Electronic Supplementary Information

Introducing a protective interlayer of TiO_2 in Cu_2O-CuO heterojunction thin film as a highly stable visible photocathode

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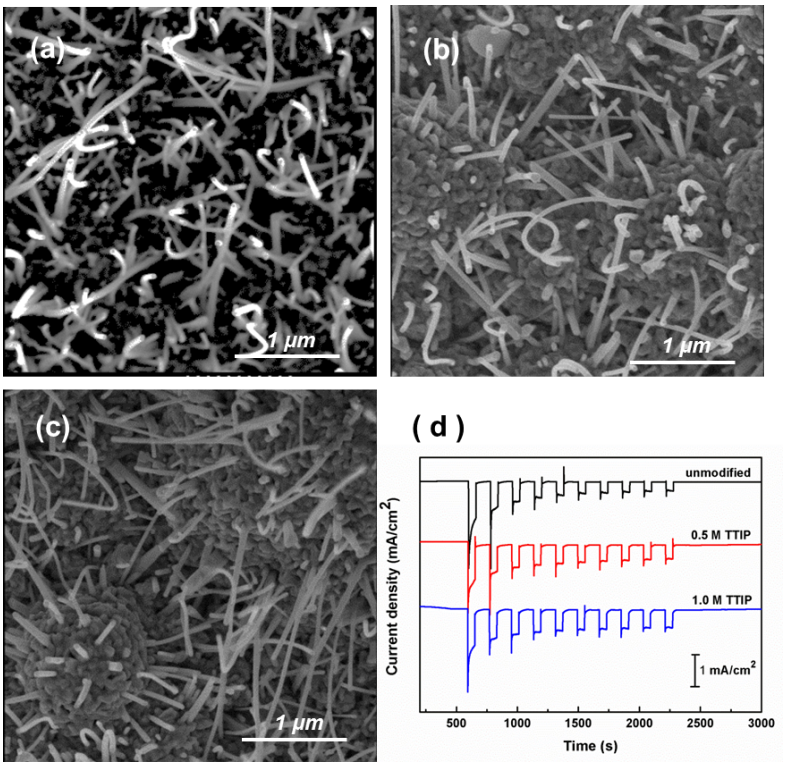
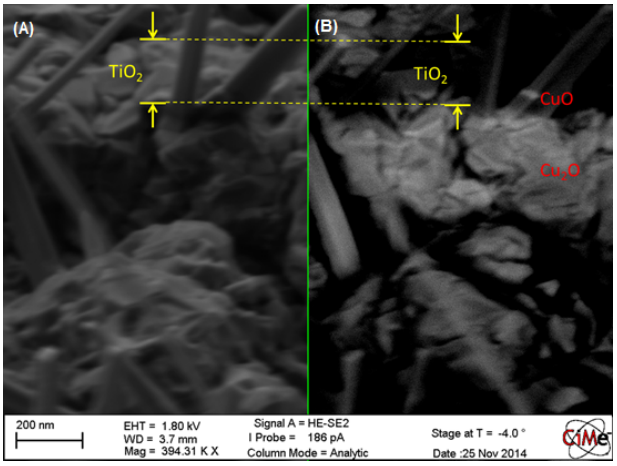


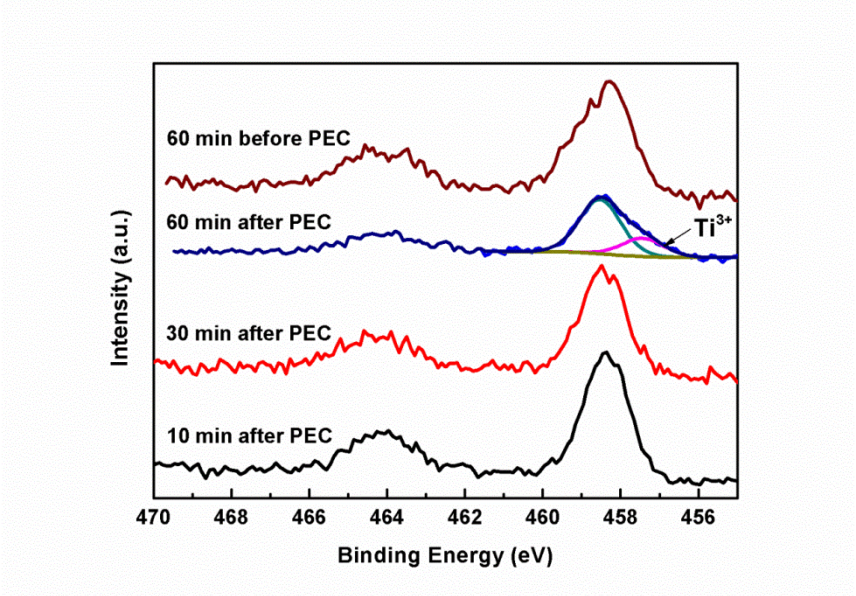
ESI Fig. S1 SEM images of (a) unmodified Cu_2O-CuO photoelectrodes; (b) TiO_2-modified Cu_2O-CuO photoelectrodes with 0.5 M TiO_2 precursor and (c) 1.0 M TiO_2 precursor; (d) corresponding visible light (>420 nm) photocurrent generation.



ESI Fig. S2 Scanning electron and back scattered electron images of Cu_2O-CuO thin film coated with TiO_2 for 30 mins.

The thickness of TiO_2 layer (30 min treatment) was estimated using a 45° tilted back scattered electrons (BSE) imaging obtained on a Zeiss MERLIN microscope. **Figure A** shows the morphology of the film surface consists of TiO_2, Cu_2O and CuO nanowire components. The TiO_2 component can be distinguished in the right image (**Figure B**) which was formed from the back scattered electrons. It shows the presence of Cu element in brighter colour and Ti element in dark colour. The thickness of the TiO_2 was therefore estimated to be ca. 140 nm.

Note that the thickness of TiO_2 across the thin film's surface may not be evenly distributed due to the nature of the dip-coating method. In this work, indeed, we did not consider the TiO_2 thickness (as we understood it would be much thinner compare with the bulk Cu_2O layer (ca. 20 µm)) as critical as the TiO_2 coverage on the surface. The level of TiO_2 coverage indicated in the **Figure 3** in the original manuscript was found important in determining its protective effectiveness against the redox reactions at the Cu_2O-electrolyte interface.



ESI Fig. S3 Ti 2p spectra of Cu_2O-CuO photoelectrodes modified with precursor of TiO_2 at different duration (10 min, 30 min and 60 min).