

Supporting Information

In situ photo-derived MnOOH collaborating with Mn₂Co₂C@C dual cocatalysts boost photocatalytic overall water splitting

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Contents

Part I: Experimental Section

Part II: Supplementary Results

Part III: References

Part I: Experimental Section

Chemical reagents

Potassium hexacyanocobaltate ($K_3[Co(CN)_6]$), sodium citrate tribasic dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$), manganese acetate ($Mn(CH_3COO)_2 \cdot 4H_2O$), strontium carbonate ($SrCO_3$), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and manganese nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$) were sourced from Aladdin. TiO_2 (P25) was purchased from Degussa. Urea was bought from Damao Chemical Reagent Factory. All the involved chemical reagents were used as purchased and not further purified.

Materials preparation

Preparation of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ and $Mn_2Co_2C@C/Mn_2N_{0.86}$. Typically, $Mn(CH_3COO)_2 \cdot 4H_2O$ (6.5 mmol) and $C_6H_5Na_3O_7 \cdot 2H_2O$ (6.5 mmol) were dissolved in 400 mL deionized water. $K_3Co(CN)_6$ (6.0 mmol) was then added to the above solution. The solution was vigorously stirred for 48 hours. The precipitate of Prussian blue analogue (denoted as PBA-CoMn) was separated by centrifugation, and dried at 80°C overnight. The $Mn_2Co_2C@C/Mn_2N_{0.86}$ (denoted as MCMN for simplicity) nanocomposites were obtained by the pyrolysis of PBA-CoMn at 600°C for 4 hours in N_2 flow.

Preparation of $Mn_2Co_2C@C$. Typically, $Co(NO_3)_2 \cdot 6H_2O$ (1.0 mmol) and $Mn(NO_3)_2 \cdot 4H_2O$ (5.0 mmol) were dissolved in 100 mL deionized water, named as solution A. $K_3Co(CN)_6$ (4.0 mmol) was dissolved in 100 mL deionized water, named as solution B. Solution B was then added to solution A under vigorous stirring. The mixed solution was agitated for 5 min then aged for 24 hours. The precipitate was separated

by centrifugation, and dried at 80°C overnight. The Mn₂Co₂C@C nanoparticles were obtained by the pyrolysis of PBA-CoMn at 800°C for 2 hours in N₂ flow.

Preparation of hollow carbon spheres. The Mn₂Co₂C@C nanoparticles were dispersed in HCl solution (1.0 M) and then stirred for 8 hours. After centrifuged and dried, the hollow carbon spheres (denoted as HCS) were obtained.

Preparation of g-C₃N₄. 50 g of urea was placed in a porcelain crucible and heated at 550°C for 2 hours (ramping rate 5°C min⁻¹) in static air. Finally, g-C₃N₄ powder was obtained after cooling to room temperature.

Preparation of Mn₂Co₂C@C/Mn₂N_{0.86}/g-C₃N₄, g-C₃N₄/Mn₂Co₂C@C and g-C₃N₄/hollow carbon spheres. 0.3 g of g-C₃N₄ powder and different weight percentages of Mn₂Co₂C@C/Mn₂N_{0.86} powder (15, 20, 25, 30 and 35 wt %) were together dispersed in 1.0 mL of ethanol, and ground in an agate mortar until the volatilization of ethanol. Then another 1.0 mL of ethanol was added, and the mixture was ground until the volatilization of ethanol again. After the mechanically grinding procedure, the Mn₂Co₂C@C/Mn₂N_{0.86} nanocomposites were uniformly loaded on the surface of g-C₃N₄ with a firm contact. Finally, the products were obtained after dried at 80°C for 4 hours, and denoted as MCMN/CN-15, MCMN/CN-20, MCMN/CN-25, MCMN/CN-30 and MCMN/CN-35, respectively. The g-C₃N₄/Mn₂Co₂C@C (15 wt % percentage of Mn₂Co₂C@C) and g-C₃N₄/hollow carbon spheres (15 wt % percentage of hollow carbon spheres) photocatalysts were obtained by using the identical method, and denoted as CN/MC-15 and CN/HCS-15, respectively.

Preparation of g-C₃N₄-Pt. 0.2 g of g-C₃N₄ powder was dispersed in 85.0 mL water and 15.0 mL triethanolamine, then the calculated H₂PtCl₆ solution was added. The mixed solution was evacuated and irradiated by UV-vis light for 2 hours. Finally, the mixed suspension was filtered, washed and dried, the g-C₃N₄-Pt (1 wt %) was obtained as a reference.

Preparation of Mn₂Co₂C@C/Mn₂N_{0.86}/SrTiO₃. Firstly, SrCO₃ (50 mmol) and TiO₂ (P25, 50 mmol) were mixed evenly, then heated at 1150°C for 10 hours (ramping rate 5°C min⁻¹) in static air. Finally, SrTiO₃ powder was obtained after cooling to room temperature. Mn₂Co₂C@C/Mn₂N_{0.86}/SrTiO₃ samples were obtained by using the same way of preparing the Mn₂Co₂C@C/Mn₂N_{0.86}/g-C₃N₄ samples. Samples with Mn₂Co₂C@C/Mn₂N_{0.86} percentages of 5 wt %, 10 wt % and 15 wt % in the photocatalysts were labelled as MCMN/STO-5, MCMN/STO-10 and MCMN/STO-15, respectively.

