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Dopant Effects on Copper Oxide Photoelectrochemical Cell Water Splitting

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Abstract

The electrical conductivity of a film has a dramatic influence on the lifetime of photo-excited electrons. As a result, the electrical conductivity of an electrode plays an important role in the performance of a photoelectrochemical (PEC) cell. In this study, we demonstrated that the conductivity of a semiconductor CuO film can be varied by introducing different dopants, such as Li, Mg, and seven other 3d or 4d orbital transition metals. Compared to the intrinsic CuO film, the conductivity was increased/decreased by up to two orders of magnitude with addition dopants and this led to a wide range of resulting photocurrent densities an essential index in the study of materials for PEC splitting of water for renewable hydrogen generation.

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1. Introduction

Water splitting hydrogen generation via a photoelectrochemical (PEC) cell is one of the cleanest processes and more importantly there is near zero carbon footprint when using this renewable hydrogen energy [1-3]. In a water splitting PEC cell, sun light (photon) is first absorbed by the electrode material and the high energy electrons excited by photons then trigger the redox chemical reaction at the electrode-electrolyte interface to convert water into hydrogen and oxygen. In this process, the fast electron transfer and less resistivity for the electron transfer can highly increase the efficiency of the system. Copper oxide, CuO, a p-type semiconductor, has been shown to have a bandgap around 1.4-1.8 eV [4-8] and a suitable

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band position for the water reduction reaction (H^+ to H_2). However, due to its relatively high resistance, the majority photon excited electrons might not have the chance to move to the electrode-electrolyte interface for the reaction. As a result, lowering the resistance by increasing the conductivity of the photocathode material, CuO, is essential. In this study, a series of dopants are added into CuO by a flame spray pyrolysis process. In a fast particle formation and quenching process, the dopants have higher chance to form a uniform phase with CuO, i.e. the dopants are soluble in CuO, without much segregation happening. We also correlate the relationship between the conductivity and the PEC efficiency in terms of photocurrent density based on six 3d and one 4d orbital transition metals and an alkaline earth metal, Mg.

2. Experimental

2.1. Doped Copper Oxide Photocathodes Preparation

Doped copper oxide nanoparticles were prepared by a flame spray pyrolysis (FSP) system. The precursors were prepared by 1 M copper nitrate solution [$Cu(NO_3)_2 \cdot 3H_2O$] (Strem Chemicals Inc., USA) and with 2 at% as dopant chemicals, i.e. magnesium, chromium, manganese, iron, cobalt, nickel, zinc, and silver. The dopant precursors were either nitrates or acetates except nickel chloride as the precursor for nickel dopant. All the chemicals are reagent grade. The nanoparticles were formed by the decomposition of precursor in a methane flame. Particles were collected on a filter paper (W. L. Gore & Associated Inc., USA) by a vacuum pump. More detailed setup can be found in our previous study [9]. Particles were suspended in ethanol. The slurry was then spin coated (Headway PWM32 Spinner, USA) on a conduction indium-tin-oxide coated microscope slides (SPI supplies, USA). Repeated the same spin coating process for four times to reach thickness ca. 850 nm. The film was then sintered in a muffle furnace (Thermo Scientific Thermolyne, USA) at 450 °C for 1 hr.

2.2. Characterization

A Philips PW 1800 diffractometer with a graphite monochromator with an incident radiation of Cu $K\alpha$ ($\lambda=1.54 \text{ \AA}$) was used in the XRD chemical component analysis. The photoelectrochemical study was conducted under a three-electrode configuration in 1M KOH (pH 14). Ag/AgCl in saturated KCl (Gamry Instruments, USA) and platinum gauze were used as reference electrode and counter electrode, respectively. The light source was a 150 W full spectrum solar simulator and a AM1.5G filter with a measured intensity of 1 sun (1000 W/m^2) at 25 °C. All the electrochemical characterization was done by a potentiostat (eDAQ, Australia). The electrical conductivity of the films was determined by electrochemical impedance spectroscopy (EIS) carried out on a potentiostat/galvanostat (Solartron, USA).

3. Result and Discussion

The result of the crystalline analysis by XRD for the flame spray pyrolysis prepared 2 at % doped-CuO particles were shown in Figure 1. The dopants includes alkaline earth metal Mg, 3d transition metals such as Cr, Mn, Fe, Co, Ni, Zn and 4d transition metal Ag. All the doped materials showed monoclinic CuO phase only, indicating that the dopants did not form a second phase. There is no obvious crystal orientation change with dopant introduced. The crystalline size for these particles was estimated to be around 30 nm based on the Scherrer equation.

