Photoelectrochemical performance of ZnCdSe-sensitized WO₃ thin films

Ruchi Gakhar and Dev Chidambaram*

Materials Science and Engineering, University of Nevada, Reno, NV, USA

*dcc@unr.edu

Abstract

Due to its wide gap, WO₃ mostly absorbs only the ultraviolet radiation, resulting into lower charge collection and thus necessitating the coupling (doping or sensitization) of WO₃ with low band gap materials so as to achieve the photoexcitation and charge separation. This study reports the sensitization of WO₃ films with ternary quantum dots (ZnCdSe) by SILAR technique for the first time. The porous WO₃ layer was spray deposited using ammonium metatungstate as precursor. The structural, surface morphological and optical properties of the sensitized WO₃ thin films were studied. Photoelectrochemical (PEC) studies of the sensitized films showed superior performance to that of unmodified WO₃ films. Photocurrent density of 8.53 mA/cm² (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 WO₃ film and WO₃/TiO₂ 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 TiO₂, results in a better charge transfer from sensitizer to the substrate material.

Keywords: quantum dots, spray pyrolysis, SILAR, water splitting; XPS

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 (versus 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 (versus 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 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 $\text{Zn}_x\text{Bi}_2\text{S}_{3+x}$ which

46 led to a photocurrent density of 7 mA cm^{-2} [18]. The photocurrent density obtained for various doped
47 and sensitized WO_3 systems have been tabulated in Table 1.

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

55 **Experimental**

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

64

65 The deposited films were observed to be uniform and well adherent to the substrate. These films were
66 annealed at 550°C for 2 hours under oxygen atmosphere. After annealing, films acquired characteristic
67 yellow color of stoichiometric WO_3 . The films were sprayed for various number of WO_3 cycles,

68 however, the films with 150 spray cycles was found to be optimum. Therefore, the WO₃(150) films were
69 used further for sensitization.

70 WO₃ films were coated with TiO₂ buffer layer prior to ZnCdSe sensitization. This step is expected to
71 result in better charge separation and reduced charge recombination in the hybrid system, as the
72 conduction band (CB) edge of TiO₂ lies above than that of WO₃ [17, 20]. The procedure involved
73 immersion of annealed WO₃ films into 40mM aqueous TiCl₄ solution in a closed vessel at 70 °C for 2
74 hours. Then, the films were rinsed thoroughly with ethanol and then annealed in air at 450 °C for 2 hours
75 [17].

76 ZnCdSe nanocrystals were deposited onto TiO₂ coated WO₃ thin film using the SILAR technique.
77 Sensitization with ZnCdSe quantum dots offers two-fold advantage, the lower band gap of ZnCdSe
78 allows it to absorb more energy and the higher energy conduction band edge of ZnCdSe (compared to
79 TiO₂) results in a better charge transfer from sensitizer to the substrate. The solvent used for precursor
80 solution was 50/50 vol.% ethanol/H₂O and deposition time was 1 minute. The deposition was carried out
81 under ambient temperature and pressure conditions. The samples were prepared with 6, 9, 12 and 15
82 cycles of deposition, where one SILAR cycle comprised of immersion of annealed WO₃ film in 0.02M
83 Zn(NO₃)₂ solution for one minute, followed by rinsing in ethanol/H₂O solvent and subsequent
84 immersion in 0.02 M Cd(CH₃CO₂)₂ solution, and finally in a Na₂Se solution (generated *in-situ* by the
85 reduction of Se metal with 0.04 M NaBH₄). The films were then annealed at 400 °C under N₂ atmosphere
86 for 1 hour. The prepared films were then used as working electrodes for the PEC measurements.

