Assembling graphitic-carbon-nitride with cobalt-oxide-phosphate to construct an efficient hybrid photocatalyst for water splitting application

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Supporting Information
All chemical compounds were purchased from Sigma Aldrich and used as received without any further purification. Mesoporous graphitic carbon nitride (mpg-CN\textsubscript{x}) was synthesized following the method described by Wang et al.\cite{1} Typically 3 g cyanamide and 12.15 g Ludox HS40 solution was employed as precursor (silica/cyanamide mass ratio was 1.5). This procedure resulted in production of highly porous mpg-CN\textsubscript{x} with typical surface area of 373 m\textsuperscript{2}\cdot g\textsuperscript{-1}.

To prepare mpg-CN\textsubscript{x} based electrodes for electrochemical investigation, 3 mg of mpg-CN\textsubscript{x} power was suspended in stock solution containing 0.8 mL deionised H\textsubscript{2}O, 0.2 mL ethanol and 10 µL Nafion\textsuperscript{®} 117 solution (wt. 5%) and subjected to ultra-sonication for 15 min. 1 µL of this suspension was drop-casted on a cleaned carbon glassy electrode surface (S = 0.071 cm\textsuperscript{2}) and air-dried.

Transmission electron microscopic (TEM) analysis was conducted using a TEM JEOL 2100F, operating at 200kV. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed in coupling with TEM analysis. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a VG ESCALAB 220i-XL spectrometer. The XPS spectra were examined by curve fitting using a combination of Gaussian and Lorentzian line shapes. Electrochemical analysis was done using a CHI, model 852, potentiostate. Three electrodes configuration was employed with mpg-CN\textsubscript{x} working electrode, Pt wire counter electrode and Ag/AgCl/3M KCl reference electrode.

1. **Photo-assisted assembling mpg-CN\textsubscript{x}/CoPi/Ag photocatalyst**

A suspension of 100mg mpg-CN\textsubscript{x} nanoparticles in 30mL pH 7 phosphate buffer solution (KPi 0.1M) containing 0.5mM Co(NO\textsubscript{3})\textsubscript{2} and 15mM AgNO\textsubscript{3} was loaded into a gas-tight schlenk tube (Sigma Aldrich). The schlenk tube was covered by aluminium paper to avoid light-decomposition of AgNO\textsubscript{3} salt before commencing the reaction. Research grade nitrogen
gas was then bubbled through the solution to remove dissolved oxygen. The solution was then illuminated with visible light provided by a 150W Xe lamp, equipped with a 400 nm cut-off filter. The light intensity arrived to the schlenk tube was adjusted to be 100 mW.cm$^{-2}$. During the reaction, the solution was vigorously stirred and the gas produced in the head cap of the schlenk was manually sampled and analysed by a gas chromatography.

Once photodeposition was over, the mpg-CN$_x$/CoPi/Ag nanoparticles were centrifuged from the solution, carefully washed with DI water, ethanol and then dried in vacuum oven before used for subsequent characterisation.

2. Preparation of mpg-CN$_x$/CoPi

2.1 Loading Co$^0$ metallic nanoparticles

Loading of Co$^0$ nanoparticles was done following the method previously described [2]. Briefly, 100 mg mpg-CN$_x$ was suspended in 100 mL DI water together with pre-determined amount of Co(NO$_3$)$_2$.6H$_2$O. The suspension was vigorously stirred and carefully saturated with research grade nitrogen gas to remove any dissolved O$_2$. 50 equivalents of freshly prepared 0.156 M NaBH$_4$ solution was slowly added into the suspension. The resultant mpg-CN$_x$/Co$^0$ nanoparticles were centrifuged, carefully washed with DI water and ethanol, and dried in a vacuum oven.

2.2 Photoassisted oxidation of Co$^0$ nanoparticles to CoPi

100 mg of mpg-CN$_x$/Co$^0$ nanoparticles were suspended in 30 mL phosphate buffer at pH 7 containing 100 mM Na$_2$S$_2$O$_8$ which has been saturated with nitrogen gas. The suspension was then illuminated with visible light for 2-4 hours to achieve the CoO/CoPi equilibrium. The equilibrium state was assumed to be when oxygen evolution rate of the system was constant. After this the resultant mpg-CN$_x$/CoO/CoPi (denoted as mpg-CN$_x$/CoPi for simplicity)
nanoparticles were centrifuged, carefully washed with DI water, ethanol and dried in vacuum oven before being used for experiments and characterisation studies.

3. Assay photocatalytic activities of mpg-CN₅/CoPi

30 mg of mpg-CN₅/CoPi nanoparticles were suspended in 20 mL phosphate buffer solution (0.1M, pH 7) to which 100 mM Na₂S₂O₈ was added and dissolved. Prior to experiments, the suspension was saturated with nitrogen gas, in an air-tight closed Schlenk tube. When all traces of O₂ had been removed, the catalytic suspension was illuminated by visible light (100 mW.cm⁻², λ > 400nm). During illumination, the suspension was stirred and the gas produced in the head cap of the Schlenk tube was manually sampled and analysed by gas chromatography.

Similar setup was employed to in-situ convert mpg-CN₅/CoPi into mpg-CN₅/H₂-CoCat and to assay photocatalytic hydrogen generation properties. The reaction suspension was made of 30 mg mpg-CN₅/CoPi suspended in 20 mL phosphate buffer solution (0.1M, pH 7) containing 10% (v/v) methanol. When photocatalytic experiment was over, resultant mpg-CN₅/H₂-CoCat powder was collected and intensively washed with water and ethanol. It was then deposited onto carbon glassy electrode to fabricate mpg-CN₅/H₂-CoCat electrode (see this above) for electrochemical investigation.
Supplementary Results

**Figure S1:** Cyclic voltammograms recorded in a pH 7 phosphate solution (KPi 0.1M) on a mpg-CNₓ/CoPi/Ag or an untreated mpg-CNₓ electrode. Potential scan rate was 50mV.s⁻¹.

**Figure S2:** Schematic presentation for the two-steps preparation of mpg-CNₓ/CoPi hybrid photocatalyst
**Figure S3**: Co$2p$ XPS analysis on mpg-CN$/CoPi$.

**Figure S4**: Cyclic voltammogram recorded in a pH 7 phosphate buffer solution on a mpg-CN$/CoPi$ electrode. Potential scan rate was 50mV.s$^{-1}$. 

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Figure S5: I-V curves recorded on an untreated mpg-CN$_x$ electrode (red curve) and a mpg-CN$_x$/H$_2$-CoCat electrode (black curve) in a pH 7 phosphate buffer solution (0.1M). Potential scan rate was 2mV.s$^{-1}$.

References:
