Supporting Information

A critical study of the generality of the two step two electron pathway for water splitting by application of a C_3N_4/MnO_2 photocatalyst

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1 Experimental Section

Preparation of C_3N_4. Carbon nitride (C_3N_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_3N_4.

Preparation of C_3N_4/MnO_2 Photocatalysts. $KMnO_4$ (0.63 mmol, 0.1 g) and 0.6 g C_3N_4 (obtained by heating urea at 550℃ 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℃ 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 (Holand) 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/cm^2 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 A° molecular sieve columns and N_2 carrier). The first four 24 h experiments were done with Ar as a carrier gas and no N_2 was detected ruling out air leaking or corrosion of the C_3N_4 catalyst releasing N_2.

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 C_3N_4/MnO_2 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 H_2 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 $mW \cdot cm^{-2}$ by ILT 950 spectroradiometer (International Light Technologies) and the irradiation area is controlled as 4.52 cm^2. The number of incident photons (N) is 2.34×10^{21} calculated by Equation S1. The produced H_2 molecules quantity is 74.4 μmol in 24 h (Fig. S18). The amount of H_2 gas produced in the subsequent 24 h is used to calculate quantum efficiency according to the Equation S2 shown below.

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

So,

$$QE = \frac{2 \times \text{the number of evolved } H_2 \text{ molecules}}{\text{the number of incident photons}} \times 100\%$$

$$= \frac{2 \times 74.4 \times 10^{-6} \times 6.02 \times 10^{23}}{2.34 \times 10^{21}} \times 100\% = 3.82\% \qquad \text{Equation S2}$$

3 Electron-transfer number (n) calculation.

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

$$n = \frac{4I_{disk}}{I_{disk} + I_{ring} / N} \qquad \text{Equation S3}$$

Here N is the RRDE collection efficiency, determined to be 0.24. Reversible system $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ is used for RRDE electrode collection efficiency measurement. In details, The RRDE electrode is dipped into 0.01 mol/L $K_3[Fe(CN)_6]$ in 0.1 mol/L KCl solution and rotated under different rotation rates (ω = 100, 400, 900, 1600, 2500 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 $[Fe(CN)_6]^{4-}$ 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_{ring}/I_{disk} is almost constant under various ω. The average of collection efficiency N is 0.24.

4 The whole photocatalysis water splitting process on MnO_2/C_3N_4.

The whole photocatalysis water splitting process on MnO_2/C_3N_4 includes four reactions as follow:

$$C_3N_4 \xrightarrow{hv} e^- + p^+ \qquad \text{Equation S4}$$

$$2H_20 + 2p^+ \longrightarrow H_2O_2 + 2H^+ \qquad \text{Equation S5}$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad \text{Equation S6}$$

$$2H_2O_2 \xrightarrow{MnO_2} 2H_20 + O_2 \qquad \text{Equation S7}$$

Table S1 Photocatalytic activities of different loading ratios of C_3N_4/MnO_2 for water splitting under visible light irradiation (λ>420 nm) for 24 h. The incient light intensity is fixed at 18.4 mW cm^{-2}. The QE for H_2 evolution is measured using 300 W Xe lamp with a 420 nm band-pass filter. The catalyst concentration is 1 g/L.

MnO_2: C_3N_4 (mass ratio, g/g)	**H_2 (O_2) evolution amount* (μmol)**	**QE* at 420 nm (%)**
0.011	15.6 (7.7)	0.24
0.054	81.4 (40.8)	2.17
0.136	132.8 (66.5)	3.82
0.528	116.7 (58.4)	3.32
0.973	112.1 (56.0)	2.96
2.049	75.2 (37.4)	1.83
5.155	27.2 (13.5)	0.65

* These data are the average results based on three parallel experiments.

