High-Throughput Methods for the Investigation of Photoelectrochemical Hydrogen Production from $Zn_{1-x}Co_xO$ Thin Films

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The solar driven photolysis of water has long been identified as one of the "holy grails" of chemistry because of its potential impact as a clean, renewable, method of fuel production. It is well known that the photoelectrochemical activity of ZnO is limited by two primary factors: (1) poor solar spectrum photon absorption (due to a wide bandgap of 3.2 eV), and (2) photocorrosion in electrolytes [1]. The combinatorial chemistry methodology of rapid synthesis and high-throughput characterization has expedited the discovery of improved of solid-state materials for a variety of applications. We have applied both traditional and combinatorial methods to improve the opto-electrochemical properties of hydrogen producing photocatalytic metal oxides. Previous researchers have identified cobalt-doping as a means to improve visible photon absorption in ZnO, however, only a handful of cobalt-loadings were prepared and studied [2-5]. Herein, we present results of a 120-member $Zn_{1-x}Co_xO$ ($0 < x < 0.068$) thin film library that spans 27 different cobalt concentrations with at least 4 replicates each, Fig. 1.

$Zn_{1-x}Co_xO$ samples (200 nm thick) were electrochemically deposited using a rapid serial synthesis system, Fig. 2. Zn:Co stoichiometry in the film was controlled by ratios of $ZnCl_2$ and $Co(NO3)_2$ in the independent electrochemical deposition cells. This synthetic route followed the ZnO preparation proposed by Gal. et. al. [6]. XPS was used to determine Zn:Co stoichiometries of the doped films, and it was found that the cobalt was predominantly Co^{2+}. XRD confirmed the wurtzite structure for all samples. UV-Vis spectroscopy showed increase visible absorption of the cobalt-doped samples through two means: (1) characteristic *d-d* transitions from the Co^{2+} ion, and (2) decreased bandgap.

A high-throughput photoelectrochemical screening system was developed to characterize the photocatalytic activity of the samples. Fig. 3 shows the zero-bias photocurrent of the samples in 0.2M KNO_3 (aq.). A ~ 1 W/cm^2 Xe lamp was used for illumination. Under UV-Vis illumination, the photocurrent of the samples asymptotically decreased with increasing cobalt. Under Vis-only illumination, however, photocurrent initially decreases but then rises rapidly to a maximum at Co = 4.4% with a value nearly four times greater than that of pure ZnO. High-throughput photoelectrochemical screening showed greatly increased photoactivity under applied bias, and it was confirmed by action spectra that the Co^{2+} photon absorptions and decreased bandgap of cobalt-doped films observed in UV-Vis spectroscopy gave rise to the increased photocurrent. Flat-band potential measurements indicated a negligible change in the conduction band edge for cobalt-doped samples compared to ZnO, implying that the bandgap shift must arise from an increase in valence band energy.

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REFERENCES

1. Inoue, T. et. al.., Bulletin of the Chemical Society of Japan **52**, 3217 (1979).
2. Fichou, D. et. al., Journal of Electroanalytical Chemistry, **188**, 167 (1985).
3. Jakani, M. et. al., Journal of Solid State Chemistry, **56**, 269 (1985).
4. Bahadur, L. and Rao, T.N., Solar Energy Materials and Solar Cells, **27**, 347 (1992).
5. Hirano, T. and Kozuka, H., Journal of Materials Science, **38**, 4203 (2003).
6. Gal, D. et. al., Thin Solid Films, **361**, 79 (2000).

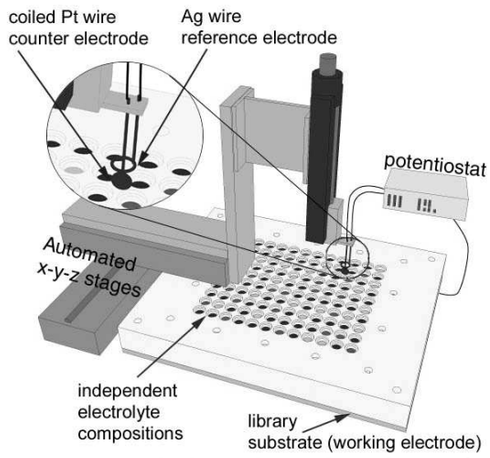

Figure 1. Automated electrochemical synthesis of 120 samples using scanning counter and reference electrodes.

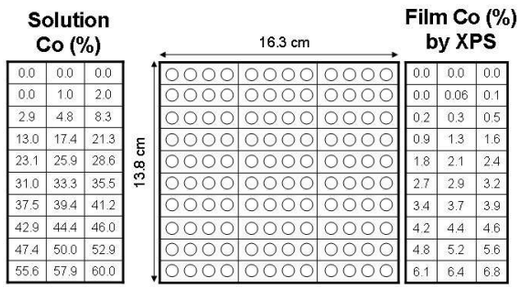

Figure 2. Library design for 120 $Zn_{1-x}Co_xO$ films ranging from $0 < x < 0.068$.

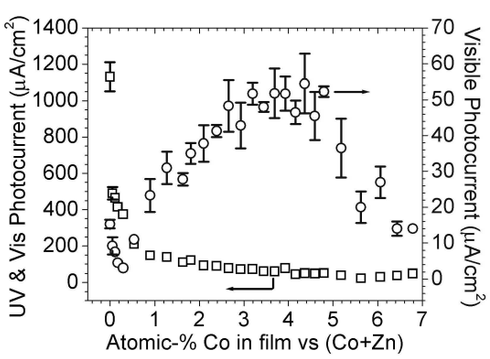

Figure 3. Photocurrent results in 0.2M KNO_3. Left axis reflects full Xe lamp illumination while the right axis exhibits results with a UV cut-off filter in place.