Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

Supporting Information

Efficient solar photoelectrosynthesis of methanol from carbon dioxide using hybrid CuO/Cu_2O semiconductor nanorod arrays

Ghazaleh Ghadimkhani,[a] Norma R. de Tacconi,[a,*] Wilaiwan Chanmanee,[a] Csaba Janaky[a,b] and Krishnan Rajeshwar[a,]

Sample Details

Table S1. CuO/Cu_2O nanorod photoelectrodes prepared by a two-step strategy (TH and ED) along with the respective parent materials

Photoelectrode name	1st step = thermal (TH)	2nd step = Cu_2O electrodeposition (ED)
TH/ED1	Cu foil heated at 400C, 4 h	Cu_2O electrodeposited for 1 min
TH/ED5	Cu foil heated at 400C, 4 h	Cu_2O electrodeposited for 5 min
TH/ED10	Cu foil heated at 400C, 4 h	Cu_2O electrodeposited for 10 min
TH/ED15	Cu foil heated at 400C, 4 h	Cu_2O electrodeposited for 15 min
TH/ED25	Cu foil heated at 400C, 4 h	Cu_2O electrodeposited for 25 min
TH/ED30	Cu foil heated at 400C, 4 h	Cu_2O electrodeposited for 30 min
TH	Cu foil heated at 400C, 4 h	N/A
ED30	N/A	Cu_2O electrodeposited for 30 min

Experimental Details

Chemicals and Materials. Cu substrates (foil and mesh) were from Alfa Aldrich and 99.99% purity. Chemical reagents used in the study were of analytical grade and were used without further purification.

Preparation of CuO/Cu_2O nanorod photoelectrodes. The hybrid CuO/Cu_2O nanorod arrays were fabricated by a two-step process performed on freshly cleaned copper. Thus, copper (foil or mesh) substrates were pretreated with 1.0 M HCl, then sonicated in isopropanol, acetone and deionized water respectively and finally dried under nitrogen gas. In the first step, freshly cleaned Cu substrates were subjected to thermal oxidation in presence of air using a box furnace for 4 hr at 400^0C. A temperature program was used and consisted in heating the samples up to 400 °C (at 25°/min), and after 4 h of isothermal heat, the temperature was allowed to return naturally to room temperature.

In the second step, Cu_2O crystallites were electrodeposited on the thermally grown CuO nanowires from a basic solution of lactate-stabilized copper sulfate using a conventional potentiostat (CHI electrochemical workstation 720C). The electrolytic bath was prepared with deionized (DI) water (Corning Megapure) and contained 4 M cupric sulfate and 3 M lactic acid. The bath pH was adjusted to 9 by addition of concentrated sodium hydroxide solution; the temperature of the bath was maintained at 60^0C during electrodeposition. A Pt foil and a Ag/AgCl (satd. KCl) were used as counter electrode and reference electrode respectively. The electrodeposition time was varied to investigate the structural and also photoactivity of the resulting heterostructures. All potentials were measured vs. Ag/AgCl ref. electrode but they are shown with respect to SHE, using Ag/AgCl = -0.197 V vs. SHE.

Experimental conditions for the preparation of several CuO/Cu_2O nanorod arrays are reported in Table S1. Heterostructures are designated as TH for thermal CuO nanowires and TH/EDτ for thermal CuO plus electrodeposited Cu_2O for selected electrodeposition times, τ. All core/shell nanostructures have CuO core nanowires of ca. 100-nm diameter (adjusted by the thermal treatment of Cu substrate) while the shell thickness was varied by adjusting the Cu_2O electrodeposition time, τ. The electrodeposition potential was always kept at -0.2 V vs. SHE and τ was varied from 1 min to 30 min.

Instrumentation for electrochemical and photoelectrochemical characterization. The photoelectrochemical performance of the prepared Cu_2O/CuO nanorod photoelectrodes was studied using a CH electrochemical workstation 600C instrument (www.chinstruments.com), in a custom-designed two-compartment, three-electrode electrochemical cell. Ag/AgCl (satd. KCl) and Pt foil were used as reference electrode and counterelectrode respectively although all potentials are quoted with respect to the SHE reference scale. The electrolyte used was 0.1 M Na_2SO_4. Solutions were saturated with N_2 or with CO_2 as needed by continual bubbling through the sealed cell. The photocurrent-potential profiles were recorded under 0.2 Hz chopped solar irradiation (AM 1.5) from a solar simulator (Newport 91160-1000).

Bulk photoelectrolysis was also performed in a two-compartment sealed electrochemical cell. The CH electrochemical workstation 600C was used to apply a constant potential of -0.2 V. Light irradiation was provided by the full output of the Newport solar simulator specified above.