87

88

89 **Characterization**

90 UV-visible absorption spectra of prepared photoelectrodes were obtained with a Shimadzu UV-2401PC
91 UV-Vis diffuse reflectance spectrophotometer and BaSO₄ was used as the reflectance standard. X-ray
92 diffraction patterns of the electrodes were recorded using a Rigaku Smartlab 3kW X-ray diffractometer
93 using Cu K α wavelength ($\lambda = 1.541 \text{ \AA}$; 40 kV, 44 mA). The measurements were recorded in the 2θ range
94 from 20° to 60° in Parallel Beam (PB) mode, with a scan speed of $1^\circ/\text{min}$ and step width of 0.06° . Surface
95 of the films were analyzed using a PHI 5600 model X-ray photoelectron spectrometer (XPS) with a
96 monochromatic AlK α (1486.6 eV) excitation source. The spectrometer was calibrated to the Ag 3d_{5/2}
97 line at $368.27 \pm 0.05 \text{ eV}$. The XPS spectra were recorded at 14 kV and 300 W, with an analysis area of
98 $800 \mu\text{m}^2$. The survey spectra were acquired at pass energy of 29.35 eV and narrow scans at 23.95 eV.
99 Charging effects were corrected using the adventitious C 1s line at 284.6 eV. The peaks were fitted
100 using SDP v4.6 Gaussian fitting software from XPS International. The photoelectrochemical (PEC)
101 responses of the samples were measured in a conventional three-electrode system with ZnCdSe-
102 sensitized WO₃ films (surface area of 1 cm^2) as the working electrodes, coiled platinum wire as counter
103 electrode, Ag/AgCl as reference electrode and an aqueous solution containing 0.35 M Na₂SO₃ and 0.25
104 M Na₂S as electrolyte. The measurements were conducted under ambient conditions in a custom-made
105 quartz window cell with a Gamry® Reference 600 potentiostat. A 300 W Xe lamp solar simulator
106 supplied by Newport served as incident light source. The visible light intensity through standard AM
107 1.5G filter was tuned to 100 mW/cm^2 measured using a Newport Thermopile Sensor 919P-003-10.

108 **Results and Discussions**

109 Light absorption properties of the ZnCdSe QDs-sensitized WO₃ electrodes, as determined using a UV-
110 Vis spectrometer, are depicted in Fig.1. The effect of number of SILAR layers on the performance of the
111 QD-modified electrodes was investigated, and the optimal thickness for the ZnCdSe-sensitized WO₃
112 electrodes was found to be 9 layers. The spectra for WO₃/TiO₂ film shows an absorption edge at 550 nm

113 with main absorption peak around 370 nm, indicating light absorption significantly in UV region. With
114 ZnCdSe sensitization, the absorption spectrum extended to longer wavelengths (~ 750 nm), exhibiting
115 strong light absorption in almost the entire visible region. This suggests complementary enhancement
116 effects in the light absorption characteristics of WO_3 film with QDs sensitization. The incorporated
117 amount of sensitizer material on the substrate film, and hence the optical absorption generally increases
118 with increasing SILAR cycles. However, the reduction in absorption for films with higher number of
119 deposition cycles can be attributed to aggregation of nanocrystals as reported earlier [21, 22]. It should
120 be noted that after 9 cycles of deposition, the absorption spectra (for 12 and 15 cycles) shows the
121 formation of an additional absorption band at longer wavelength. Such a band at higher wavelength is
122 due to the sensitizer particles, indicating the formation of larger particles (or aggregates) on the surface
123 of the film with 12 and 15 cycles of deposition. In particular, film with 12 cycles of deposition forms
124 largest aggregates of particles compared to other cycles, where the increase in particle size has been
125 demonstrated by red-shift of the absorption onset. Similar results have been reported earlier by Peter *et al.*
126 [23, 24] and Drouard *et al.* [25]. The increase in particle size for 12 cycle film can be correlated to
127 the lowest photocurrent produced by the film (as shown in Fig. 4).

