## Photoelectrochemical Water Splitting from Earth-Abundant CuO Thin Film Photocathode: Enhancing Performance and Photo-Stability through Deposition of Overlayers

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Abstract : Cupric oxide (CuO) is a promising absorber material for the fabrication of scalable, low cost solar energy conversion devices, due to the high abundance and low toxicity of copper. It is a p-type semiconductor with a band gap of around 1.5 eV, absorbing a significant portion of the solar spectrum. One of the main challenges in using CuO as solar absorber in an aqueous system is its tendency towards photocorrosion, generating Cu2O and metallic Cu. Although there have been several reports of CuO as a photocathode for hydrogen production, it is unclear how much of the observed current actually corresponds to H2 evolution, as the inevitability of photocorrosion is usually not addressed. In this research, we investigated the effect of the deposition of overlayers onto CuO thin films for the purpose of enhancing its photostability as well as performance for water splitting applications. CuO thin film was fabricated by galvanic electrodeposition of metallic copper onto gold-coated FTO substrates, followed by annealing in air at 600 °C. Photoelectrochemical measurement of the bare CuO film using 1 M phosphate buffer (pH 6.9) under simulated AM 1.5 sunlight showed a current density of ca. 1.5 mA cm-2 (at 0.4 VRHE), which photocorroded to Cu metal upon prolonged illumination. This photocorrosion could be suppressed by deposition of 50 nm-thick TiO2, deposited by atomic layer deposition. In addition, we found that insertion of an n-type CdS layer, deposited by chemical bath deposition, between the CuO and TiO2 layers was able to enhance significantly the photocurrent compared to without the CdS layer. A photocurrent of over 2 mA cm-2 (at 0 VRHE) was observed using the photocathode stack FTO/Au/CuO/CdS/TiO2/Pt. Structural, electrochemical, and photostability characterizations of the photocathode as well as results on various overlayers will be presented.

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