Supporting Information

A critical study of the generality of the two step two electron pathway for water splitting by application of a C$_3$N$_4$/MnO$_2$ photocatalyst

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1 Experimental Section

Preparation of C$_3$N$_4$. Carbon nitride (C$_3$N$_4$) was synthesized following previous reports. [3] 10 g of urea powder was put into an alumina crucible with a cover and then heated to 550 °C with a heating rate of 5 °C/min in a muffle furnace and maintained at this temperature for 3 h. The light yellow powder obtained after cooling was C$_3$N$_4$.

Preparation of C$_3$N$_4$/MnO$_2$ Photocatalysts. KMnO$_4$ (0.63 mmol, 0.1 g) and 0.6 g C$_3$N$_4$ (obtained by heating urea at 550°C for 3 hours) were added into 500 mL ultrapure water, and stirred for 12 h. After centrifuging for 3 times to remove the excess KMnO$_4$, 10 mL oleinic acid was added into the turbid liquid. Stirring it again for 24 h. The resulting product was centrifuged and washed with acetone, ethyl and water many times till all the oleinic acid was removed. The product is then dried at 60°C in an oven till it becomes a powder. The weight of the final product is 0.6066 g.
**Photocatalyst Characterization.** The crystalline structure of the resultant products was characterized by X-ray powder diffraction (XRD) by using a X'Pert-ProMPD (Holland) D/max-γAX-ray diffractometer with Cu Kα radiation (λ=0.154178 nm). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images and EELS spectra were obtained with a FEI/Philips Tecnai 12 BioTWIN transmission electron microscope and a CM200 FEG transmission electron microscope, respectively. The TEM samples were prepared by dropping the solution onto a copper grid with carbon support film and dried in air, respectively. Room temperature UV–Vis absorption was recorded on a Lambda 750 (Perking Elmer) spectrophotometer in the wavelength range of 300–800 nm. The Fourier transform infrared (FTIR) spectrum was recorded on a FTIR spectrometer (Spectrum One, Perkin Elmer) using a standard KBr pellet technique. X-ray photoelectron spectroscopy (XPS) was obtained by using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatised Mg Kα X-ray (hν = 1283.3 eV). Ultraviolet photoelectron spectroscopy (UPS) measurements are performed with an unfiltered HeI (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV.

**Photocatalysis activity tests.** The photocatalytic reactions of the composite photocatalysts were carried out in an outer irradiation-type photoreactor (Pyrex glass) connected to a closed gas-circulation system. Approximately 0.100 g photocatalysts were dispersed by a magnetic stirrer in 100 mL ultrapure water. The suspension was thoroughly degassed to remove air and irradiated using a 300 W Xe-lamp (PLS-SXE 300, Beijing Trusttech Co. Ltd, China). A cutoff filter (Kenko L-42) was employed for the visible light (λ>420 nm) irradiation and band-pass filters were used for measurements of the hydrogen generation quantum efficiency. The power density measured for the λ>420 nm irradiation was 18.4 mW/cm² and for the band-pass filters one order of magnitude lower. The photocatalytic gas evolution rate was analyzed using an online SP-6890 gas chromatograph (TCD detector, 5 Å molecular sieve columns and N₂ carrier). The first four 24 h experiments were done with Ar as a carrier gas and no N₂ was detected ruling out air leaking or corrosion of the C₃N₄ catalyst releasing N₂.
**Electrochemical measurements.** The hydrogen peroxide generation tests were performed using a rotating ring-disk electrode (RRDE) at a scan rate of 10 mV/s. A platinum wire was the auxiliary electrode and a saturated calomel electrode (SCE, saturated KCl) was the reference electrode. The working electrodes were prepared by spreading 10 μL 0.1 g/L catalysts dispersed in ethanol on a Pt disk (3.0 mm in diameter)-Pt ring RRDE system (Jiangsu Jiangfen Electroanalytical Instrument Co. Ltd.). The I-V curves of the electrodes were tested in a conventional three-electrode electrochemical cell with a platinum wire as the auxiliary electrode and a SCE as the reference electrode. The working electrode is 10 μL 0.1 g/L C₃N₄/MnO₂ dripped on glassy carbon electrode in 100 mL ultrapure water solution at a scan rate of 20 mV/s. The current signal was recorded with a CHI 660C workstation (CH Instruments, Chenhua, Shanghai, China). All electrochemical experiments were carried out at room temperature.

**2 Quantum efficiency calculation.**

The apparent quantum efficiency (QE) for H₂ evolution is measured using a 420 nm band-pass filter. The wavelength is from 400 nm to 440 nm. The average intensity of irradiation is determined to be 2.84 mW·cm⁻² by ILT 950 spectroradiometer (International Light Technologies) and the irradiation area is controlled as 4.52 cm². The number of incident photons (N) is 2.34×10²¹ calculated by Equation S1. The produced H₂ molecules quantity is 74.4 μmol in 24 h (Fig. S18). The amount of H₂ gas produced in the subsequent 24 h is used to calculate quantum efficiency according to the Equation S2 shown below.

\[
N = \frac{E \lambda}{hc} = \frac{2.84 \times 10^{-3} \times 4.52 \times 24 \times 3600 \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 2.34 \times 10^{21} \quad \text{Equation S1}
\]

So,
3 Electron-transfer number (n) calculation.