128

129 The XRD patterns obtained from WO_3 thin films before and after sensitization are shown in Fig. 2. The
130 XRD pattern of spray deposited WO_3/TiO_2 thin film (shown in curve a) exhibited strong diffraction
131 peaks corresponding to that of monoclinic $\gamma\text{-WO}_3$ phase (JCPDS card No. 43-1035, marked as *) [26].
132 The absence of peaks due to TiO_2 may be due to the fact that the TiO_2 layer is much thinner than the
133 WO_3 layer and is unlikely to be detected by the XRD. The XRD spectrum of sensitized
134 $\text{WO}_3/\text{TiO}_2/\text{ZnCdSe}$ electrode (shown in curve b) showed presence of additional peaks corresponding to
135 CdSe phase (JCPDS card no. 19-0191, marked as #). It is important to note that while there were no

136 peaks observed corresponding to Zn, a significant shift in 2θ values of CdSe peaks (towards higher 2θ)
137 was observed. Such shift signifies the presence of dopants in CdSe phase. More specifically, the shift
138 towards higher 2θ indicates the presence of smaller atoms as dopants. Hence, this observation confirms
139 the presence of Zn within the CdSe phase. The XRD peaks corresponding to the CdSe phase are broad,
140 suggesting the small crystallite size of the deposited material.

141 The elemental analysis of composite film showed the presence of all three elements - Zn, Cd and Se on
142 the surface of WO_3 . Fig. 3 shows the core-level XPS scans of W 4f, Zn 2p, Cd 3d and Se 3d regions of
143 sensitized $\text{WO}_3/\text{TiO}_2/\text{ZnCdSe}$ film and the peak-fitting parameters are summarized in Table 1. W4f has
144 a spin-orbit doublet ($4f_{7/2}$ and $4f_{5/2}$) with intensity ratio 4:3 and difference in binding energy of 2.1 eV.
145 The two peaks appearing at binding energies 35.6 and 37.7 eV, correspond well with the reported values
146 [27]. The Zn 2p spectrum of the doublet peaks with the binding energies of 1021.5eV and 1044.6eV are
147 shown in Fig. 3(b), corresponding to $\text{Zn}2p_{3/2}$ and $\text{Zn}2p_{1/2}$, respectively. These binding energies and the
148 difference between two binding energies to 23.1 eV are associated with the Zn^{2+} [28]. The $3d_{3/2}$ and
149 $3d_{5/2}$ spin-orbit splitting of the Cd 3d level occurs at binding energy values of 411.7 and 405.0eV,
150 respectively, while the Se $3d_{5/2}$ spin-orbit coupled doublet appeared at binding energy values of 53.8
151 (main contribution) and 54.6eV (second contribution), respectively. The binding energy values obtained
152 for Cd and Se are in good agreement with the literature values [29, 30].

153

154 To quantitatively address the photoactivity of ZnCdSe QDs-sensitized WO_3 photoanodes, photocurrent
155 density versus potential curves recorded under light illumination (1 sun or 100 mW cm^{-2}) are depicted in
156 Fig. 4. The increase in photocurrent with applied anodic potential represents the n-type character of the
157 films. The unsensitized WO_3/TiO_2 film showed a low photocurrent density of 0.55 mA/cm^2 under visible
158 light irradiation. To demonstrate the significance of TiO_2 layer coated on the surface of WO_3 before

159 sensitization, the photocurrent obtained from the film without TiO₂ coating has also been shown in Fig.
160 4. As observed, the film showed a photocurrent of only 0.07 mA/cm². The enhancement in photocurrent
161 with TiO₂ coating can be attributed to the better charge transfer process occurring in the composite film.
162 As the conduction band (CB) edge of TiO₂ (-0.1 V versus NHE) lies above that of WO₃ (+0.4 versus
163 NHE), the electron transport in the hybrid structure occurs in a cascade form. When the electron-hole
164 pairs are generated in ZnCdSe, electrons can be first transferred more easily from the CB of TiO₂ and
165 then to the CB of WO₃ rather than directly to WO₃. This process results in better charge separation and
166 reduced charge recombination in the hybrid system. Similar effect has been reported earlier [17, 20].
167