SEM and XRD Characterization of CuO/Cu_2O nanorod photoelectrodes. The morphology of the films was characterized using a Hitachi S-5000H field emission scanning electron microscope (SEM) operated at an acceleration voltage of 20.0 kV. X-ray diffraction (XRD) patterns were obtained on a Siemens D-500 powder diffractometer using CuK_α as the source radiation.

Gas Chromatography with MS detection. Liquid aliquots were periodically taken during the photoelectrolysis to be analyzed in a gas chromatograph (GC) equipped with a mass spectrometer as detector (GC-MS). The aliquots were subjected to supporting electrolyte removal by shaking overnight with Amberlite IRN-150 ion-exchange resin (cleaned and vacuum dried just before use) and then injected into the GC-MS instrument. For analysis of the liquid aliquots, a Shimadzu GC-MS-2010SE chromatograph with a MS QP2010 detector and a AOC-

20S sampler was used. The chromatographic column was Shimadzu SHRX105MS (30-m length and 0.25-mm inner diameter, part # 220-94764-02) set at 45 °C. The MS detector was set at 250 °C, and helium was used as the carrier gas. Calibration curves for different methanol concentrations in water showed that the methanol peak eluded at 1.52 min with a corresponding m/z = 31.

Figures

The electrodeposition (ED) of Cu_2O on a Cu substrate without and with a thermal oxidation treatment (TH) is compared in Fig. S1. The different morphology of the two substrates is also included in Fig. S1. It is worth noticing that the electrodeposition charge is seen to vary almost linearly with time for both electrodes and from the respective slopes a surface aspect ratio increase of 6-7 was found for the thermal oxidized electrode. Observe also that Cu_2O is continuously electrodeposited in spite of its p-type conductivity.

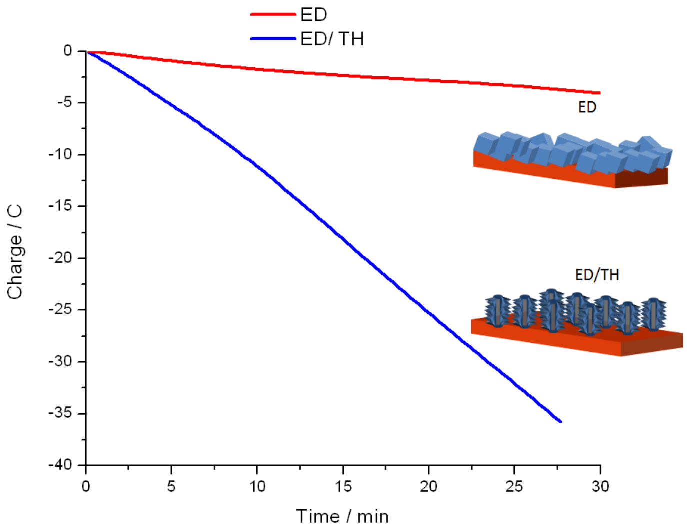

Fig. S1. Charge evolution during the electrodeposition of Cu_2O on freshly polished Cu and on thermal oxidized Cu electrodes at -0.20 V vs. SHE for 30 min in a solution containing 0.4 M $CuSO_4$ and 3 M lactic acid adjusted to pH 9. Color sketches are included to clarify the two contrasting substrates used for Cu_2O electrodeposition.

To analyze the product photogenerated on CuO/Cu_2O nanorod photoelectrodes, bulk photoelectrolyses under continuous simulated solar irradiation were performed at -0.2 V vs. SHE in a CO_2 saturated solution. Representative photocurrent/time profile for a TH/ED10 electrode is shown in Fig. S2. Observe that the photocurrent decreases during the first 30 min and then recovers to reach a constant value of 1.05 mA after ~ 2 hours irradiation (Fig. S2a). Dark currents values of one order lower (0.1 mA) corroborate that the electrode remains photoactive all over the photoelectrolysis time (see insert on the right side of Fig. S2).