Characterization

X-ray powder diffraction (XRD) patterns were recorded by a Rigaku Ultima IV X-ray diffractometer. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images were obtained from a FEI Glacios Cryo-TEM microscope. Scanning electron microscopy (SEM) images were obtained from a FEI Quanta 200 microscope. Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60 thermal analyser in an Ar flow. The contents of Mn and Co elements were detected by using an inductively coupled plasma atomic emission spectrometry (ICP-AES: Thermo Fisher IRIS Intrepid II XSP). Surface structure was detected by an Thermo VG Scientific

ESCALAB 250 X-ray photoelectron spectrometer. UV-visible diffuse reflectance spectra (UV-vis DRS) were obtained from a Shimadzu UV-3600 UV-visible spectrophotometer. Photoluminescence (PL) spectra were detected by a fluorescence spectrophotometer with an excitation wavelength of 389 nm. PL decay plots were obtained from an Edinburgh Instruments F980 fluorescence lifetime spectrophotometer. Electron Paramagnetic Resonance (EPR) spectra were recorded by a Bruker EPR A300-10/12 spectrometer in a DMPO solution with methanol dispersion for DMPO- $\cdot\text{O}^{2-}$ and aqueous dispersion for DMPO- $\cdot\text{OH}$, respectively.

Photocatalytic overall water splitting

Photocatalytic overall water splitting tests were carried out in a closed photocatalytic reaction system (Labsolar-6A, Beijing Perfectlight). A 300 W Xe-lamp (PLS-SXE300D, Beijing Perfectlight) was used as the light source. In a typical experiment, 20 mg of photocatalyst was suspended in 100 mL pure water in a Pyrex glass reaction cell at 15°C by a flow of cooling water. Before irradiation, the photocatalytic reaction system was evacuated for 30 min to remove air completely. The evolved H_2 and O_2 were detected by an online gas chromatograph (GC7900, TCD with Ar as the carrier gas).

The stability of photocatalyst was tested. After 10 hours of reaction, the generated H_2 and O_2 were evacuated completely, followed by another 10 hours of reaction. According to the H_2 generation under monochromatic light illumination, the apparent quantum efficiency (AQE) was calculated by Eq. 1,^{1,2}

$$\text{AQE} = \frac{2 \times N_{\text{H}_2} (\text{S}^{-1} \cdot \text{cm}^{-2})}{P_{\lambda} (\text{mW} \cdot \text{cm}^{-2}) \div E_{\lambda} (\text{mW} \cdot \text{s}^{-1})} \times 100 \% \quad (1)$$

where N_{H_2} is the molecules number of the produced H_2 , λ is the wavelength of the irradiated monochromatic light, E_λ and P_λ is the average photon energy and the light intensity of per unit area at corresponding λ , respectively.

Photoelectrochemical measurements

A mixed solution of 10 μ L 5 wt% Nafion solution, 5.0 mg of photocatalyst and 1.0 ml ethanol was sonicated to a homogeneous dispersion. 100 μ L mixed solution was dropped on a FTO glass substrate ($2 \times 1 \text{ cm}^2$), after dried, the working electrode was obtained.

Photoelectrochemical measurements were carried out by an electrochemical workstation (CHI 650E) with a three electrode system. The Pt foil electrode and Ag/AgCl (saturated KCl) electrode were used as a counter electrode and a reference electrode, respectively. A Na_2SO_4 solution (0.5 M) was used as electrolyte for all the tests except for the electrocatalytic oxygen evolution reaction (OER). A 300 W Xe-lamp with a 400 nm cut-off filter was used as the light source. The transient photocurrent curves were recorded at bias 0.3 V. The electrochemical impedance spectra (EIS) were recorded at amplitude of 5 mV and frequency of 0.01-10⁵ Hz. The Mott-Schottky (MS) plots were recorded at amplitude of 5 mV and frequency of 1000 Hz. The flat band potentials (V_{fb}) were estimated based on the MS plots by means of Eq. 2.³

$$\frac{1}{C^2} = \left[\frac{2}{e_0 \cdot \epsilon \cdot \epsilon_0 \cdot N_d \cdot A^2} \right] \left[E - E_{fb} - \frac{KT}{e} \right] \quad (2)$$

Where C is the space charge layer capacitance, N_d stands for the electron donor density, e_0 stands for the electron charge, E denotes the applied potential, ϵ and ϵ_0

represent the material's permittivity and permittivity of vacuum, respectively. V_{fb} is calculated by extrapolating the fitted line at $C^{-2} = 0$. The polarization curves of electrocatalytic hydrogen evolution reaction (HER) were recorded at a scan rate of 5 $mV s^{-1}$. The polarization curves of electrocatalytic OER were recorded at a scan rate of 5 $mV s^{-1}$ in a KOH solution (1.0 M). To obtain potential to reversible hydrogen electrode (RHE), Eq. 3 was employed.

$$E_{RHE} = E_{AgCl} + 0.059pH + E_{AgCl}^0 (E_{AgCl}^0 = 0.197V) \quad (3)$$

Part II: Supplementary Results

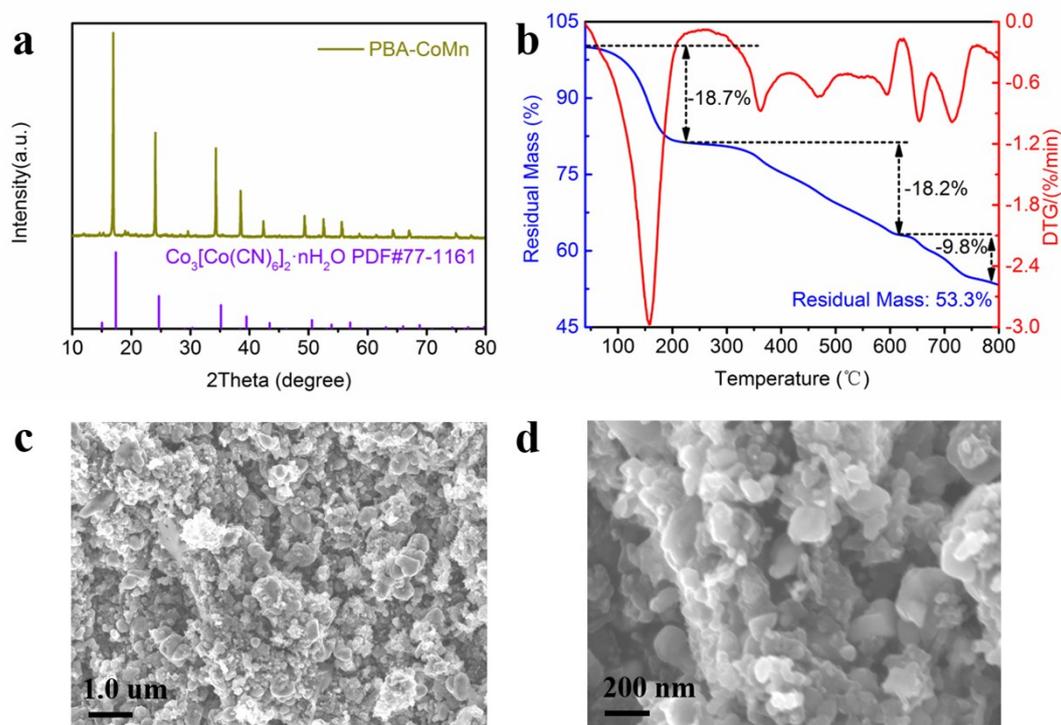


Figure S1. The XRD pattern (a) and TG analysis (b) of PBA-CoMn. The SEM images (c, d) of MCMN.

XRD pattern (**Figure S1a**) confirms that the peaks of PBA-CoMn closely match cubic Co₃[Co(CN)₆]₂·nH₂O (JCPDS 77-1161). The slight shift to lower angles for the PBA-CoMn, relative to Co₃[Co(CN)₆]₂·nH₂O, owing to the substitution of Co²⁺ by Mn²⁺ having a larger radius. Determined by ICP-AES, the exact contents of Co and Mn in the MCMN are 22.12 wt % and 30.20 wt %, that is, the molar mass ratio of Co/Mn is close to 4:6, respectively. In addition, the weight percentage of N-doped graphitic carbon is 47.68 wt %. And the N-doped graphite carbon comes from the pyrolysis and graphitization of cyanogroup.

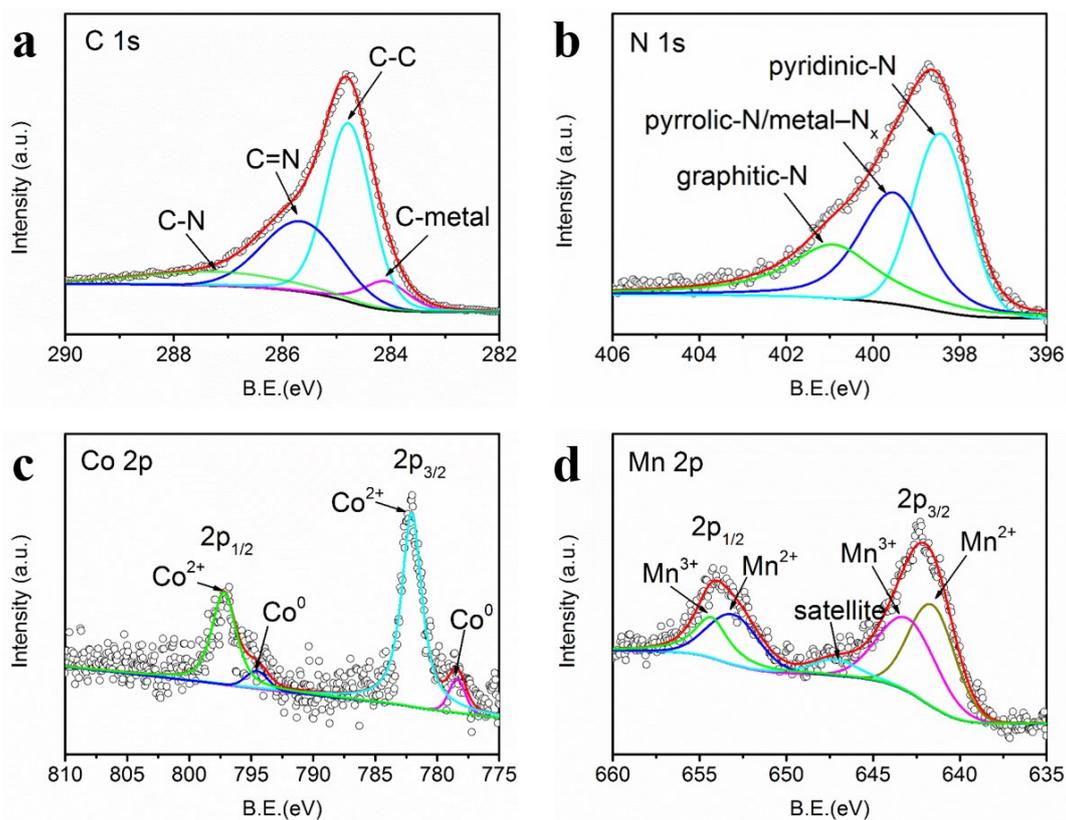


Figure S2. The high-resolution XPS spectra of MCMN: C 1s (a), N 1s (b), Co 2p (c) and Mn 2p (d).

Figure S2 shows the high-resolution C, N, Co and Mn spectra of MCMN. The high-resolution C 1s spectra can be divided into four peaks, three peaks are the C–C band (284.78 eV), C=N bond (285.65 eV) and C–N (287.24 eV) of N-doped graphitic carbon shell, respectively.⁴ The peak of 284.11 is indexed to the C–metal band of Mn₂Co₂C.⁵ The high resolution N 1s spectra show three peaks of doped N elements at 398.44 eV (pyridinic–N), 399.53 eV (pyrrolic–N/Co–N_x) and 404.91 eV (graphitic–N).⁶ The binding energies of 782.06 and 797.12 eV in the Co 2p spectra are assigned to Co²⁺,⁷ ascribed to the surface oxidation of Mn₂Co₂C. The binding energy of 778.40 eV and 794.54 are assigned to Co⁰ in an alloy.^{4, 5} The high-resolution Mn 2p spectra can be divided into

five peaks, two peaks at binding energies of 641.59 and 653.07 eV are associated with Mn^{2+} , and the other two peaks of 643.03 and 654.32 eV are associated with Mn^{3+} , suggesting the presence of $\text{Mn}_2\text{N}_{0.86}$,⁵ while the one of 647.20 eV are the satellite peak.

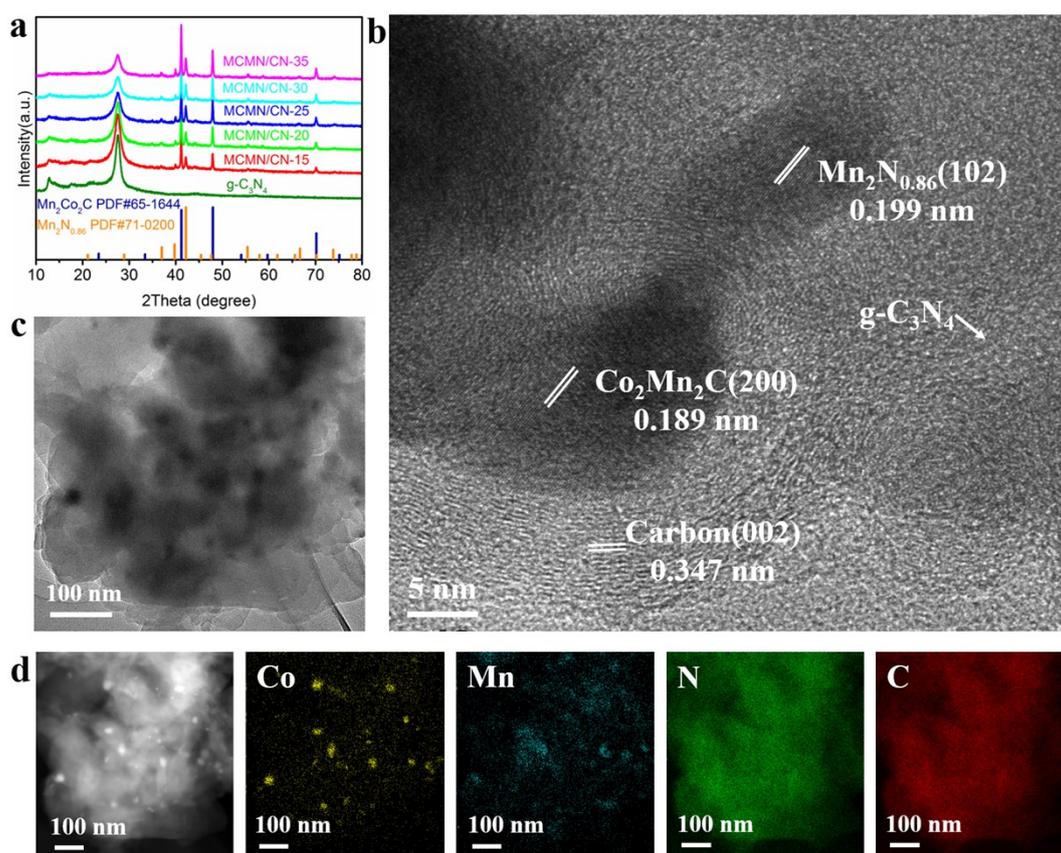


Figure S3. The XRD patterns (a) of MCMN/CN photocatalysts. The HTEM (b), TEM (c), STEM (d) images and the corresponding elemental mappings of MCMN/CN-15.

As presented in **Figure S3a**, the XRD pattern of $\text{g-C}_3\text{N}_4$ exhibits two peaks at $2\theta = 13.26$ and 27.52° indexed to the (100) and (002) lattice planes, respectively.⁸ The XRD patterns of MCMN/CN photocatalysts match well with MCMN and $\text{g-C}_3\text{N}_4$. Notably,

the intensities of characteristic diffraction peaks of MCMN increase gradually with the increased content, whereas those of the g-C₃N₄ decrease, indicating that the crystal structure of g-C₃N₄ is markedly covered by the loading of MCMN on its surface.

The TEM image (**Figure S3c**) of MCMN/CN-15 reveals that MCMN hybrids are uniformly embedded on g-C₃N₄ nanosheets, further confirmed by STEM image and elemental mappings (**Figure S3d**). The uniform dispersions of Co and Mn confirm MCMN hybrids are evenly loaded on g-C₃N₄. HRTEM image (**Figure S3b**) proves that MCMN nanoparticles are welded onto g-C₃N₄ nanosheets. A core has lattice plane with d-spacing of 0.189 nm, corresponded to the (200) plane of Mn₂Co₂C. An adjacent lattice plane with a d-spacing of 0.199 nm is assigned to the (102) plane of Mn₂N_{0.86}. Meanwhile, Mn₂Co₂C cores are coated by N-doped graphitic carbon shells (lattice fringes of 0.347 nm). The above results confirmed that MCMN were successfully embedded on the surface of g-C₃N₄ to fabricate a high quality photocatalyst.

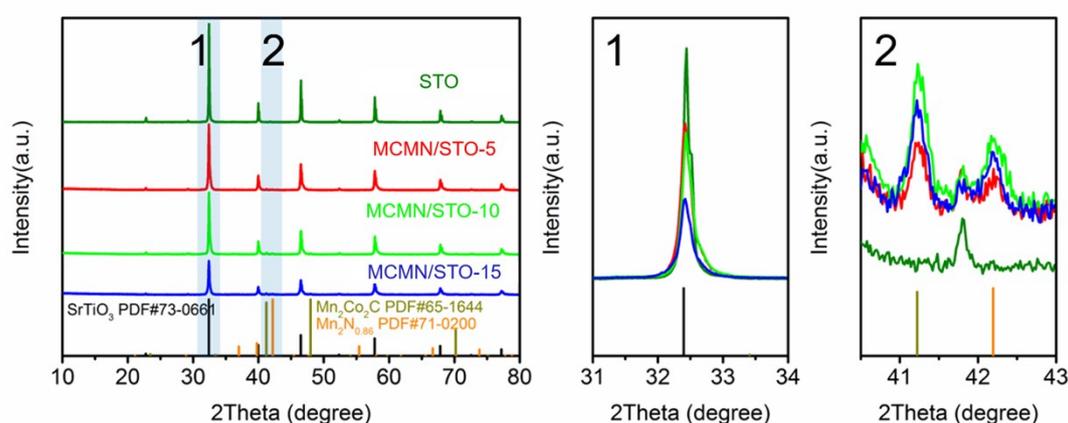


Figure S4. The XRD patterns of SrTiO₃ and MCMN/STO photocatalysts.