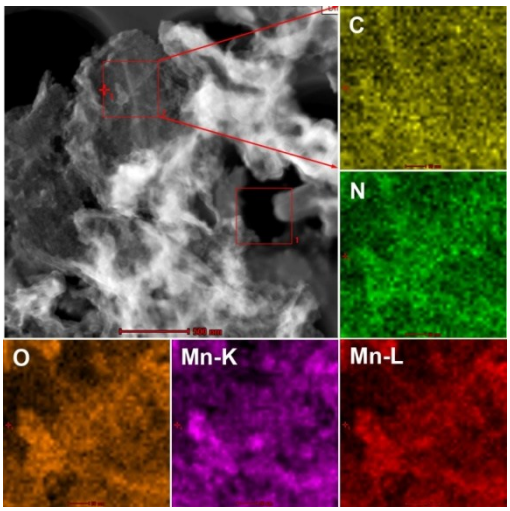

Fig. S1 The mapping patterns for the C_3N_4/MnO_2, with a MnO_2 concentration of 0.136 g_{MnO2}/g_{C3N4}.

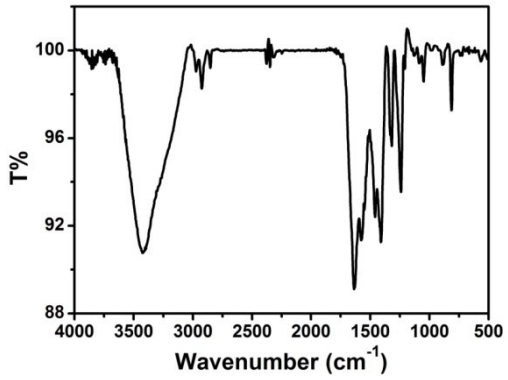

Fig. S2 The FT-IR spectra of C_3N_4/MnO_2 (the MnO_2 concentration of 0.136 g_{MnO2}/g_{C3N4}). The spectra present several major bands between 1200 cm^{-1} and 1650 cm^{-1} region, which correspondi to the characteristic stretching modes of CN heterocycles. In addition, the breathing mode of triazine units at 809 cm^{-1} is observed.

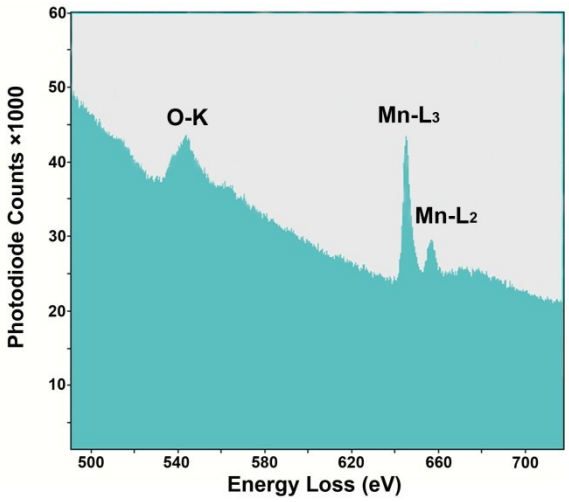

Fig. S3 Electron energy loss spectroscopy (EELS) spectra of C_3N_4/MnO_2 (the MnO_2 concentration of 5.155 g_{MnO2}/g_{C3N4}).

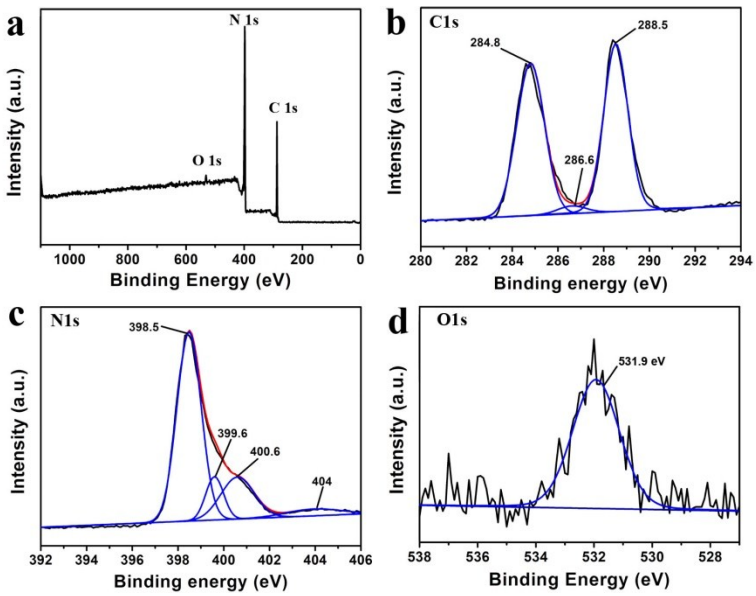

Fig. S4 XPS spectra of C_3N_4 prepared by pyrolysis of urea at 550 ℃. (a) XPS survey spectrum. (b) C1s spectrum. (c) N1s spectrum. (d) O1s spectrum.