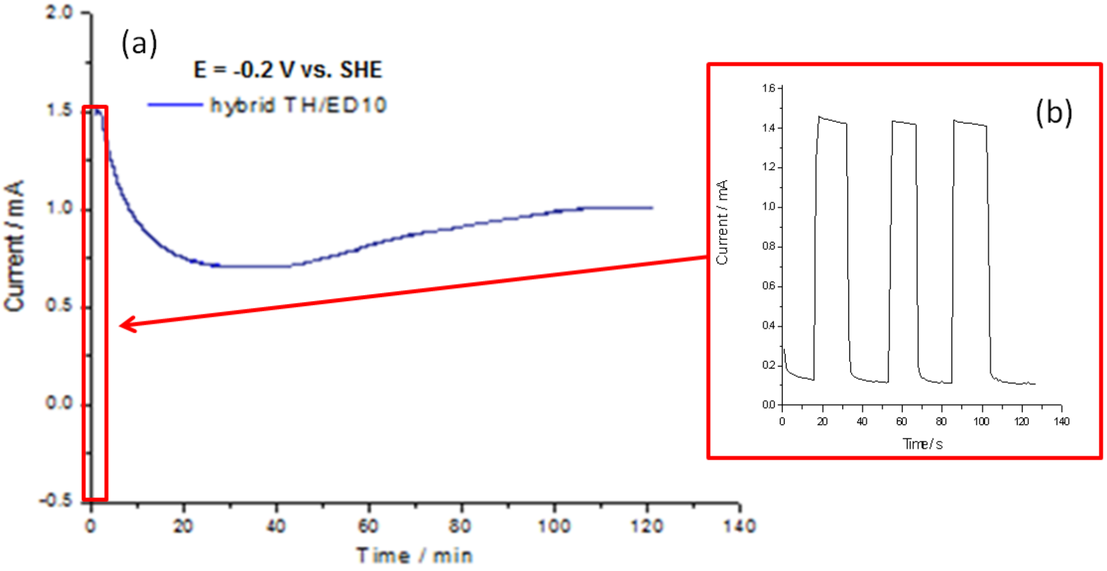

Fig. S2. Current/time under continuous (a) and chopped solar irradiation (b) at -0.2 V vs. SHE in a sealed two-compartment photoelectrochemical cell containing a Cu_2O/CuO nanorod photocathode. Light Intensity from solar simulator = 70 mW cm^{-2}. Photoelectrode area ~ 2 cm^2. Electrolyte = 0.1 M Na_2SO_4 saturated with CO_2 and maintained at room temperature.

To prove that the photoactive material is still on the electrode after photoelectrolysis, XRD data before and after 2 h photoelectrolysis in CO_2 saturated solution are compared in Fig. **S3**. Observe that before photoelectrolysis (Fig. S3a) three distinctly distinguishable crystalline phases are clearly discernible: CuO, Cu_2O and Cu. The first originated from the thermal treatment, the second resulted from both TH and ED, while the third phase is that of the underlying Cu substrate. The CuO and Cu_2O XRD peaks after photoelectrolysis (Fig. S3b) corroborate that these two phases are still intact on the electrode.

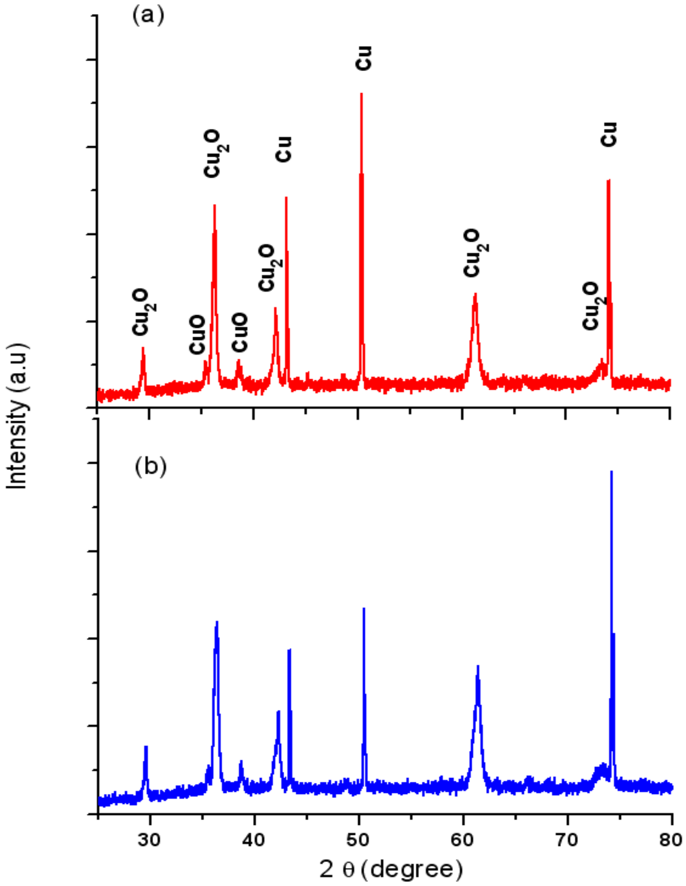

Fig. S3. XRD spectra of a TH/ED30 Cu/Cu_2O hybrid nanorod film before (a) and after being subjected to photoelectrolysis at -0.2 V vs. SHE in a CO_2-saturated aqueous solution. The CuO/Cu_2O nanorod film was prepared on a copper foil whose XRD peaks are clearly discernible before and after photoelectrolysis.