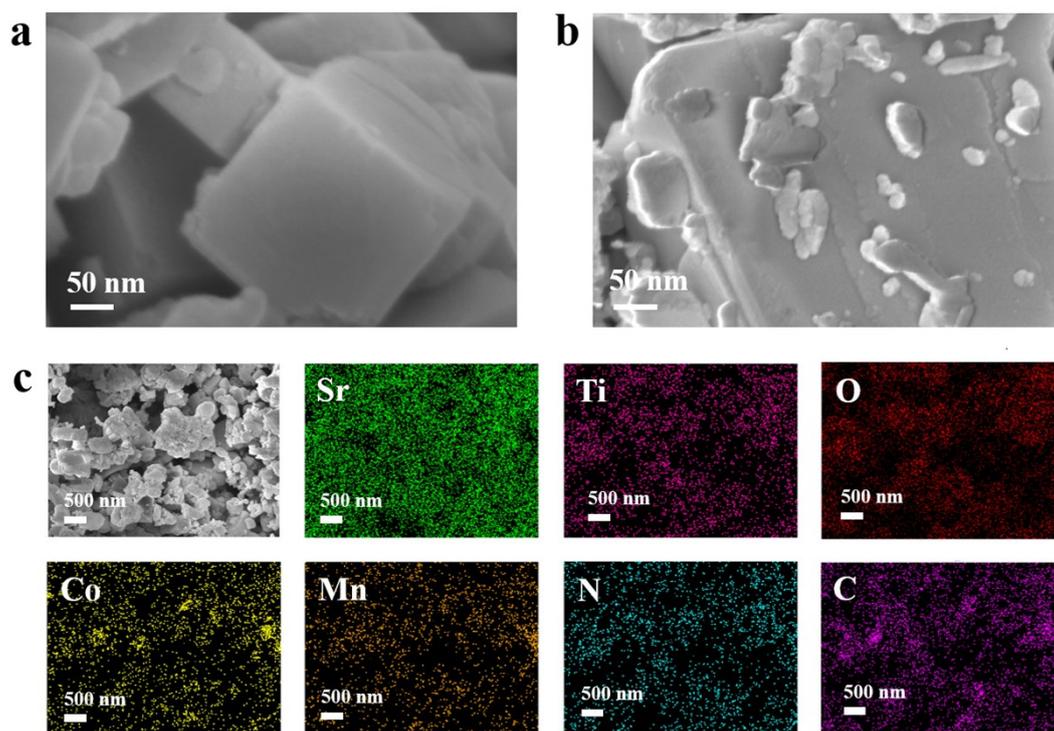


Figure S5. The SEM image of SrTiO₃ (a), the SEM images of MCMN/STO-10 (b, c) and the corresponding elemental mappings of picture c.

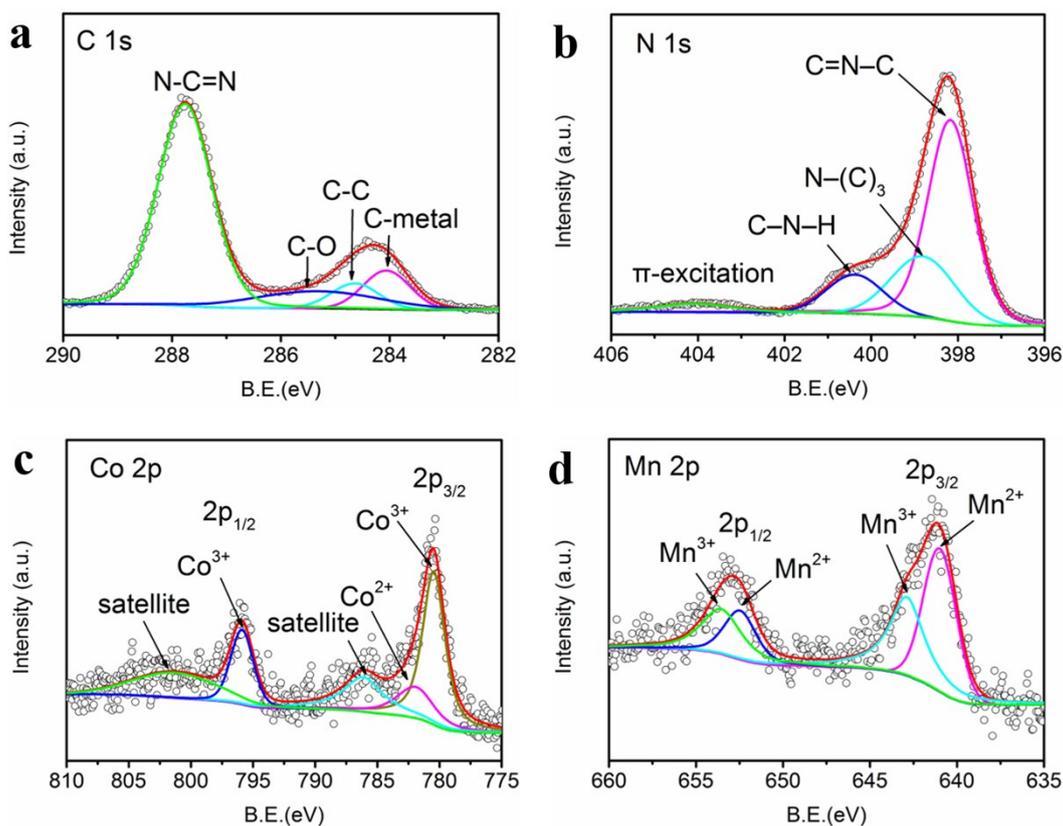


Figure S6. The high-resolution XPS spectra of recycled MCMN/CN-30: C 1s (a), N 1s (b), Co 2p (c) and Mn 2p (d).