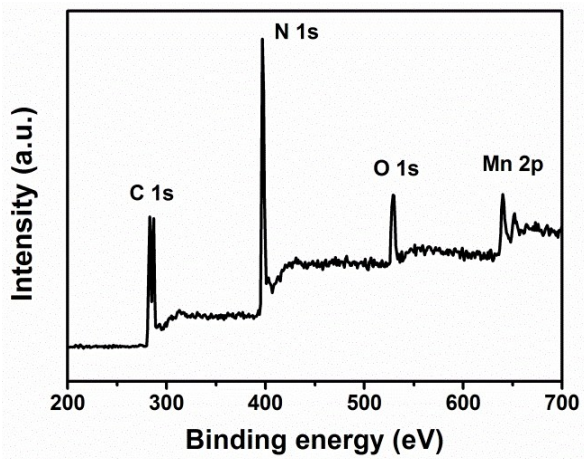

Fig. S5 The XPS survey spectra of the C_3N_4/MnO_2 (the MnO_2 concentration of 0.136 g_{MnO2}/g_{C3N4}).

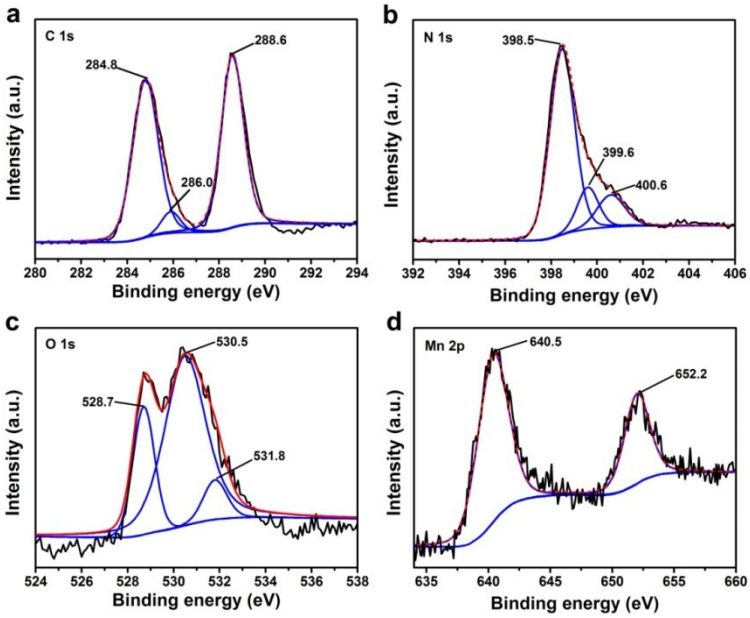

Fig. S6 The XPS spectra of the C_3N_4/MnO_2. (a) C 1s spectra. (b) N 1s spectra. (c) O 1s spectra. (d) Mn 2P spectra.

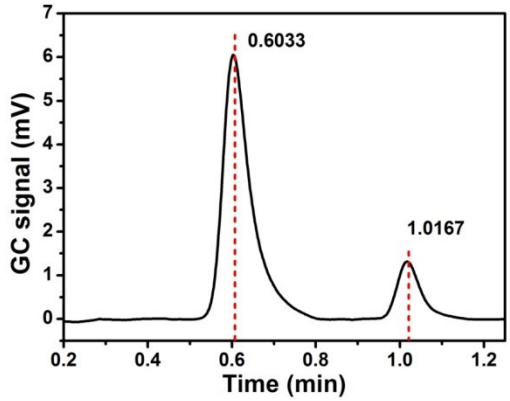

Fig. S7 A typical gas chromatograph trace of evolved hydrogen and oxygen. The gas chromatograph signal peaks at 0.6033 and 1.0167 min are attributed to H_2 and O_2 evolution respectively with a true intensity ratio of 2:1.

