Electron Acceptor of Ni Decorated Porous Carbon Nitride Applied In Photocatalytic Hydrogen Production

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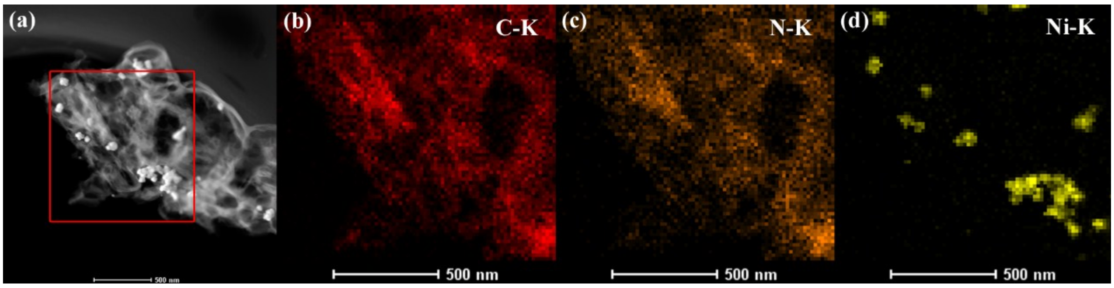


Fig. S1 TEM elemental mapping images of C, N, and Ni of CM-Ni10.

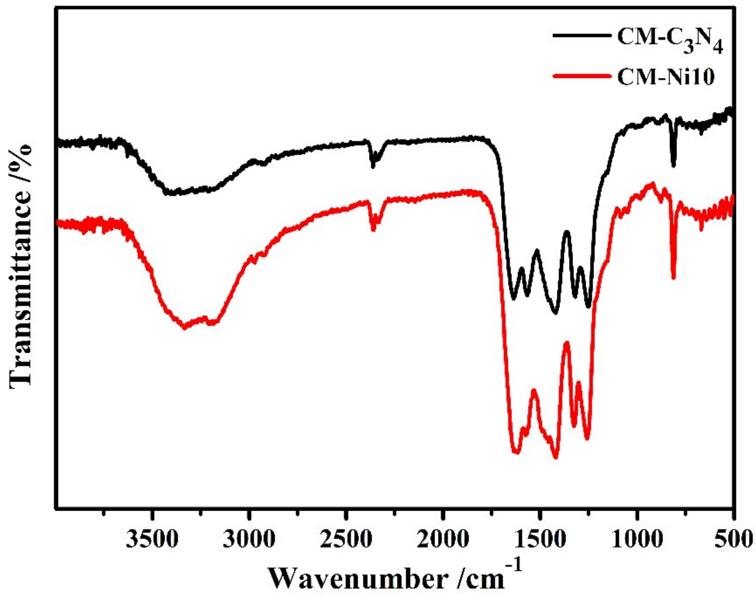


Fig. S2 FTIR spectra of CM-C_3N_4 and CM-Ni10 samples.

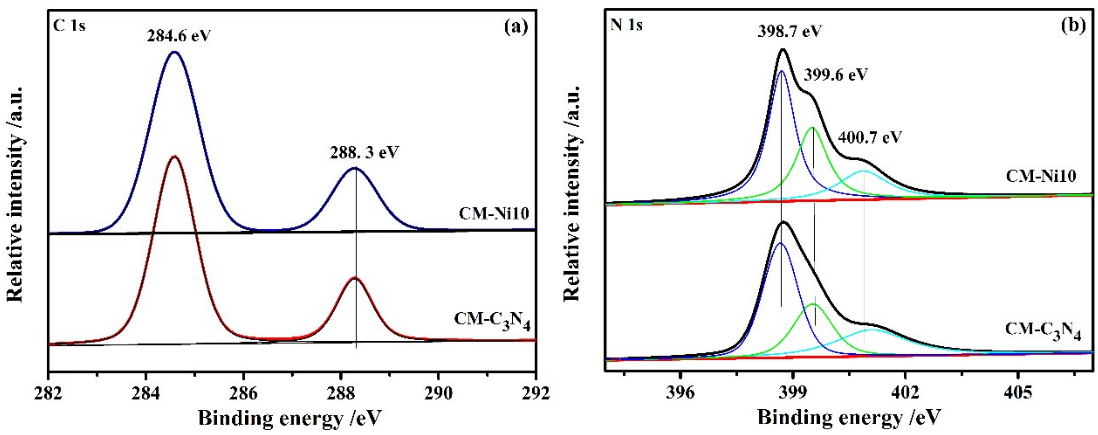


Fig. S3 The comparison of the curvefitted XPS spectra with the high resolution of C 1s and N 1s binding energy regions about CM-C_3N_4 and CM-Ni10**.**

The high resolution of C 1s and N 1s show that it has no obvious change of the CM-Ni10, compared with the CM-C_3N_4, suggesting that the metallic nickel is on the surface of the CM-C_3N_4 but not merge into the lattice.

