Supplementary Information

Dual Photocatalysis for CO$_2$ Reduction along with the Oxidative Coupling of Benzylamines Promoted by Cu/Cu$_2$O@g-C$_3$N$_4$ under Visible Irradiation

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1.0 Experimental section

1.1 Materials

Dicyandiamide (Alfa Aesar), thiourea (Alfa Aesar), copper nitrate hemi pentahydrate (Sigma Aldrich), sodium hydroxide (Alfa Aesar), D-glucose (Alfa Aesar), benzylamine (Sigma Aldrich), 4-methyl benzylamine (Sigma Aldrich), 4-methoxy benzylamine (Sigma Aldrich), 4-chlorobenzylamine (Sigma Aldrich), 4-fluoro benzylamine (Sigma Aldrich), 4-nitro benzylamines were procured and used as received. Absolute ethanol (Alfa Aesar) and double distilled water were used to synthesize the nanomaterials.

1.2 Synthesis of photocatalysts

1.2.1 Synthesis of g-C_3N_4

g-C_3N_4 was synthesized by following the literature procedure.[1] In brief, dicyandiamide and thiourea were ground in a 4:1 ratio for 15 min. The fine powder was placed in a muffle furnace and annealed in air at 550 °C for 4 h. The pale-yellow powder of g-C_3N_4 was collected after cooling the mixture at room temperature.

1.2.2 Synthesis of Cu/Cu_2O@g-C_3N_4 heterojunction

In the typical synthesis, a certain amount of $Cu(NO_3)_2.5/2H_2O$ (0.5, 1.0, 1.5, 2.0, & 2.5 mmol bases of Cu_2O) was dissolved in 50 mL of water in a round bottom flask with continuous stirring of 30 min. NaOH of 3 mol/L concentration (2, 4, 6, 8, & 10 mL) was added to this solution for precipitation and stirred again for 30 min. D-glucose (0.2, 0.4, 0.6, 0.8, & 1.0 g) was added to the precipitates followed by addition of 1000 mg g-C_3N_4 powder with continuous stirring. This solution was heated at 60 °C for 30 min to reduce Cu^{2+} to Cu^+, which was confirmed by the appearance of brown-red slurry in the solution. Thus, obtained precipitates were separated by vacuum filtration and washed with water and ethanol several times. The wet precipitates of the composite were placed in an oven at 60 °C overnight to remove the moisture content.

1.3 Characterization techniques

The particle size and ultrafine surface morphology of catalyst were determined by High-resolution transmittance electron microscopy on FEI-TecnaiG^2 Twin TEM operating at an acceleration voltage of 200 kV. A very diluted sample prepared by dispersion of the minimum quantity of catalyst in isopropyl alcohol was deposited on the holey carbon support TEM grid. FT-IR spectra of the material obtained by Perkin-Elmer spectrum RX-1 IR spectrophotometer having a potassium bromide window. X-ray diffractogram determined the crystallinity of material and plane, recorded at Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu K$_\alpha$ radiation (λ= 0.15418 nm). UV-vis spectra of material were recorded on Perkin-Elmer lambda-19 UV-VIS-NIR spectrophotometer using a 10 mm quartz cell, using $BaSO_4$ as a reference. N_2 sorption was carried out for the catalyst to determine the bulk properties, such as BET surface area (S_{BET}), BJH porosity, pore volume and mean pore diameter at 77 K by using VP; Micromeritics ASAP 2010. Thermal analyzer TA-SDT Q-600 analyzed the thermal stability of the material. The TGA-DTA patternswere recorded in the temperature range of 40-800°C under N_2 flow with a 10°C/min heating rate. The photoelectrochemical (PEC) analysis was obtained with the help of Versastat-4 potentiostat (Princeton applied research) by a three-electrode system. The catalytic material on ITO plates was used as the working electrode, Pt wire as an auxiliary electrode, and Ag/AgCl as a reference electrode. The binders used are ethylcellulose, acetic acid, and terpineol. Ethylcellulose (50 mg) and photocatalyst (25 mg) are used in 2:1 ration, while acetic acid (10 μL) and terpineol (50 μL) are in 1:5. These two mixtures were mixed in a mortar-pestle for 20 min for complete mixing. Potassium bicarbonate is used as an electrolyte in all the CV and LSV experiments. Bruker Advance-II 500 MHz used to collect ^1H &^{13}C NMR of various formanilide with operating frequency at 500 MHz.

1.4 Photocatalytic experiment of amine coupling and CO_2 reduction

The photocatalytic experiments were performed in a 60 mL cylindrical vessel placed in a cardboard box fitted with a 20 W white LED light. 1 mmol of benzylamine was dissolved in 20 mL of acetonitrile solvent in the reaction system. N_2 bubbled into the reaction mixture for 10 min to evacuate the dissolved air, followed by CO_2 for 20 min to saturate the reaction mixture under continuous stirring at room temperature and atmospheric pressure conditions. After that, 50 mg of catalyst was added to the reaction mixture, followed by bubbling of CO_2 for 10 min. The resulting reaction vessel was placed under the light irradiation using (20 W LED, Model No. HP-FL-20W-F-Hope LED Opto-Electric Co., Ltd., $\lambda > 400$ nm) to begin the oxidation of benzylamine and reduction of CO_2. The progress of the reaction was monitored by TLC of the collected samples every 2 h interval. In addition, the collected reaction mixture was filtered through a syringe filter (Millipore, 0.45 μ, 33 mm), and 0.2 μL of the separated reaction mixture was injected into GC-FID (Perkin-Elmer, stibwaxCP Sil 24CB LOW BLEED/MS 30 mm, 0.25 μm, CP 5817,flow rate of 0.5 mL min^{-1}, injector temperature 330 °C, and FID detector temperature 350 °C) to calculate the conversion of benzylamine and yield of *N*-benzylidene benzylamine and methanol. After 16 h, a minimum of the reaction mixture was separated and injected into GC-FID. The products of benzylamine oxidation were confirmed by GC-MS and ^{1}H and ^{13}C NMR studies with the help of authentic samples.

References

1.   A. Kumar, P. K. Prajapati, M. Aathira, A. Bansiwal, R. Boukherroub and S. L. Jain, *J. Colloid Interface Sci.*, 2019, **543**, 201-213.