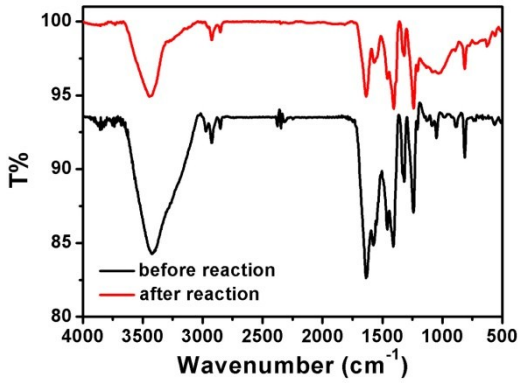

Fig. S8 FT-IR spectra of C_3N_4/MnO_2 (g_{MnO2}/g_{C3N4}=0.1) powders after 100 cycles of 24 h water splitting.

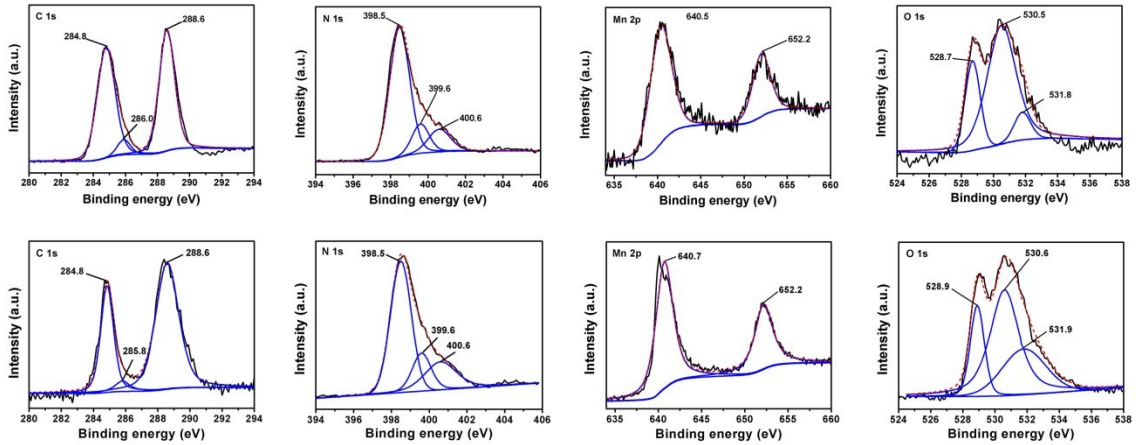

Fig. S9 XPS spectra of C_3N_4/MnO_2 (g_{MnO2}/g_{C3N4}=0.1) before (a-c) and after (d-f) 100 cycles of 24 h water splitting. (a, d) C1s spectrum. (b, e) N1s spectrum. (c, f) Mn 2p spectrum. (d,g) O1s spectrum.

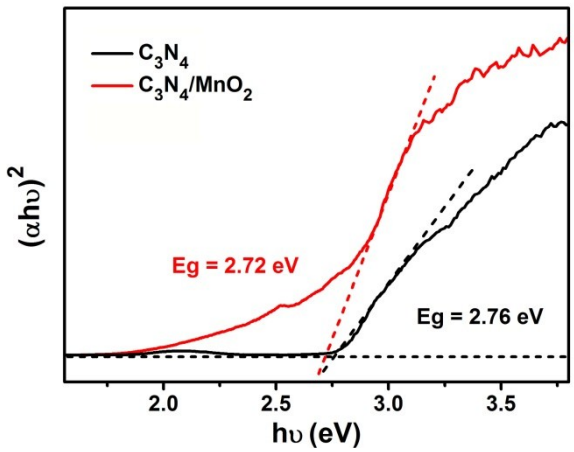

Fig. S10 Tauc plots ($(\alpha h\upsilon)^2$ vs. $h\upsilon$ curves) of C_3N_4 (black trace) and C_3N_4/MnO_2 (red trace). The MnO_2 loading was 0.136 g_{MnO2}/g_{C3N4}.

