Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Simultaneous glucose sensing and bio-hydrogen evolution from direct photoelectrocatalytic glucose oxidation on robust Cu_2O-TiO_2 electrodes

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S1. Experimental Procedure:

Preparation of CuO thin films

The CuO thin films were prepared by spray-pyrolysis technique. The pre-cleaned fluorinated tin oxide (FTO) coated glass substrates were placed on the over head heater maintained at 300 ºC. The aqueous solution of 0.25 M $CuCl_2.2H_2O$ (Sigma Aldrich) in 50 ml of deionized water was used as precursor. The solution was pumped into the air stream in the spray nozzle at a rate of 10 ml/min by means of a syringe pump, for a preset time of 10 min. An air stream of 25 L/min, measured at 1 bar, was utilized to atomize the solution. The constant pressure at 0.4 kg/cm^2 was provided during the spray process. The aerosol after contact the substrate evaporates and undergoes decomposition reaction on the substrate surface to produce CuO thin film. The flow rate of the sol in the spray nozil is 10 ml/min.

Preparation of thin TiO_2 layer onto CuO_x films

The as-prepared CuO electrode by spray-pyrolysis technique is transformed into RF sputtering chamber. The titanium (Ti) target (99.995% purity, ULVAC Technologies Inc. Japan) is used for making TiO_2 films. The Ti target was sputtered at 3 x 10^{-3} Pa back pressure for 10 minutes with flow of O_2: Ar = 1:1 (v/v) under 200 W RF power. The operating temperature is about 300 ºC. The resultant TiO_2 thin layer coated CuO electrodes was used without further treatment. The thickness of the electrodes CuO and Cu_2O/TiO_2 were estimated using surface profilometer and found to be ~1.24 micron and ~1.25 micron thickness, respectively. These values were verified with AFM section analysis between uncoated substrate and coating area.

Characterization techniques:

The crystalline phases of the CuO films were studied by X-ray diffraction (XRD) using a diffractometer (Rigagu Denki Japan) with CuKα radiation. The morphology of CuO electrode was characterized using the field emission scanning electron microscope (JSM-7500F JEOL)). The surface topography of CuO film analyzed using atomic force microscopy (AFM), (Nanoscope, Dimension-3100 Multimode), and the AFM tip was a silicon-SPM sensor (tapping mode), thickness 4 µm, length 125 µm and width 30 µm. The chemical environment of CuO and CuO-TiO2 films were analyzed by x-ray photoelectron spectroscopy (XPS) using an angular resolved electron analyzer with a monochromated Al Kα source (Theta Probe, Thermo Fisher Scientific).

Electrochemical and photoelectrochemical measurements

The electrochemical analysis was done using three electrode systems. The as-prepared CuO films (electrode area 1 cm^2) and TiO2 thin film coated CuO electrodes were used as the working electrode, Ag/AgCl as the reference and Pt foil as the counter electrode. 0.1 M of NaOH (Sigma Aldrich) was used as the electrolyte for all EC measurements. Cyclic voltammograms were recorded using the advanced potentiostat (PGSTAT-30 from Autolab) with the scanning voltage in the range of –0.8 V to 0.8 V. The photocurrent measurements were recorded using a UV-Visible solar simulator with a 300 W xenon arc-lamp (Hayashi- LA 251-Xe). The light intensity was calibrated using a silicon photodiode (100 $mWcm^{-2}$).

For glucose oxidation measurements, the following chemicals were used as received from Sigma Aldrich Chemicals; D-(+)-Glucose (99.5%), L-Ascorbic acid (99 %), Uric acid and dopamine hydrochloride. The PEC chamber was sealed to prevent gas leakage. Gas samples were collected at applied potential of 0.7V vs (Ag/AgCl) for 1 hr duration from the head space using an air-tight gas syringe through the manual sampling port in the top of the chamber (flexible cork made of Teflon) and further subjected to gas chromatographic analysis to evaluate the constituents of the gaseous products. The average values of hydrogen evolution quantity from three different photoelectrocatalytic processes has been summarized and reported. After three cycles of test the photocurrent value of the electrode was reduced less than 3% compare with first cycle. This comment has been included in the revised manuscript.

