High-Throughput Methods for the Investigation of Photocatalytic Hydrogen Production from $\text{Zn}_x\text{Co}_y\text{O}$ Thin Films

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The solar driven photoysis 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 photocatalytic activity of $\text{ZnO}$ 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 $\text{ZnO}$, however, only a handful of cobalt-loadings were prepared and studied [2-5]. Herein, we present results of a 120-member $\text{Zn}_x\text{Co}_y\text{O}$ ($0 < x < 0.068$) thin film library that spans 27 different cobalt concentrations with at least 4 replicates each. Fig. 1. $\text{Zn}_x\text{Co}_y\text{O}$ samples (200 nm thick) were electrochemically deposited using a rapid serial synthesis system, Fig. 2. $\text{ZnO}$ stoichiometry in the film was controlled by ratios of $\text{ZnCl}_2$ and $\text{Co(NO}_3)_2$ in the independent electrochemical deposition cells. This synthetic route followed the $\text{ZnO}$ preparation proposed by Gal et al. [6]. XPS was used to determine $\text{Zn:Co}$ stoichiometries of the doped films, and it was found that the cobalt was predominantly $\text{Co}^{2+}$. 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 $\text{Co}^{2+}$ 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 $\text{ZnO}$. High-throughput photoelectrochemical screening showed greatly increased photoactivity under applied bias, and it was confirmed by action spectra that the $\text{Co}^{2+}$ 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 $\text{ZnO}$, implying that the bandgap shift must arise from an increase in valence band energy.

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REFERENCES


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

Figure 2. Library design for 120 $\text{Zn}_x\text{Co}_y\text{O}$ 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.