168 Therefore, the sensitization was carried out on WO₃ films coated with TiO₂ layer. Sensitization of
169 unmodified WO₃ films with ZnCdSe quantum dots resulted in abrupt increase in the photocurrent
170 density. The average photocurrent densities were measured to be 5.18, 8.53, 3.07 and 3.88 mA/cm² (at 0
171 V Vs Ag/AgCl) for WO₃/TiO₂ films sensitized with ZnCdSe for 6, 9, 12 and 15 cycles. As expected, the
172 number of SILAR cycles strongly affect the photoelectrochemical response of the resulting
173 photoanodes, which display marked variations within the series. The initial rise in photocurrent with
174 increase in number of SILAR cycles (upto 9 cycles) can be seen as a direct consequence of increased
175 loading of sensitizer material. With more sensitizer loading, the light absorption characteristics and thus,
176 the photoconversion efficiency are augmented. However, further increase in SILAR cycles (12 and 15
177 cycles) result in overloading of QDs, which can prove disadvantageous for the PEC performance of
178 photoanodes, ascribed to the blocking of mesopores of underlying substrate [31, 32]. Another reason is
179 that the thicker layers do not contribute much towards the charge transfer process from the sensitizer to
180 substrate, as they are not in direct contact with the substrate [33]. Therefore, the optimum current

density was obtained for film sensitized with 9 cycles annealed at 400°C, which is ~120-fold and ~14-fold higher than that of unsensitized WO₃ film and WO₃/TiO₂ film, respectively.

To further demonstrate the effect of sensitization on PEC performance of photoanodes, the fill factor (FF), and conversion efficiency (η) corresponding to unsensitized WO₃/TiO₂ and sensitized WO₃/TiO₂/ZnCdSe(9) films have been calculated and listed in Table 2 alongwith open circuit potential (V_{oc}), short circuit current (I_{sc}) values. The conversion efficiency obtained in this study is higher than the values reported earlier for WO₃ system [34, 35]. The current obtained in the present study is highest compared to the doped and sensitized WO₃ systems investigated earlier [13-18, 20, 36-38] (see Table 3). It is also worthy to note that the open-circuit potential (OCP) for the WO₃/TiO₂ is observed at -0.48 V. However, the photocurrent onsets shifts to more negative values for the WO₃/TiO₂/ZnCdSe(n) films. These results indicate that better charge separation and electron accumulation occur in the sensitized films. The experiments were performed in duplicates. While the films followed the same trend (9 cycles deposition film produced highest photocurrent compared to others), the photocurrent values differed by $\pm 10\%$ which is typical case for SILAR based composite films.

Conclusions

In summary, the design of WO₃/TiO₂/ZnCdSe heterostructure for PEC water splitting has been reported for the first time. The incorporation of ZnCdSe QDs with WO₃ extends the absorption spectrum of the composite film significantly into visible region up to 750 nm. The variation in number of SILAR cycles found to have a considerable effect on the photoelectrochemical response of the resulting photoanodes. With 9 cycles of deposition (WO₃/TiO₂/ZnCdSe(9) film), optimum thickness was obtained, and a photocurrent density as high as 8.53 mA/cm² (at 0 V Vs Ag/AgCl) was achieved. Such high current

202 efficiency (almost 120 times higher than that of unsensitized WO_3 film) indicate the potential of
203 ZnCdSe-sensitized WO_3 film as promising candidate for PEC applications.

204

205 **Acknowledgements**

206 The authors sincerely thank Dr. S.K. Pilli for scientific discussions at the beginning of this study. The
207 work was supported by Department of Energy under contracts DE-FC36-06-GO86066 and DE-
208 EE0003158.

