

## Supplementary Information

### In-situ synthesis of photocatalytic CuAl<sub>2</sub>O<sub>4</sub>-Cu hybrid nanorod arrays

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**Preparation of anodic aluminum oxide (AAO) template:** Aluminum foil (99.99%), 0.3-mm thick, is annealed in air at 500 °C for 4 h in furnace. Al pieces, 3 cm × 3 cm in size, were degreased by acetone in ultrasonic for 5 min, rinsed in distilled water and electropolished in a mixture of ethanol and perchloric acid until visually mirror-like surface at 20 V. Prior to anodization, the back and edges of electrodes were sealed with wax to produce an electrode with only one face exposed. Anodization were carried out in a 2.5 M phosphoric acid at 20 °C for 20 min under a voltage of 15 V against a graphite counter electrode. This procedure produces a porous AAO template of pore fraction about 40% by volume. The pore thickness was about 700 nm with mean diameter approximates to 50 nm.

**Synthesis of CuAl<sub>2</sub>O<sub>4</sub>-Cu nanorods:** Using a two-electrode system consisting of a graphite plate as the counter electrode and AAO as the working electrode, electrochemical deposition of CuAl<sub>2</sub>O<sub>4</sub>-Cu is performed in a pH 3 ~ 4 electrolyte of CuSO<sub>4</sub> (35 g L<sup>-1</sup>), MgSO<sub>4</sub> (20 g L<sup>-1</sup>) and boric acid at 13 V under continuous ac mode for 60 seconds, frequency was kept at 60 Hz for all samples. MgSO<sub>4</sub> was added to improve the stability of anodic oxide film by preventing breakdown of barrier layers. The temperature of electrolyte was kept at 20(±1)°C by water cooling system. The electrolyte was refreshed after every five samples to compensate Cu<sup>2+</sup> depletion.

**Preparation of nanorod TiO<sub>2</sub> film:** The film characterized by TiO<sub>2</sub> nanorods was fabricated as the reported process by Jin-Ming Wu et al. (Environ. Sci. Technol., 2007, **41**, 1723-1728).

**Preparation of CuAl<sub>2</sub>O<sub>4</sub> film and powders:** The CuAl<sub>2</sub>O<sub>4</sub> film was fabricated by a sol-gel and dip coating method. 0.2 M Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and 0.4 M Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were mixed and dissolved into deionized water under magnetic stirring. Citric acid solution (citric acid: metal ions molar ratio was 2:1) was slowly poured into above liquid. After stirred for 30 min at about 333 K, ammonia was added to adjust the pH to 2.0–3.0. The solution was kept at 333 K until deep blue gel was formed. Pure Ti plate was used as substrates. The surfaces were previously cleaned with oxalic acid in 273 K water bath and dried, then coated by the dip-coating method at a withdrawal rate of 1 cm/min for 5 times. For formation of CuAl<sub>2</sub>O<sub>4</sub> powders, the rest of the

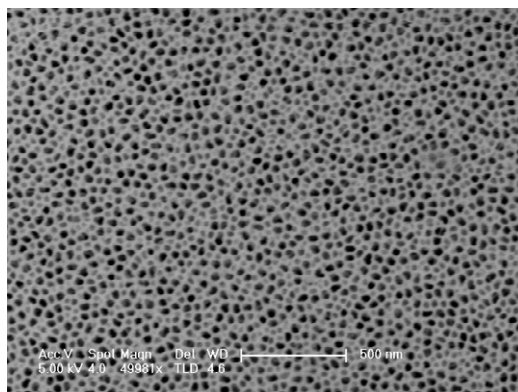
sol-gel was heated up to 423K until the gel was dried. Both samples were calcinated at 1073 K for 2 h in air to obtain the spinel  $\text{CuAl}_2\text{O}_4$  crystalline .

**Characterization:** Phase identification was performed by means of X-ray diffraction (XRD) using a D8 ADVANCE X-Ray Polycrystalline Diffractometer (Bruker, Germany) with Cu  $K\alpha$  radiation ( $\lambda = 0.154056 \text{ \AA}$ ). Scanning electron microscopy (SEM) images were acquired on a SIRION 200 scanning electron microscope (FEI, USA) equipped with an INCA energy dispersive Spectrometer (EDS) system (Oxford Instrument, UK). TEM image of the hybrid nanorods are obtained by a High-resolution Transmission Electron Microscopy (JEM 100-CX, JEOL). To prepare samples, nanorods were liberated in 0.6 M phosphoric acid at 60 °C. The liberated rods were then rinsed multiple times in distilled water and were finally dispersed in methanol. At each stage, rods were sonicated in an ultrasonic bath for 1 min, and solvent exchange was carried out by centrifuging, extracting the supernatant, and adding fresh solvent. To prepare the TEM sample, one drop of the final suspension in methanol was placed on a Mo TEM grid and the methanol was allowed to evaporate. HR-TEM studies were performed on a JEM-100CX model operating with a 300 keV electron beam. Diffuse reflection spectroscopy (DRS) measurements in the UV-Vis region were carried out on a CARY 500 spectrophotometer (USA) equipped with an integrating sphere, using  $\text{BaSO}_4$  as reference.