S2. Surface wettablity analysis

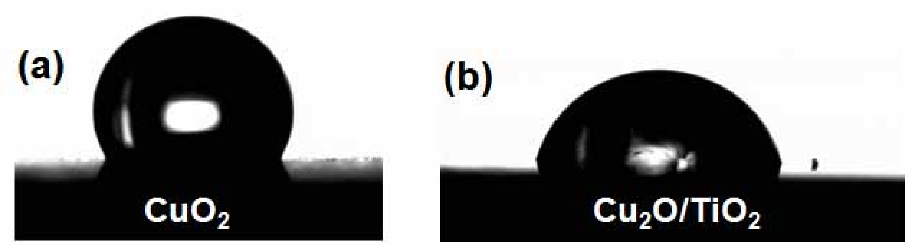
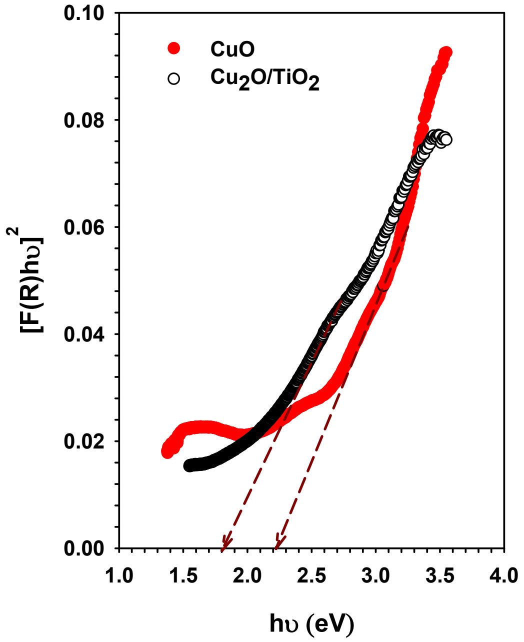


Figure S2. Contact angle measurements on (a) CuO$_2$ and (b) Cu$_2$O/TiO$_2$ electrodes.

The water contact angle measurements were carried out using contact angle meter (KYOWA, model DM-301). The water volume of 1 µl is taken for all measurements. The water contact angles on CuO$_2$ and Cu$_2$O/TiO$_2$ electrodes were measured at three different position and an average values were considered. We found that water contact angle of CuO$_2$ electrode 132.8º reduced to 76.7º under TiO$_2$ coating (Fig. S1). This inferred that the hydrophobic nature of CuO$_2$ surface is modified as hydrophilic by TiO$_2$ coating.

S3. Optical property



The optical absorption and diffused reflectance spectra of the electrodes were recorded in the range of 350–900 nm using a V670 JASCO UV-Vis spectrophotometer. The optical density (OD) of the pristine and TiO_2 post-coated CuO electrodes has been estimated as $F(R)^{1/2} = [(1-R^2)/2R]^{1/2}$ in Kubelka-Munk units (Fig.2b). The optical density of CuO is markedly enhanced at UV as well as visible light wavelength region owing to phase transformation of CuO to Cu_2O by TiO_2 post-coating, respectively. Interestingly, the band gap energy is shifted from ~2.2 eV to ~1.82 eV confirm the crystalline phase transformation from Cu^+ to Cu^{2+} as is observed from XPS spectra (Fig. 2 in the main manuscript).

S4. Glucose selectivity analysis

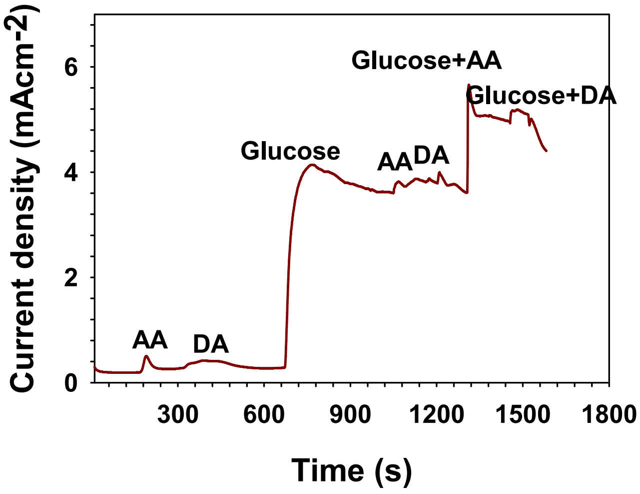


Figure S4. The amperometric responses of the interfering species on the Cu_2O/TiO_2 electrode with 1 mM glucose, and 0.05 mM of ascorbic acid (AA) and dopamine (DA).