References

- [1] N.A. Galiote, R.L. Parreira, J.M. Rosolen, F. Huguenin, Self-assembled films from WO₃: Electrochromism and lithium ion diffusion, *Electrochemistry Communications*, 12 (2010) 733-736.
- [2] S.K. Deb, Opportunities and challenges in science and technology of WO₃ for electrochromic and related applications, *Solar Energy Materials and Solar Cells*, 92 (2008) 245-258.
- [3] H. Li, Y. Lv, X. Zhang, X. Wang, X. Liu, High-performance ITO-free electrochromic films based on bi-functional stacked WO₃/Ag/WO₃ structures, *Solar Energy Materials and Solar Cells*, 136 (2015) 86-91.
- [4] H. Zheng, Y. Tachibana, K. Kalantar-zadeh, Dye-sensitized solar cells based on WO₃, *Langmuir*, 26 (2010) 19148-19152.
- [5] W. Yu, L. Shen, F. Meng, Y. Long, S. Ruan, W. Chen, Effects of the optical microcavity on the performance of ITO-free polymer solar cells with WO₃/Ag/WO₃ transparent electrode, *Solar Energy Materials and Solar Cells*, 100 (2012) 226-230.
- [6] Y. Miseki, H. Kusama, H. Sugihara, K. Sayama, Cs-modified WO₃ photocatalyst showing efficient solar energy conversion for O₂ production and Fe (III) ion reduction under visible light, *The Journal of Physical Chemistry Letters*, 1 (2010) 1196-1200.
- [7] S. Jayaraman, T.F. Jaramillo, S.-H. Baeck, E.W. McFarland, Synthesis and characterization of Pt-WO₃ as methanol oxidation catalysts for fuel cells, *The Journal of Physical Chemistry B*, 109 (2005) 22958-22966.
- [8] K. Huang, Q. Pan, F. Yang, S. Ni, X. Wei, D. He, Controllable synthesis of hexagonal WO₃ nanostructures and their application in lithium batteries, *Journal of Physics D: Applied Physics*, 41 (2008) 155417.
- [9] E. Llobet, G. Molas, P. Molinas, J. Calderer, X. Vilanova, J. Brezmes, J. Sueiras, X. Correig, Fabrication of highly selective tungsten oxide ammonia sensors, *Journal of the Electrochemical Society*, 147 (2000) 776-779.
- [10] M. Butler, Photoelectrolysis and physical properties of the semiconducting electrode WO₂, *Journal of Applied Physics*, 48 (1977) 1914-1920.
- [11] S. Deb, Optical and photoelectric properties and colour centres in thin films of tungsten oxide, *Philosophical Magazine*, 27 (1973) 801-822.
- [12] D. Scaife, Oxide semiconductors in photoelectrochemical conversion of solar energy, *Solar Energy*, 25 (1980) 41-54.
- [13] X.F. Cheng, W.H. Leng, D.P. Liu, J.Q. Zhang, C.N. Cao, Enhanced photoelectrocatalytic performance of Zn-doped WO₃ photocatalysts for nitrite ions degradation under visible light, *Chemosphere*, 68 (2007) 1976-1984.
- [14] K.H. Ng, L.J. Minggu, M.B. Kassim, Gallium-doped tungsten trioxide thin film photoelectrodes for photoelectrochemical water splitting, *International Journal of Hydrogen Energy*, 38 (2013) 9585-9591.