Figure S6 shows the high-resolution C, N, Co and Mn spectra of recycled-MCMN/CN-30. The high-resolution C 1s spectra can be divided into four peaks, two peaks are C–O band (285.32 eV) and N–C=N bond (287.76 eV) of $g\text{-C}_3\text{N}_4$.^{9, 10} The other peaks of 284.06 and 284.64 eV are indexed to the C–metal band of $\text{Mn}_2\text{Co}_2\text{C}$ and the C–C of graphitic carbon shell, respectively.^{4, 5} The high resolution N 1s spectra show four peaks of $g\text{-C}_3\text{N}_4$ at 398.17 eV (C=N–C), 398.81 eV [N–(C₃)], 400.38 eV (C–N–H) and 404.09 eV (π -excitation).¹¹ The binding energies of 780.45 and 795.88 eV in the Co 2p spectra are assigned to Co^{3+} ,¹² ascribed to the surface oxidation of $\text{Mn}_2\text{Co}_2\text{C}$. The binding energy of 781.92 eV is assigned to Co^{2+} of $\text{Mn}_2\text{Co}_2\text{C}$,¹³ while the ones of 786.13

and 801.27 eV are the satellite peaks. The high-resolution Mn 2p spectra can be divided into four peaks, two peaks at binding energies of 640.99 and 652.47 eV are associated with Mn²⁺, and the other two peaks of 642.88 and 653.54 eV are associated with Mn³⁺.¹⁴ In addition, the energy separation between Mn 2p_{1/2} and Mn 2p_{3/2} is 11.87 eV, demonstrating the presence of MnOOH.¹⁴ Based on the XRD, HRTEM and XPS results, it is summarized that the recycled-MCMN/CN-30 is comprised of g-C₃N₄, Mn₂Co₂C@C and MnOOH, in which the Mn₂Co₂C@C and MnOOH are loading on the surfaces of g-C₃N₄ with tight and robust structures.