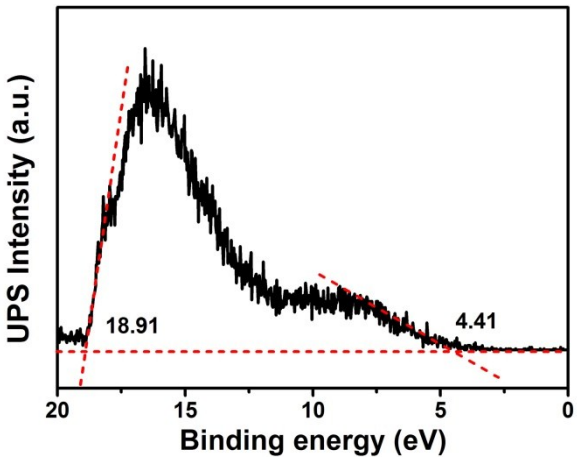

Fig. S11 The UPS spectra of the C_3N_4/MnO_2. The MnO_2 loading was 0.136 g_{MnO2}/g_{C3N4}.

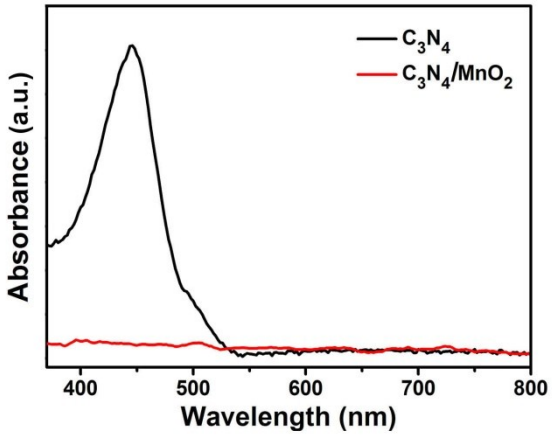

Fig. S12 The H_2O_2 amount in the reaction solution after visible light irradiation (300 W Xe lamp with a cutoff filter to acquire $\lambda > 420$ nm, the intensity is 18.4 mW cm^{-2}) for 12 h. The reaction system is 100 mg catalyst dispersed in 100 mL water. (black trace) C_3N_4 as catalyst, (red trace) C_3N_4/MnO_2 as catalyst (the MnO_2 loading was 0.136 g_{MnO2}/g_{C3N4}.).

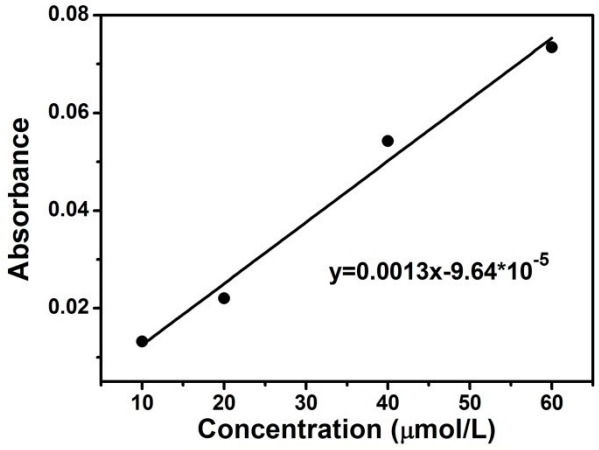

Fig. S13 The calibration curve and the fitting equation of the H_2O_2 concentration versus 446 nm absorbance, which are determined by measuring known concentrations of H_2O_2.

