**Supporting Information**

**Enhancing the pure water splitting using carbon-iron oxide-carbon nitride (Fe2O3-C/CN) heterostructure**

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**1. Synthesis of Fe2O3 catalysts**

Fe2O3 was produced hydrothermally without the presence of a carbon layer. More precisely, a total of 2 grams of FeCl3.6H2O and 15 milliliters of water were introduced into an autoclave with a total capacity of 100 milliliters. The suspension was agitated until a clear solution was obtained. Afterward, a 15 mL solution of 0.2-M NaOH was gradually added to the previously produced FeCl3 solution. The mixture was continually stirred for a few minutes, resulting in the formation of a yellow suspension. The suspension was then sealed in the autoclave and heated at a temperature of 90°C for 5 hours. The final results were obtained by subjecting the sample to centrifugation and repeatedly washing it with ethanol and water in alternating steps. The obtained yellow precipitate was subjected to overnight drying at a temperature of 80 °C, resulting in the formation of β-FeOOH. The carbon-free phase of α-Fe2O3 was synthesized by annealing the β-FeOOH at a high temperature of 300 oC for a few hours.

**2. Synthesis of Fe2O3/CN heterostructure**

Usually, a two-step method was utilized. More precisely, a powder of CN weighing 100 mg was thoroughly crushed with 5 wt% of Fe2O3 powder using a mortar and ethanol. The solid obtained was thereafter moved to a spacious vessel that was lined with aluminum foil. The substance was exposed to the open air and heated at a temperature of 300 °C for 2 hours. Eventually, the composite was rinsed with water and the composite was dried in a vacuum furnace, resulting in the formation of Fe2O3/CN.

**3. Photocatalytic reaction for pure water splitting**

The photocatalytic pure water splitting reaction was carried out in a specially designed side-irradiated Pyrex cell with a total capacity of 100 mL. A quantity of 10 mg of the prepared photocatalyst was dispersed into 80 mL of deionized (DI) water, which underwent sonication for approximately 15 minutes to ensure uniform dispersion. Subsequently, the resulting suspension underwent a 25-minute purge with argon (Ar) gas to remove any gases absorbed within the suspension. For illumination, a visible light source incorporating a cut-off filter (≥ 420 nm) derived from a 300 W Xenon (Xe) lamp was employed to drive the photocatalytic reaction. To mitigate scattering losses, the Pyrex cell was encased in aluminium (Al) foil. The evolution of gases (H2/O2) from the reaction was measured by gas chromatography. The stability test was conducted similarly, except in every cycle the photocatalyst suspension was removed from the light source and again degassed for about 25 to 30 minutes to remove the dissolved oxygen.

**4. Photoelectrochemical measurements.**

The transient photocurrent response, Mott-Schottky (MS) analysis, polarization curve determination, and electrochemical impedance spectroscopy (EIS) measurements of photocatalytic materials were conducted using a CHI760D electrochemical workstation manufactured by Chenhua Instruments Co., Shanghai. Throughout the (photo)electrochemical assessments, a 0.5 M sodium sulfate (Na2SO4) aqueous solution served as the electrolyte within a standard three-electrode configuration consisting of a working electrode (the sample), a reference electrode (Ag/AgCl in saturated KCl), and a counter electrode (Platinum wire). The transient photocurrent response was recorded under illumination from a 300 W Xenon (Xe) lamp coupled with an AM 1.5 simulated solar light filter. For the fabrication of the working electrodes, 1 mg of the prepared sample and 10 μL of 5% Nafion (DuPont) were uniformly dispersed in a 1.0 mL mixture of water and ethanol (volume ratio = 1:1), followed by sonication for 1 hour to ensure a homogeneous suspension. Subsequently, 10 μL of the suspension was delicately deposited onto the surface of a glassy carbon electrode (GCE, diameter = 3 mm) and allowed to air-dry naturally for approximately 8 hours at ambient temperature to form the working electrode.

**5. Calculation of solar to hydrogen conversion efficiency (STH)**

In this study, we determine the solar-to-hydrogen conversion efficiency (STH) of the composite photocatalyst (Fe2O3-C/CN) using the following equation:

|  |  |
| --- | --- |
|  | (S1) |

The variables r*H*2, ΔG, Psun, and *S* correspond to the rate of hydrogen evolution, Gibb's free energy, the intensity of solar light (1.5 AMG), and the area of the Pyrex cell, respectively.

**6. Instrumentation.**

X-ray diffraction (XRD) patterns were acquired using a PANalytical X-pert MPD Pro diffractometer employing Ni-filtered Cu Kα irradiation (wavelength = 1.5406 Å). Fourier transform infrared (FTIR) spectra were obtained utilizing a Bruker Vertex 70 FTIR spectrophotometer via the KBr pellet method. Morphological and microstructural characterization was conducted employing an FEI Tecnai G2 F30 S-Twin transmission electron microscope (TEM) equipped with an OXFORD MAX-80 energy-dispersive X-ray detector (EDX). Scanning electron microscopy (SEM) analysis was performed using a JEOL JSM-7800F instrument at an accelerating voltage of 3 kV to examine sample size and morphology. X-ray photoelectron spectroscopy (XPS) measurements were carried out employing a Kratos spectrometer (AXIS Ultra DLD) utilizing standard and monochromatic Al Kα excitation (hν = 1486.6 eV), with the adventitious carbon peak (C1s) at 284.8 eV serving for calibration. Nitrogen adsorption-desorption isotherms were obtained at 77 K using an Accelerated Surface Area and Porosimetry Analyzer (ASAP 2020, Micromeritics). Steady-state photoluminescence (PL) properties were evaluated at room temperature using a time-resolved PTIQM-4 fluorescence spectrophotometer at an excitation wavelength of 337 nm. UV-vis absorption spectra were recorded using a Hitachi U-4100 UV-vis-near-IR spectrophotometer to analyze the optical properties of the prepared samples. The carbon content in Fe2O3-C and Fe2O3-C/CN was determined by elemental analysis, namely the vario MACRO cube Elemental analyzer. EPR spectra were recorded at room temperature under visible light irradiation. The samples were irradiated with a 300 W Xe lamp equipped with a UV cut-off filter (λ > 420 nm) to simulate visible light conditions. The detection of superoxide radicals (O₂⁻•) and hydroxyl radicals (•OH) was performed using DMPO (5,5-dimethyl-1-pyrroline N-oxide) as a spin-trapping agent.