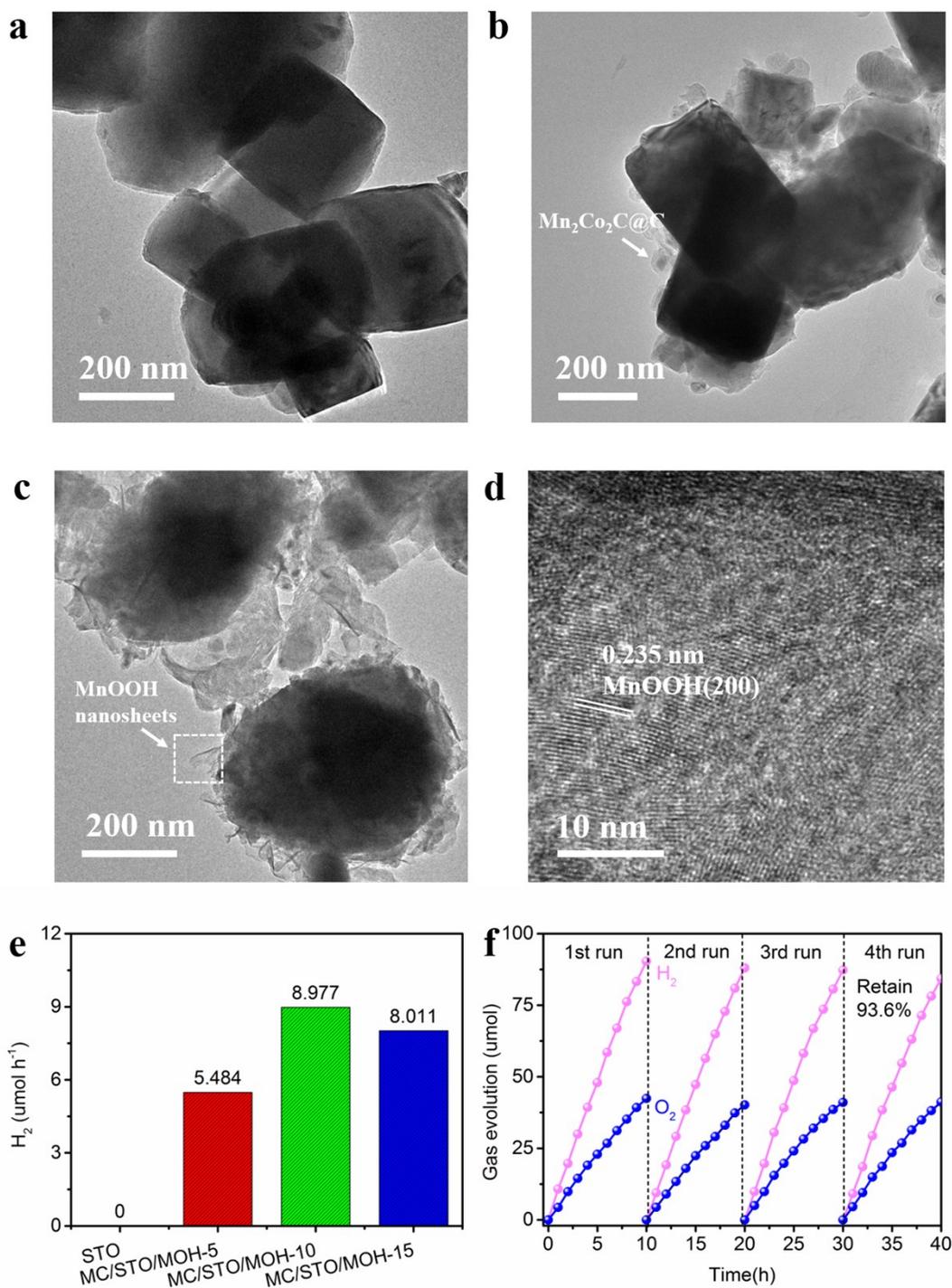


Figure S7. The TEM and HRTEM images: (a) SrTiO_3 , (b) as-prepared MCMN/STO-10, (c) MC/STO/MOH-10, (d) selection in c. The photocatalytic performances under UV-vis light irradiation in pure water (50 mg of photocatalyst): (e) average H_2 evolution rates of MC/STO/MOH samples, (f) stability tests of MC/STO/MOH-10.

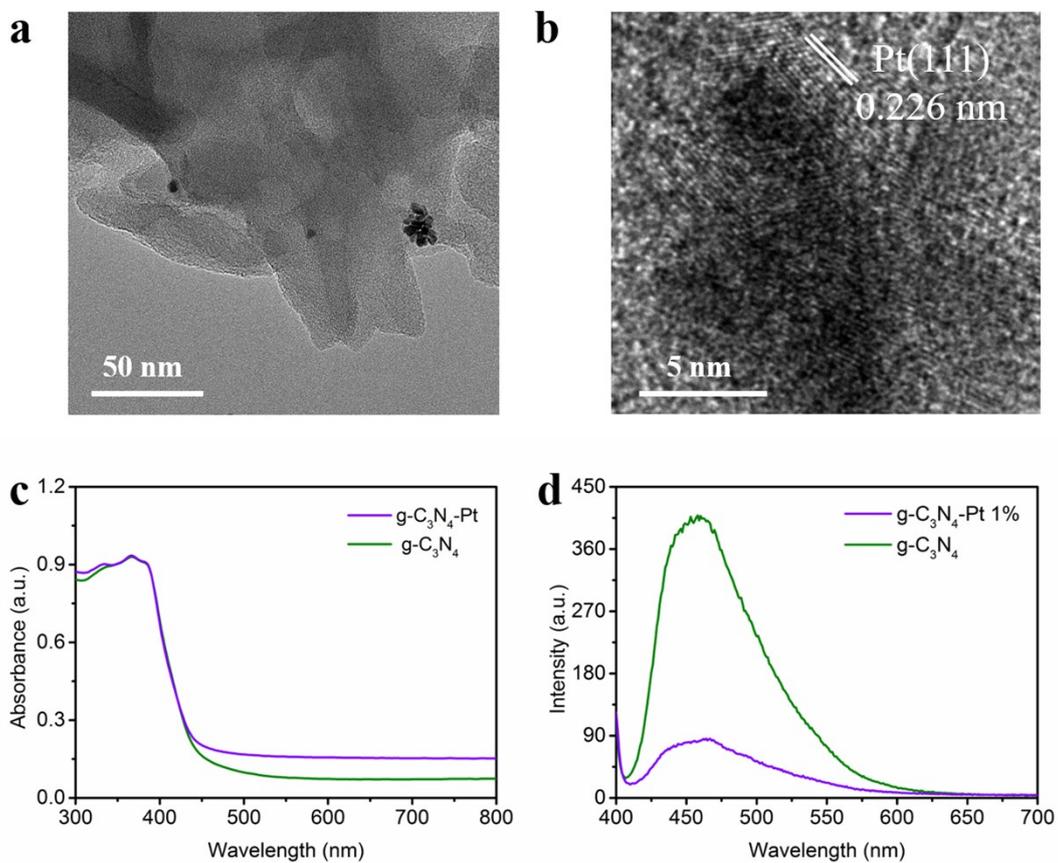


Figure S8. The TEM (a) and HRTEM (b) images of $g\text{-C}_3\text{N}_4\text{-Pt}$, The UV-vis diffuse reflectance spectra (c) and photoluminescence spectra (d) of $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4\text{-Pt}$.