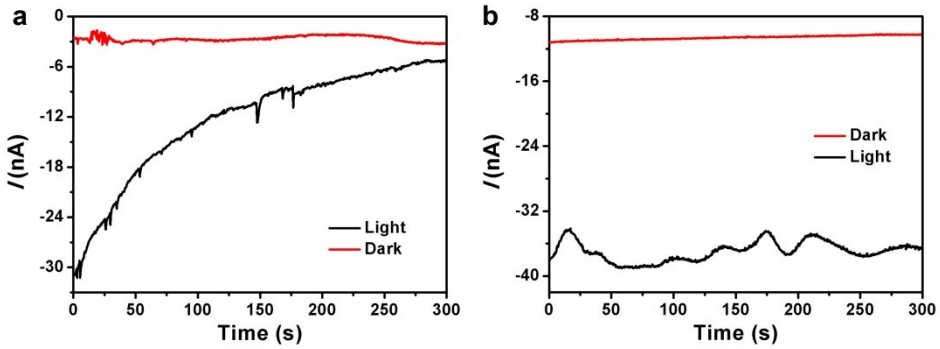

Fig. S14 The current-time curve of (a) C_3N_4 and (b) C_3N_4/MnO_2 (g_{MnO2}/g_{C3N4}=0.136). The photocurrents were measured at a bias which nulls the current under dark conditions in ultrapure water solution under 300 W Xe lamp with a λ>420 nm cut-off filter. The light intensity is 18.4 mW cm^{-2}. The C_3N_4 curve (black trace in a) shows a rapid decrease of the photocurrent indicating poisoning of the catalyst surface by H_2O_2. The C_3N_4/MnO_2 curve (black trace in b) shows current oscillations between 33.5-38 nA due to cycles of H_2O_2 generation, adsorption, decomposition by MnO_2 and diffusion.

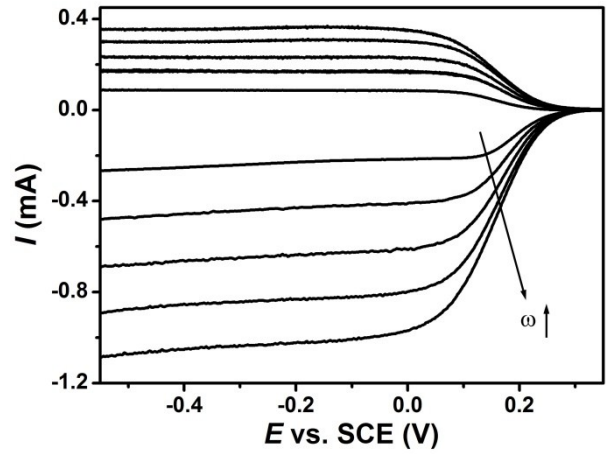

Fig. S15 I-V curves of bare RRDE in 0.1 M KCl containing 0.01 M $K_3Fe(CN)_6$ under rotation rates: 100, 400, 900, 1600 and 2500 rpm (from inner to outer).

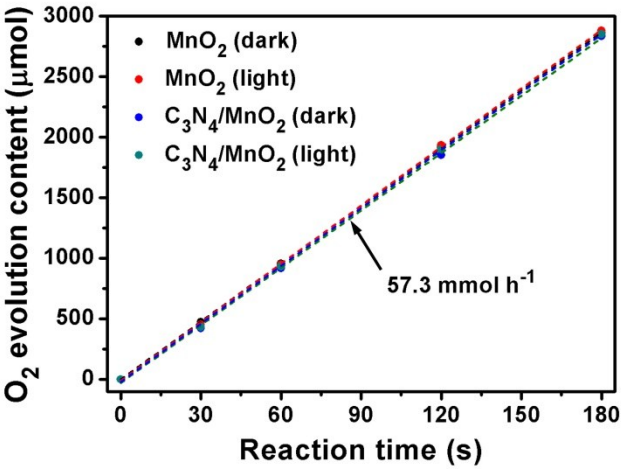

Fig. S16 O_2 evolution rate from hydrogen peroxide decomposition catalyzed by C_3N_4/MnO_2 (0.136 g_{MnO2}/g_{C3N4}) or MnO_2 as a function of reaction time under either dark or light irradiation. Reaction conditions: 100 mg of C_3N_4/MnO_2 or 0.01 g MnO_2 and 100 ml 0.5 M N_2-saturation H_2O_2 aqueous solution; light source: 300 W Xe-lamp fitted with a cutoff filter (L-42) to remove light of $\lambda < 420$ nm.