**Fig. S1.** a) XRD patterns of simulated MOF, MIL-235, and synthesized MIF-MIL-235.

SEM

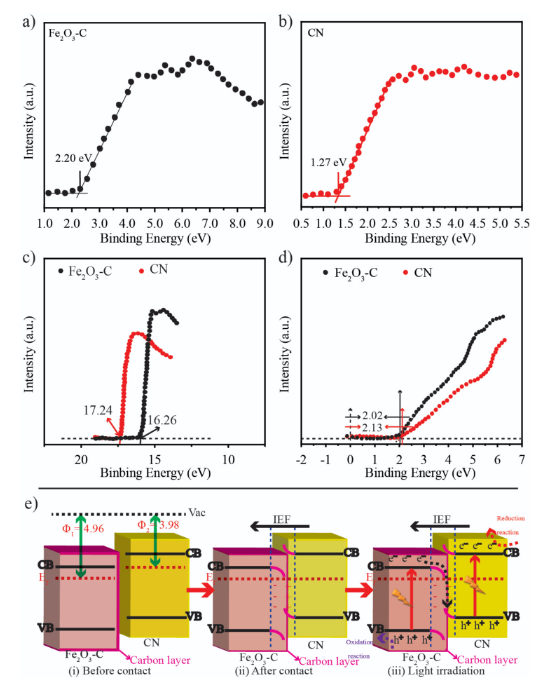
**Fig. S2.** SEM images of a) CN, b) 3% Fe2O3-C/CN, c) 5% Fe2O3-C/CN and d) Fe2O3-C photocatalysts.



**Fig. S3.** STEM and Mapping analysis of b) C, c) O, and d) Fe, respectively.

Table S1

|  |  |  |
| --- | --- | --- |
| **Sample** | **Surface area (m2/g)** | **Peak pore radius (nm)** |
| **1. CN** | **22.96** | **1.72** |
| **2. Fe2O3-C** | **22.37** | **1.90** |
| **3. 5%Fe2O3-C/CN** | **44.19** | **7.40** |



**Fig. S4.** a-b) XPS-VB curves of Fe2O3-C, and CN photocatalysts, c, d) UPS analysis of Fe2O3-C, and CN, respectively, while e) represents the Z-scheme mechanism between Fe2O3-C and CN.

Band Position calculation (based on the **UPS** outcomes**)** is as follows:

…………………………………………. (S2)

………………………………………………(S3)

……………. (S4)

…………... (S5)

where Ecut-off is the secondary electron cut-off edge of the samples.

…………………………………………………… (S6)

From the following eq

…………………………………………. (S7)



**Fig. S5.** a-b) Mott-Schottky plots for Fe2O3-C and CN photocatalysts measured at different frequencies in a Na2SO4 electrolyte.



**Fig. S6.** a) Hydrogen and oxygen evolution rate at 5 wt. % of Fe2O3/CN photocatalyst during pure water splitting under visible light illumination, b) the corresponding mass activity.



**Fig. S7.** a, c) DMPO spin-trapping EPR spectra of the composite in the dark, b, d) EPR signals of DMPO-•OH and DMPO •O2−, respectively.



**Fig. S8.** a-c) XRD FTIR and TEM analysis of optimized composite before and after the photocatalytic reaction.

**Fig. S9.** a-c) Hydrogen and oxygen evolution rate of all synthesized composite photocatalysts (i.e. Fe2O3-C/CN) for pure water splitting under visible light illumination.

Table S2

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **Sacrificial agents/Cocatalyst** | **Light source** | **H2/O2 evolution rate (μmol g-1h-1)** | **References** |
| 5% Fe2O3-C/CN | - | 300 W Xe lamp (λ> 420 nm) | 499/199 | Present work |
| Co3(PO4)2/g-C3N4 | - | Solar light | 375.6/177.4 | Ref. 1 |
| g-C3N4/Fe2P/red-P | - | 300 W Xe lamp (λ> 420 nm) | 429/- | Ref. 2 |
| γ-Fe2O3/C3N4 | - | 300 W Xe lamp (λ> 420 nm) | 23.3/12 | Ref. 3 |
| 2D/2D Fe2O3/g-C3N4 | Pt/TEOA- | Visible (Xe 350 W) 𝜆 > 420 nm | 398/- | Ref. 4 |
| g-C3N4@Fe2O3/Co-Pi | TEOA | 300 W Xe lamp (λ> 420 nm) | 450 | Ref. 5 |
| 0D/2D α-Fe2O3/g-C3N4 | TEOA/Pt | 300 W Xe lamp (λ> 420 nm) | 182/- | Ref. 6 |
| α -Fe2O3/g-C3N4 | TEOA/Pt | 300 W Xe lamp (λ> 420 nm) | 77.6/- | Ref. 7 |

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