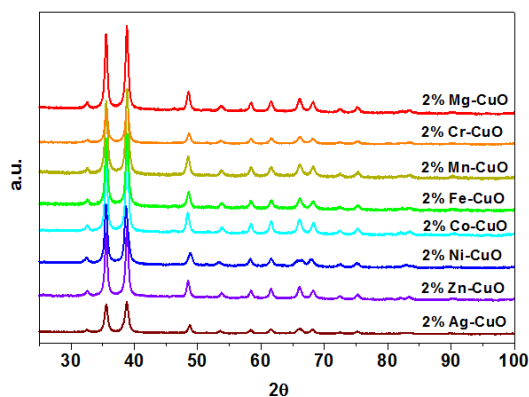


Fig. 1. XRD for 2 at% doped-CuO photocathodes prepared by flame spray pyrolysis and spin coating process in this study.

The photocurrent density for various dopants added into CuO with concentration of 2 at% under bias voltage of -0.55 V vs. Ag/AgCl applied is shown in Table 1. The experiment was carried in pH 14 solution with a three-electrode system under AM1.5G spectrum at 1 sun irradiation. Besides from those dopants in this study, 2 at% Li doped CuO from Chiang et al. [6], was also included for the comparison. In Table 1, it is seen that Li shows the best performance in terms of photocurrent density generated by the light irradiance. This is explained by the two orders of magnitude increase in conductivity [6]. Ni, Co, Ag, Zn and Mg are following after Li for the relatively high photocurrent density generated. For example, in our previous study [6], the intrinsic CuO film prepared by spin coating has the electrical conductivity ca. 3×10^{-6} S/cm and for these dopants with positive effect on photocurrent density, i.e. Ni, Co, Ag, Zn, and Mg, the electrical conductivity is also found to be higher and ranging from 4.4×10^{-6} to 1.8×10^{-5} S/cm. In contrast, dopants like Cr, Mn, and Fe contribute to lower the conductivity to ca. $10^{-8} \sim 10^{-9}$ S/cm and thus highly decrease the photocurrent density.

Table 1. Film conductivities vs. photocurrent density for various dopants introduced (2 at% doped CuO film photoelectrode) at bias voltage of -0.55 V vs. Ag/AgCl.

Dopant	Conductivity (S/cm)	Photocurrent density (mA/cm ²) at -0.55 V vs. Ag/AgCl
none	3×10^{-6}	0.31
Li [6]	1.00×10^{-4}	1.52
Ni	1.80×10^{-5}	1.07
Zn	9.22×10^{-6}	0.417
Co	8.88×10^{-6}	0.77
Mg	8.43×10^{-6}	0.417
Ag	4.43×10^{-6}	0.63
Cr	8.33×10^{-8}	0.138
Fe	7.63×10^{-8}	0.192
Mn	6.19×10^{-9}	0.142

An interesting finding is shown in Table 1, conductivity of the film vs. photocurrent density. As the conductivity increases approximately one order of magnitude (comparing to the intrinsic CuO film) by

introducing Ni as dopant, the photocurrent density almost 3 times. And, as the conductivity decreases for about 2~3 order of magnitude, the photocurrent density becomes about half. However, if the conductivity is further increased to 2 orders of magnitude as Li serves as the dopant, the photocurrent density is not showing a linear increase. This might be because once the conductivity reaches a certain level when the efficiency dominant factor is no longer on the conductivity for a PEC water splitting cell, instead the surface area would take an more important role since the water splitting reaction takes place at the interface. If there is no enough surface for those photon generated electrons to react with water then no matter how conductive the cell is, the efficient will not be high.

4. Conclusion

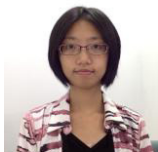
The electrical conductivity of doped CuO films has been shown with a positive effect on the photoelectrochemical cell water splitting for renewable hydrogen generation. By doping with Li, Ni, Co, Ag, Zn and Mg, the conductivity of the films increases by up to two orders of magnitude, leading to a few percent to five fold increase in photocurrent density. On the other hand, Cr, Fe and Mn dopants have negative effect in the conductivity ($10^{-8} \sim 10^{-9}$ S/cm comparing to the intrinsic CuO's conductivity 3×10^{-6} S/cm) and the efficiency of these doped CuO photocathodes are much lower.

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Biography

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