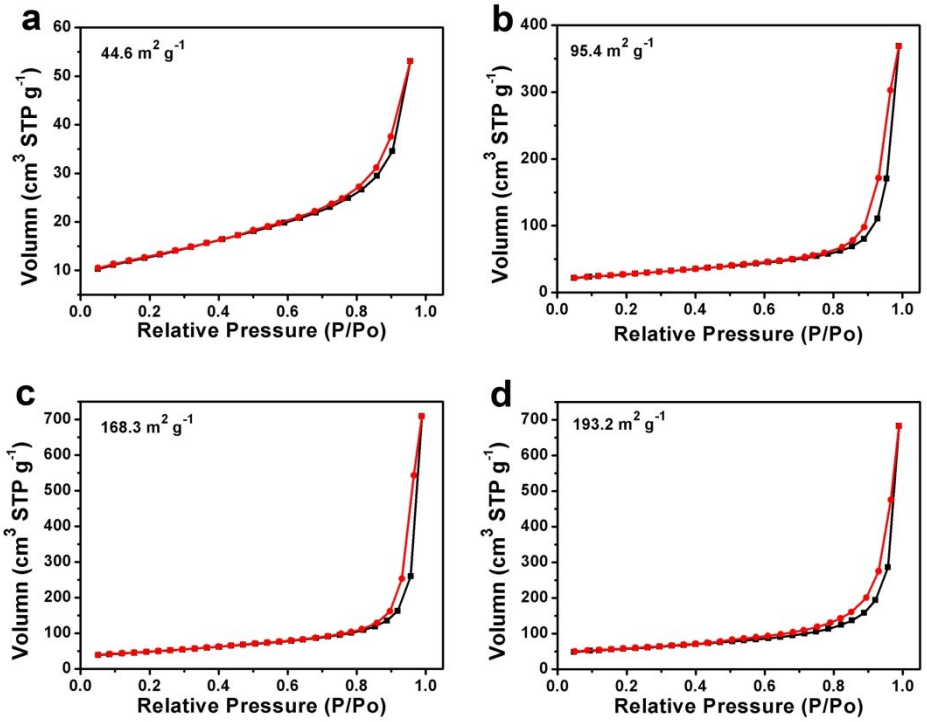

Fig. S17 N_2 adsorption and desorption isotherms at 78 K. BET surface area was measured by Tristar II 3020.

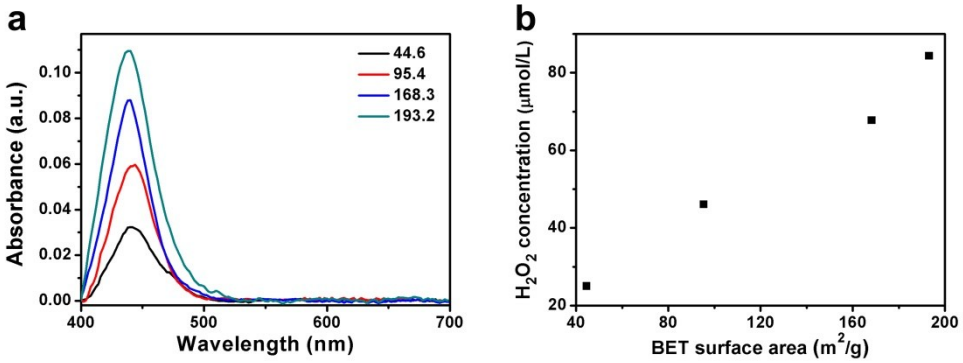

Fig. S18 (a) The H_2O_2 amount in the reaction solution after irradiation for 12 h. The reaction system is 100 mg catalyst dispersed in 100 ml water. (black trace) C_3N_4-44.6 as catalyst, (red trace) C_3N_4-95.4 as catalyst, (blue trace) C_3N_4-168.3 as catalyst, (red trace) C_3N_4-193.2 as catalyst. (b) H_2O_2 evolution for C_3N_4 with different internal surface area in the composite catalyst from the average value of BET test.

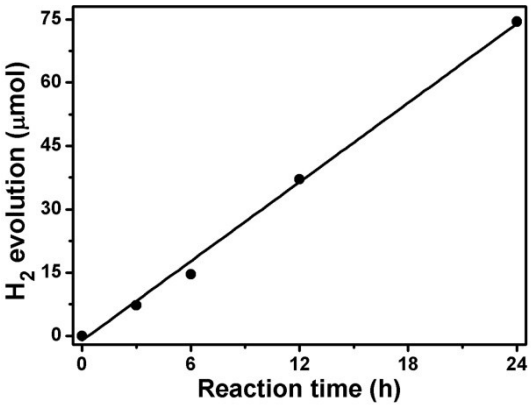

Fig. S19 The H_2 evolution curve used for determination of QE (420±20 nm). A 300 W Xe lamp with a bandpass filter were used.