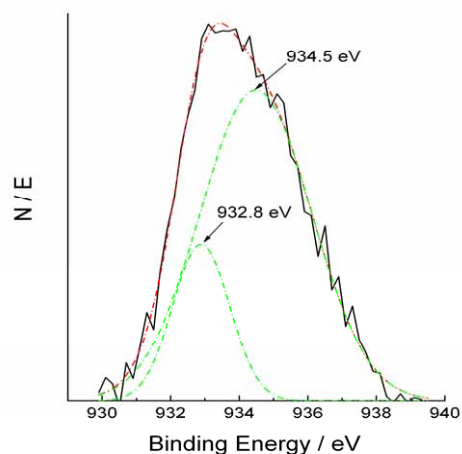
**Photocatalysis experiment:** The  $\text{CuAl}_2\text{O}_4$ -Cu nanorods filled AAO was firstly immersed in NaOH (0.5 M) at 30 °C for 3 minutes to remove the upper alumina nanostructure, and was soaked in deionized water. For all samples, film with an area of  $2 \text{ cm}^2$  was placed in a single quartz photoreactor. 15 mL of methyl orange (MO) ( $5 \text{ mg L}^{-1}$ ) was added and stirred continuously. A 350 W UV-Vis Xenon lamp ( $\lambda = 0.4 - 1 \text{ \mu m}$ ) with maximal light intensity of  $90 \text{ mW/cm}^2$  was used as light source after filtration of UV and IR light. Before light illumination, the photocatalysis system was kept in a dark environment until equilibrium concentration of MO in the solution was reached. Concentration of MO was measured by spectrometer at the absorption peak of MO ( $\lambda = 465 \text{ nm}$ ) over time. The degradation percentage (DP) was calculated with  $DP = (C_0 - C_t) / C_0 \times 100\%$ , where  $C_0$  and  $C_t$  are the absorbance of original solution

and solution photodegraded after  $t$  time. For cycling run of the  $\text{CuAl}_2\text{O}_4$ -Cu hybrid photocatalysis system, the film was soaked in dionized water for 30 minutes after each photocatalysis run, then dried and placed in the reactor. The following procedures is as the first photocatalysis run.

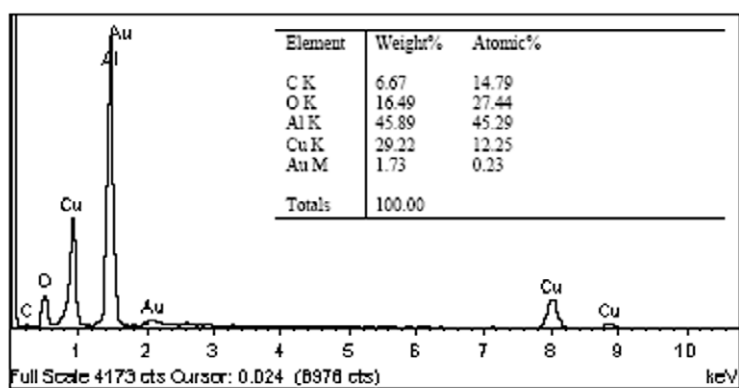
HPLC analysis of intermediates was performed on a SHIMADZU LC-2010A HT liquid chromatograph equipped with a ODS C18 column (250 mm  $\times$  4.6 mm). The eluent was methanol-water (65 / 35, v/v) at a flow rate of 0.8 ml  $\text{min}^{-1}$ . A 10  $\mu\text{l}$  of sample was injected by using autosampling device. The eluent from the chromatographic column successively enter the UV-Vis detector operated at 275 nm.



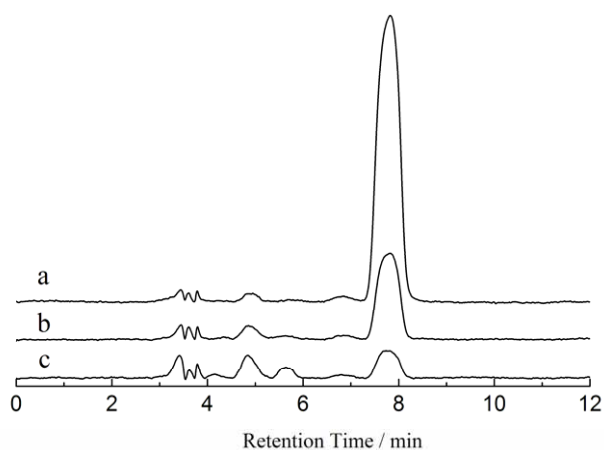
**Figure S1.** SEM image of the prepared AAO template with a mean pore diameter of 50 nm.



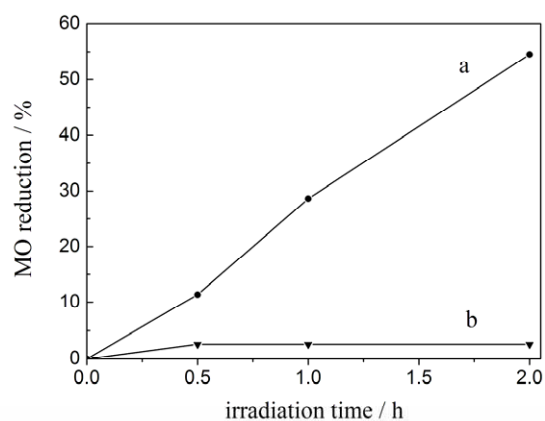
**Figure S2.** XPS spectrum of Cu 2p<sub>3</sub> for as-synthesis CuAl<sub>2</sub>O<sub>4</sub>-Cu nanorods



**Figure S3.** EDX analysis of the as-synthesized CuAl<sub>2</sub>O<sub>4</sub>-Cu hybrid nanorods



**Figure S4.** HPLC profiles of samples: (a) original MO solution, (b) after adsorption equilibrium was reached, (c) after 2 h of photocatalysis run under visible irradiation



**Figure S5.** degradation of MO in the system of  $\text{CuAl}_2\text{O}_4$  powders versus time:  
(a) under visible light irradiation, 1000 W Xenon lamp with a  $\lambda \geq 400$  nm filter, (b) in dark ambient