- [15] T. Zhang, Z. Zhu, H. Chen, Y. Bai, S. Xiao, X. Zheng, Q. Xue, S. Yang, Iron-doping-enhanced photoelectrochemical water splitting performance of nanostructured WO₃: a combined experimental and theoretical study, *Nanoscale*, 7 (2015) 2933-2940.
- [16] W. Li, F. Zhan, J. Li, C. Liu, Y. Yang, Y. Li, Q. Chen, Enhancing photoelectrochemical water splitting by aluminum-doped plate-like WO₃ electrodes, *Electrochimica Acta*, 160 (2015) 57-63.
- [17] C. Liu, Y. Li, W. Li, J. Zhu, J. Li, Q. Chen, Y. Yang, CdS quantum dots sensitized platelike WO₃ photoelectrodes with a TiO₂ buffer-layer, *Materials Letters*, 120 (2014) 170-173.
- [18] C. Liu, Y. Yang, W. Li, J. Li, Y. Li, Q. Shi, Q. Chen, Highly Efficient Photoelectrochemical Hydrogen Generation Using Zn_xBi₂S_{3+x} Sensitized Platelike WO₃ Photoelectrodes, *ACS Applied Materials & Interfaces*, 7 (2015) 10763-10770.
- [19] P.S. Patil, P.R. Patil, E.A. Ennaoui, Characterization of ultrasonic spray pyrolyzed tungsten oxide thin films, *Thin Solid Films*, 370 (2000) 38-44.
- [20] H.-i. Kim, J. Kim, W. Kim, W. Choi, Enhanced Photocatalytic and Photoelectrochemical Activity in the Ternary Hybrid of CdS/TiO₂/WO₃ through the Cascadal Electron Transfer, *The Journal of Physical Chemistry C*, 115 (2011) 9797-9805.
- [21] R. Gakhar, A. Merwin, K. Summers, S.K. Pilli, D. Chidambaram, Application of Zn_xCd_{1-x}Se-sensitized TiO₂ nanotube arrays as photoanodes for solar cells, *Journal of Materials Chemistry A*, 2 (2014) 10116–10125.
- [22] X.-F. Gao, H.-B. Li, W.-T. Sun, Q. Chen, F.-Q. Tang, L.-M. Peng, CdTe Quantum Dots-Sensitized TiO₂ Nanotube Array Photoelectrodes, *The Journal of Physical Chemistry C*, 113 (2009) 7531-7535.
- [23] D. Jason Riley, K. Upul Wijayantha, Photosensitization of nanocrystalline TiO₂ by self-assembled layers of CdS quantum dots, *Chemical Communications*, (2002) 1030-1031.
- [24] L.M. Peter, K.U. Wijayantha, D.J. Riley, J.P. Waggett, Band-edge tuning in self-assembled layers of Bi₂S₃ nanoparticles used to photosensitize nanocrystalline TiO₂, *The Journal of Physical Chemistry B*, 107 (2003) 8378-8381.
- [25] D. Stephanie, S.G. Hickey, D. Jason Riley, CdS nanoparticle-modified electrodes for photoelectrochemical studies, *Chemical Communications*, (1999) 67-68.
- [26] H. Zhang, M. Yao, L. Bai, W. Xiang, H. Jin, J. Li, F. Yuan, Synthesis of uniform octahedral tungsten trioxide by RF induction thermal plasma and its application in gas sensing, *Cryst Eng Comm*, 15 (2013) 1432-1438.
- [27] A. Katrib, F. Hemming, P. Wehrer, L. Hilaire, G. Maire, The multi-surface structure and catalytic properties of partially reduced WO₃, WO₂ and WC + O₂ or W + O₂ as characterized by XPS, *Journal of Electron Spectroscopy and Related Phenomena*, 76 (1995) 195-200.
- [28] Y. Shen, N. Xu, W. Hu, X. Xu, J. Sun, Z. Ying, J. Wu, Bismuth doped ZnSe films fabricated on silicon substrates by pulsed laser deposition, *Solid-State Electronics*, 52 (2008) 1833-1836.
- [29] B. Canava, J. Vigneron, A. Etcheberry, J.F. Guillemoles, D. Lincot, High resolution XPS studies of Se chemistry of a Cu(In,Ga)Se₂ surface, *Applied Surface Science*, 202 (2002) 8-14.

