra for unsensitized WO_3/TiO_2 film and ZnCdSe-sensitized WO_3 films; WO_3/TiO_2/ZnCdSe(n) films, where n depicts the number of SILAR cycles. The films were annealed at 400 °C under N_2 atmosphere for 1 h.