The electron-transfer number (n) is calculated as follows:

\[
\text{n} = \frac{4I_{\text{disk}}}{I_{\text{disk}} + I_{\text{ring}}} / N \quad \text{Equation S3}
\]

Here N is the RRDE collection efficiency, determined to be 0.24. Reversible system
\([\text{Fe(CN)}_6]^{4-}/[\text{Fe(CN)}_6]^{3-}\) is used for RRDE electrode collection efficiency
measurement. In details, The RRDE electrode is dipped into 0.01 mol/L \(K_3[\text{Fe(CN)}_6]\)
in 0.1 mol/L KCl solution and rotated under different rotation rates (\(\omega = 100, 400, 900,
1600, 2500 \text{ rpm}\)). Disk potential \(E_D\) is scanned from 0.35 V to -0.55 V vs. SCE at scan
rate 10 mV/s, ring potential \(E_R\) is fixed to 0.497 V vs. SCE (the reduced product
\([\text{Fe(CN)}_6]^{4-}\) can be oxidized at this potential), and the current-potential
voltammograms are recorded during the electrode rotation. Fig. S15 shows the RRDE
measurement. The ratio of \(I_{\text{ring}}/I_{\text{disk}}\) is almost constant under various \(\omega\). The average of
collection efficiency N is 0.24.

4 The whole photocatalysis water splitting process on \(\text{MnO}_2/C_3\text{N}_4\).

The whole photocatalysis water splitting process on \(\text{MnO}_2/C_3\text{N}_4\) includes four
reactions as follow:

\[
\text{C}_3\text{N}_4 \xrightarrow{\text{hv}} \text{e}^- + \text{p}^+ \quad \text{Equation S4}
\]

\[
2\text{H}_2\text{O} + 2\text{p}^+ \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ \quad \text{Equation S5}
\]

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad \text{Equation S6}
\]

\[
2\text{H}_2\text{O}_2 \xrightarrow{\text{MnO}_2} 2\text{H}_2\text{O} + \text{O}_2 \quad \text{Equation S7}
\]
Table S1 Photocatalytic activities of different loading ratios of C₃N₄/MnO₂ for water splitting under visible light irradiation (λ>420 nm) for 24 h. The incident light intensity is fixed at 18.4 mW cm⁻². The QE for H₂ evolution is measured using 300 W Xe lamp with a 420 nm band-pass filter. The catalyst concentration is 1 g/L.

<table>
<thead>
<tr>
<th>MnO₂: C₃N₄ (mass ratio, g/g)</th>
<th>H₂ (O₂) evolution amount* (µmol)</th>
<th>QE* at 420 nm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.011</td>
<td>15.6 (7.7)</td>
<td>0.24</td>
</tr>
<tr>
<td>0.054</td>
<td>81.4 (40.8)</td>
<td>2.17</td>
</tr>
<tr>
<td>0.136</td>
<td>132.8 (66.5)</td>
<td>3.82</td>
</tr>
<tr>
<td>0.528</td>
<td>116.7 (58.4)</td>
<td>3.32</td>
</tr>
<tr>
<td>0.973</td>
<td>112.1 (56.0)</td>
<td>2.96</td>
</tr>
<tr>
<td>2.049</td>
<td>75.2 (37.4)</td>
<td>1.83</td>
</tr>
<tr>
<td>5.155</td>
<td>27.2 (13.5)</td>
<td>0.65</td>
</tr>
</tbody>
</table>

* These data are the average results based on three parallel experiments.
**Fig. S1** The mapping patterns for the C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{2}, with a MnO\textsubscript{2} concentration of 0.136 g\textsubscript{MnO2}/g\textsubscript{C3N4}.

**Fig. S2** The FT-IR spectra of C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{2} (the MnO\textsubscript{2} concentration of 0.136 g\textsubscript{MnO2}/g\textsubscript{C3N4}). The spectra present several major bands between 1200 cm\textsuperscript{-1} and 1650 cm\textsuperscript{-1} region, which correspond to the characteristic stretching modes of CN heterocycles. In addition, the breathing mode of triazine units at 809 cm\textsuperscript{-1} is observed.
**Fig. S3** Electron energy loss spectroscopy (EELS) spectra of C$_3$N$_4$/MnO$_2$ (the MnO$_2$ concentration of 5.155 g$_{\text{MnO}_2}$/g$_{\text{C}_3\text{N}_4}$).

**Fig. S4** XPS spectra of C$_3$N$_4$ prepared by pyrolysis of urea at 550 °C. (a) XPS survey spectrum. (b) C1s spectrum. (c) N1s spectrum. (d) O1s spectrum.
**Fig. S5** The XPS survey spectra of the C$_3$N$_4$/MnO$_2$ (the MnO$_2$ concentration of 0.136 g$_{MnO2}$/g$_{C3N4}$).