- [30] K.R. Murali, A. Austine, B. Jayasutha, D.C. Trivedi, Photoelectrochemical cells based on CdSe films brush plated on high-temperature substrates, *Solar Energy Materials and Solar Cells*, 90 (2006) 753-759.
- [31] Y.-L. Lee, B.-M. Huang, H.-T. Chien, Highly efficient CdSe-sensitized TiO₂ photoelectrode for quantum-dot-sensitized solar cell applications, *Chemistry of Materials*, 20 (2008) 6903-6905.
- [32] S.-C. Lin, Y.-L. Lee, C.-H. Chang, Y.-J. Shen, Y.-M. Yang, Quantum-dot-sensitized solar cells: Assembly of CdS-quantum-dots coupling techniques of self-assembled monolayer and chemical bath deposition, *Applied Physics Letters*, 90 (2007) 143517.
- [33] B. Mukherjee, Y.R. Smith, V. Subramanian, CdSe Nanocrystal assemblies on anodized TiO₂ nanotubes: Optical, surface, and photoelectrochemical properties, *The Journal of Physical Chemistry C*, 116 (2012) 15175-15184.
- [34] Z. Jiao, J. Wang, L. Ke, X.W. Sun, H.V. Demir, Morphology-tailored synthesis of tungsten trioxide (hydrate) thin films and their photocatalytic properties, *ACS Applied Materials & Interfaces*, 3 (2011) 229-236.
- [35] K. Hara, Z.-G. Zhao, Y. Cui, M. Miyauchi, M. Miyashita, S. Mori, Nanocrystalline Electrodes Based on Nanoporous-Walled WO₃ Nanotubes for Organic-Dye-Sensitized Solar Cells, *Langmuir*, 27 (2011) 12730-12736.
- [36] S.J. Hong, H. Jun, P.H. Borse, J.S. Lee, Size effects of WO₃ nanocrystals for photooxidation of water in particulate suspension and photoelectrochemical film systems, *International Journal of Hydrogen Energy*, 34 (2009) 3234-3242.
- [37] S.J. Hong, S. Lee, J.S. Jang, J.S. Lee, Heterojunction BiVO₄/WO₃ electrodes for enhanced photoactivity of water oxidation, *Energy & Environmental Science*, 4 (2011) 1781-1787.
- [38] K.C. Leonard, K.M. Nam, H.C. Lee, S.H. Kang, H.S. Park, A.J. Bard, ZnWO₄/WO₃ Composite for Improving Photoelectrochemical Water Oxidation, *The Journal of Physical Chemistry C*, 117 (2013) 15901-15910.

Figures and Tables Captions

Table 1. Peak-fitting parameters for core-level scans of W4f, Zn 2p, Cd 3d and Se 3d.

Table 2. Parameters obtained from photocurrent versus potential curves corresponding to unsensitized WO_3/TiO_2 and sensitized $\text{WO}_3/\text{TiO}_2/\text{ZnCdSe}(9)$ films.

Table 3. Photocurrent density of various doped and sensitized WO_3 systems.

Fig.1. Absorption spectra for unsensitized WO_3/TiO_2 film and ZnCdSe-sensitized WO_3 films; $\text{WO}_3/\text{TiO}_2/\text{ZnCdSe}(n)$ films, where n depicts the number of SILAR cycles. The films were annealed at 400°C under N_2 atmosphere for 1 hour.

Fig. 2. Stacked X-ray diffraction patterns of (a) unsensitized WO_3/TiO_2 thin film and (b) $\text{WO}_3/\text{TiO}_2/\text{ZnCdSe}$ sample annealed at 400°C . The patterns reveal the presence of CdSe phase on the surface of sensitized film.

Fig. 3. X-ray photoelectron spectra for $\text{WO}_3/\text{TiO}_2/\text{ZnCdSe}$ composite film showing (a) W4f peak (b) Zn 2p peak (c) Cd 3d peak and (b) Se 3d peak. `

Fig. 4. Photocurrent versus potential characteristics for unsensitized WO_3 films (with and without TiO_2 layer) and ZnCdSe-sensitized WO_3 films; $\text{WO}_3/\text{TiO}_2/\text{ZnCdSe}(n)$ films, where n depicts the number of SILAR cycles measured under 100 mW/cm^2 intensity (AM 1.5 global filter). The films were annealed at 400°C under N_2 atmosphere for 1 hour.