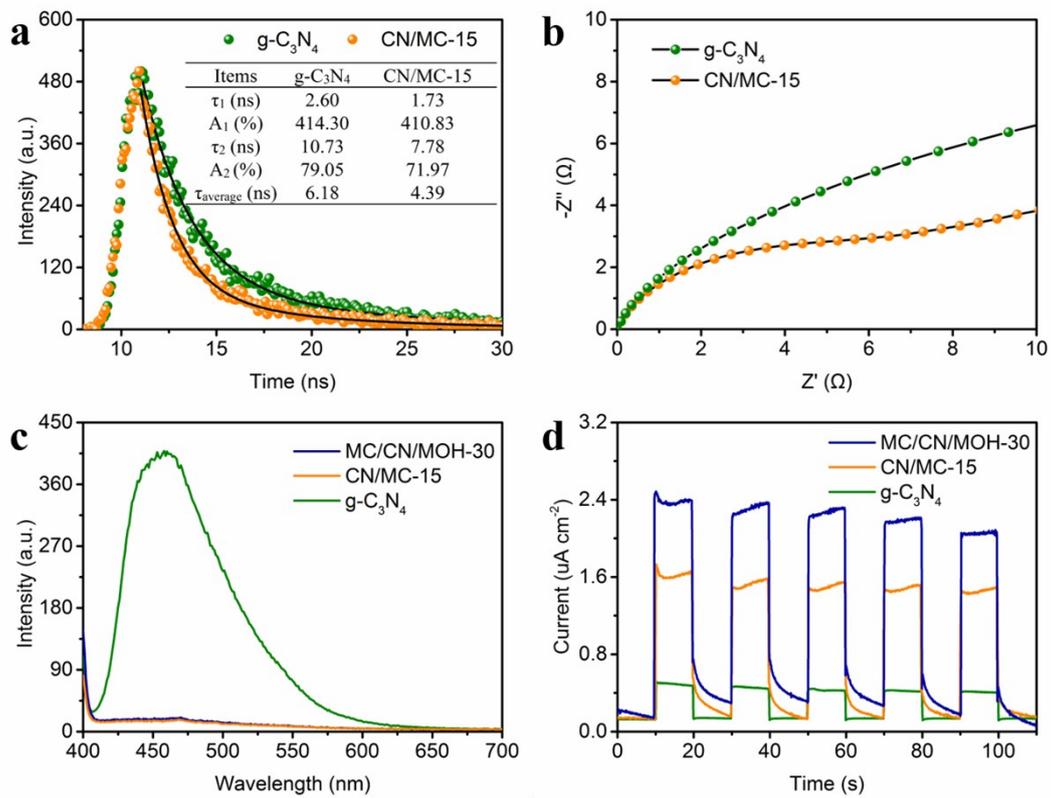


Figure S9. The transient PL spectra (a) and electrochemical impedance spectroscopy (b) of g-C₃N₄ and CN/MC-15. The PL spectra (c) and transient photocurrent response test (d) of g-C₃N₄, CN/MC-15 and MC/CN/MOH-30.

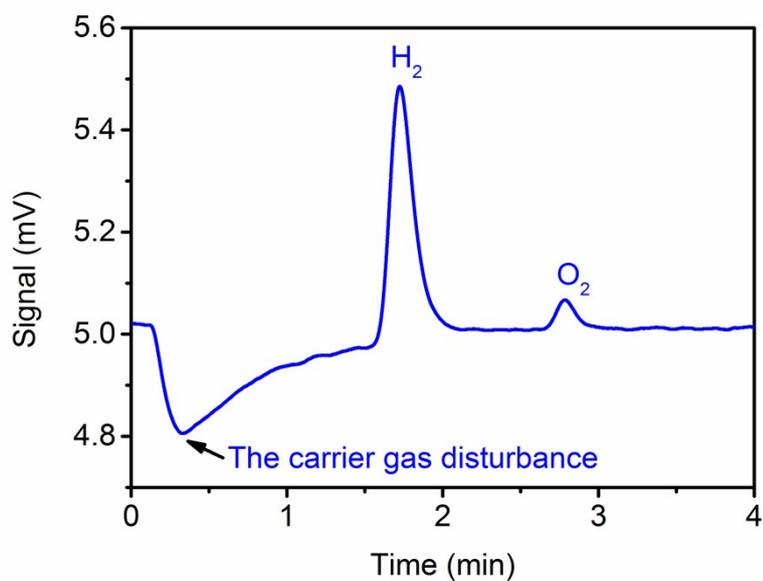


Figure S10. The actual H₂ and O₂ testing chart detected by gas chromatography over MC/CN/MOH-30 photocatalyst.

The typical GC raw data of photocatalytic overall water splitting over MC/CN/MOH-30 photocatalyst is shown in **Figure S10**, the negative peak at 0.33 min is ascribed to the carrier gas disturbance during injection. The peaks at 1.72 min and 2.78 min are assigned to H₂ and O₂, respectively. Based on the peak areas of H₂ and O₂, the amount of H₂ and O₂ can be calculated by external standard method.

Table S1. Summary of the photocatalytic H₂ evolution on g-C₃N₄ based photocatalysts for overall water splitting.

Photocatalysts	Cocatalysts	Power (Xe lamp), wavelength	Activity ($\mu\text{mol h}^{-1}$ g^{-1})	AQE	Reference (year)
g-C ₃ N ₄	Mn ₂ Co ₂ C@C/Mn OOH	300W	64.15	1.45% at 420 nm	This work
g-C ₃ N ₄	Pt/PtO _x /CoO _x	300W	61	0.3% at 405 nm	¹⁵ (2016)
g-C ₃ N ₄	Pt/Co ₃ O ₄	300W	610	/	¹⁶ (2016)
α -Fe ₂ O ₃ /g- C ₃ N ₄	Pt/RuO ₂	300W, $\lambda \geq 420$ nm	38.2	/	¹⁷ (2017)
g-C ₃ N ₄	Co ₁ -phosphide	300W, $\lambda \geq 420$ nm	126.8	3.6% at 420 nm	¹⁸ (2017)
g-C ₃ N ₄	Au	300W, $\lambda \geq 420$ nm	150.1	/	¹⁹ (2018)
CoO/g-C ₃ N ₄	/	LED, $\lambda \geq 400$ nm	50.2	1.91% at 420 nm	²⁰ (2018)
g-C ₃ N ₄	NiO	300W, $\lambda \geq 420$ nm	28	/	²¹ (2018)
g-C ₃ N ₄	Pt/Ni(OH) ₂	300W	425.7	1.8% at 420 nm	²² (2019)
g-C ₃ N ₄	Pt@Ni(OH) ₂ /Pt	300W	1330	4.2% at 420 nm	²³ (2019)
g-C ₃ N ₄ /Ti ₃ C ₂	Pt	300W, $\lambda \geq 420$ nm	627.1	8.7% at 350 nm	²⁴ (2019)
g-C ₃ N ₄ -RGO- Fe ₂ O ₃	Pt	300W	1090	/	²⁵ (2019)
MnO ₂ /g-C ₃ N ₄	Pt	300W, $\lambda \geq 420$ nm	60.6	/	²⁶ (2019)
Mn-g-C ₃ N ₄	Pt	300W, AM1.5	695.1	4.0% at 420 nm	²⁷ (2019)
P-g-C ₃ N ₄	Pt/CoP	300W, $\lambda \geq 420$ nm	213.6	6.8% at 400 nm	²⁸ (2020)
CdS/g-C ₃ N ₄	Pt/MnO _x	300W, $\lambda \geq 420$ nm	924.4	1.745% at 420	²⁹ (2020)

Part III: References

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