**Fig. S6** The XPS spectra of the C$_3$N$_4$/MnO$_2$. (a) C 1s spectra. (b) N 1s spectra. (c) O 1s spectra. (d) Mn 2P spectra.
Fig. S7 A typical gas chromatograph trace of evolved hydrogen and oxygen. The gas chromatograph signal peaks at 0.6033 and 1.0167 min are attributed to H\textsubscript{2} and O\textsubscript{2} evolution respectively with a true intensity ratio of 2:1.

Fig. S8 FT-IR spectra of C\textsubscript{3}N\textsubscript{4}/MnO\textsubscript{2} (g\textsubscript{MnO2}/g\textsubscript{C3N4}=0.1) powders after 100 cycles of 24 h water splitting.
**Fig. S9** XPS spectra of C$_3$N$_4$/MnO$_2$ ($g_{\text{MnO}_2}/g_{\text{C}_3\text{N}_4} = 0.1$) before (a-c) and after (d-f) 100 cycles of 24 h water splitting. (a, d) C1s spectrum. (b, e) N1s spectrum. (c, f) Mn 2p spectrum. (d,g) O1s spectrum.

**Fig. S10** Tauc plots ($\alpha(h\nu)^2$ vs. $h\nu$ curves) of C$_3$N$_4$ (black trace) and C$_3$N$_4$/MnO$_2$ (red trace). The MnO$_2$ loading was 0.136 $g_{\text{MnO}_2}/g_{\text{C}_3\text{N}_4}$. 
**Fig. S11** The UPS spectra of the C$_3$N$_4$/MnO$_2$. The MnO$_2$ loading was 0.136 g$_{MnO2}$/g$_{C3N4}$.

**Fig. S12** The H$_2$O$_2$ amount in the reaction solution after visible light irradiation (300 W Xe lamp with a cutoff filter to acquire $\lambda > 420$ nm, the intensity is 18.4 mW cm$^{-2}$) for 12 h. The reaction system is 100 mg catalyst dispersed in 100 mL water. (black trace) C$_3$N$_4$ as catalyst, (red trace) C$_3$N$_4$/MnO$_2$ as catalyst (the MnO$_2$ loading was 0.136 g$_{MnO2}$/g$_{C3N4}$).
**Fig. S13** The calibration curve and the fitting equation of the H$_2$O$_2$ concentration versus 446 nm absorbance, which are determined by measuring known concentrations of H$_2$O$_2$.

![Calibration Curve](image1)

**Fig. S14** The current-time curve of (a) C$_3$N$_4$ and (b) C$_3$N$_4$/MnO$_2$ (g$_{MnO2}$/g$_{C3N4}$=0.136). The photocurrents were measured at a bias which nulls the current under dark conditions in ultrapure water solution under 300 W Xe lamp with a $\lambda>$420 nm cut-off filter. The light intensity is 18.4 mW cm$^{-2}$. The C$_3$N$_4$ curve (black trace in a) shows a rapid decrease of the photocurrent indicating poisoning of the catalyst surface by H$_2$O$_2$. The C$_3$N$_4$/MnO$_2$ curve (black trace in b) shows current oscillations between 33.5-38 nA due to cycles of H$_2$O$_2$ generation, adsorption, decomposition by MnO$_2$ and diffusion.
Fig. S15 I-V curves of bare RRDE in 0.1 M KCl containing 0.01 M K$_3$Fe(CN)$_6$ under rotation rates: 100, 400, 900, 1600 and 2500 rpm (from inner to outer).

Fig. S16 O$_2$ evolution rate from hydrogen peroxide decomposition catalyzed by C$_3$N$_4$/MnO$_2$ (0.136 g$_{\text{MnO}_2}$/g$_{\text{C}_3\text{N}_4}$) or MnO$_2$ as a function of reaction time under either dark or light irradiation. Reaction conditions: 100 mg of C$_3$N$_4$/MnO$_2$ or 0.01 g MnO$_2$ and 100 ml 0.5 M N$_2$-saturation H$_2$O$_2$ aqueous solution; light source: 300 W Xe-lamp fitted with a cutoff filter (L-42) to remove light of $\lambda < 420$ nm.
**Fig. S17** N\textsubscript{2} adsorption and desorption isotherms at 78 K. BET surface area was measured by Tristar II 3020.

**Fig. S18** (a) The H\textsubscript{2}O\textsubscript{2} amount in the reaction solution after irradiation for 12 h. The reaction system is 100 mg catalyst dispersed in 100 ml water. (black trace) C\textsubscript{3}N\textsubscript{4}-44.6 as catalyst, (red trace) C\textsubscript{3}N\textsubscript{4}-95.4 as catalyst, (blue trace) C\textsubscript{3}N\textsubscript{4}-168.3 as catalyst, (red trace) C\textsubscript{3}N\textsubscript{4}-193.2 as catalyst. (b) H\textsubscript{2}O\textsubscript{2} evolution for C\textsubscript{3}N\textsubscript{4} with different internal surface area in the composite catalyst from the average value of BET test.
Fig. S19 The H₂ evolution curve used for determination of QE (420±20 nm). A 300 W Xe lamp with a bandpass filter were used.