Table 1. Peak-fitting parameters for core-level scans of W4f, 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

Table 2. Parameters obtained from photocurrent versus potential curves corresponding to unsensitized WO₃/TiO₂ and sensitized WO₃/TiO₂/ZnCdSe(9) films.

Photoanode	I _{sc} (mA/cm ²)	V _{oc} (mV)	FF	η (%)
WO ₃ /TiO ₂	0.55	-0.48	0.23	0.16
WO ₃ /TiO ₂ /ZnCdSe(9)	8.53	-0.54	0.33	1.72

Table 3. Photocurrent density of various doped and sensitized WO₃ systems.

Material	Photocurrent density (mA/cm ²)	Illumination Intensity (mW/cm ²)	Author	Reference
WO ₃	0.6 (at 1.2V Vs NHE)	100	Honget <i>al.</i>	[36]
Zn-doped WO ₃	116 x 10 ⁻³ (at 0.8V Vs SCE)	3	Cheng <i>et al.</i>	[13]
Ga-doped WO ₃	131 x 10 ⁻³ (at 0.7V Vs SCE)	100	Ng <i>et al.</i>	[14]
Fe-doped WO ₃	0.88 (at 1.23V Vs RHE)	100	Zhang <i>et al.</i>	[15]
Al-doped WO ₃	1.14 (at 1.2 V Vs Ag/AgCl)	100	Li <i>et al.</i>	[16]
WO ₃ -BiVO ₄ composite	2.78 (at 1.2 V Vs Ag/AgCl)	100	Honget <i>al.</i>	[37]
CdS/TiO ₂ /WO ₃ composite	1.6 (at 0 V Vs Ag/AgCl)	180	Kim <i>et al.</i>	[20]
ZnWO ₄ /WO ₃ composite	0.75 (at +0.7 V vs Ag/AgCl)	100	Leonard <i>et al.</i>	[38]
CdS-sensitized WO ₃	0.92 (at 0 V Vs Ag/AgCl)	100	Liu <i>et al.</i>	[17]
Zn _x Bi ₂ S _{3+x} - sensitizedWO ₃	7 (at -0.1V VsAg/AgCl)	100	Liu <i>et al.</i>	[18]

Fig.1. Absorption spectra for unsensitized WO_3/TiO_2 film and ZnCdSe-sensitized WO_3 films; $\text{WO}_3/\text{TiO}_2/\text{ZnCdSe}(n)$ films, where n depicts the number of SILAR cycles. The films were annealed at 400°C under N_2 atmosphere for 1 hour.

Fig. 2. Stacked X-ray diffraction patterns of (a) unsensitized WO_3/TiO_2 thin film and (b) $\text{WO}_3/\text{TiO}_2/\text{ZnCdSe}$ sample annealed at 400°C . The patterns reveal the presence of CdSe phase on the surface of sensitized film.

Fig. 3. X-ray photoelectron spectra for $\text{WO}_3/\text{TiO}_2/\text{ZnCdSe}$ composite film showing (a) W4f peak (b) Zn 2p peak (c) Cd 3d peak and (b) Se 3d peak.

Fig. 4. Photocurrent versus potential characteristics for unsensitized WO_3 films (with and without TiO_2 layer) and ZnCdSe -sensitized WO_3 films; $\text{WO}_3/\text{TiO}_2/\text{ZnCdSe}(n)$ films, where n depicts the number of SILAR cycles measured under 100 mW/cm^2 intensity (AM 1.5 global filter). The films were annealed at 400°C under N_2 atmosphere for 1 hour.