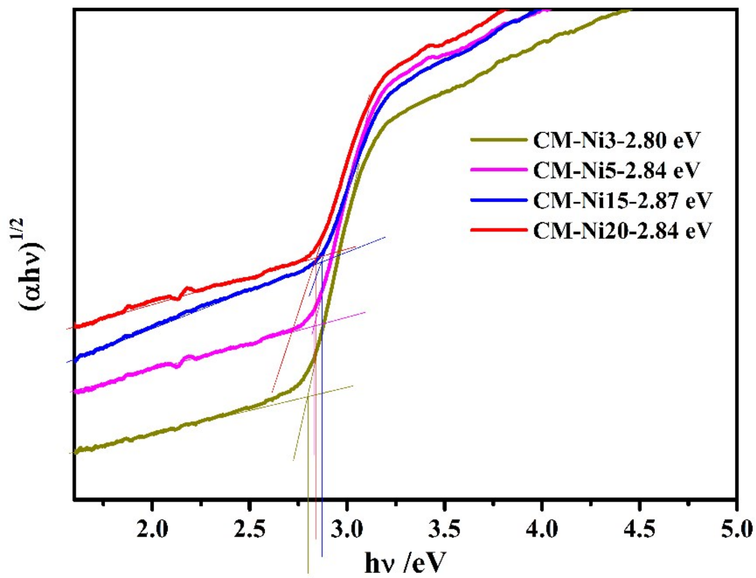
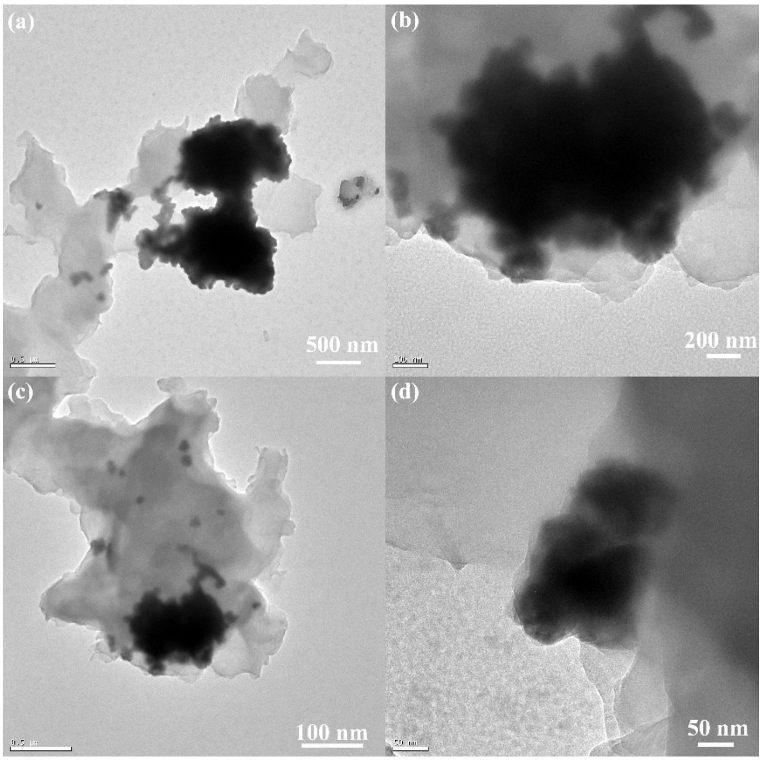


Fig. S4 Plots of the $(h\nu)^{1/2}$ vs photo energy (hν) for Ni/CM-C_3N_4 composites.



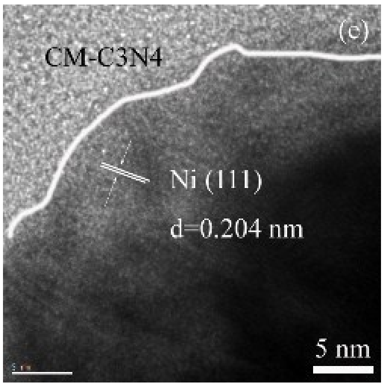


Fig. S5 TEM images of CM-Ni20 (a-d); the HRTEM image of CM-Ni20 (e).

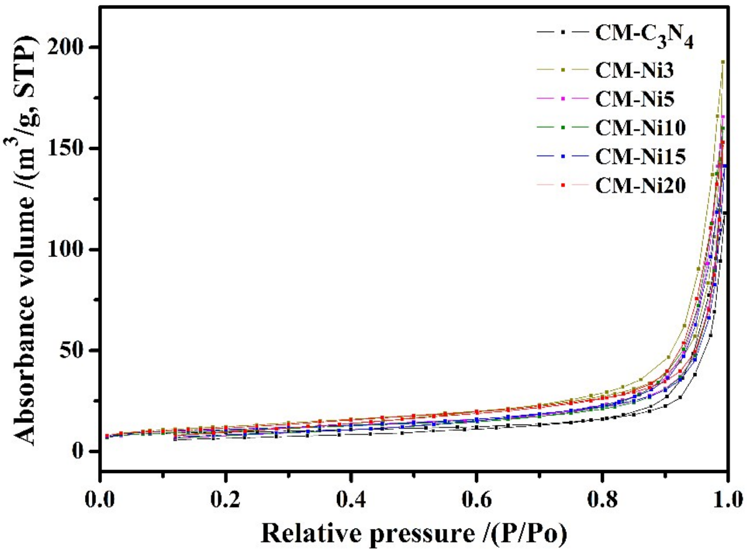


Fig. S6 Nitrogen gas sorption isotherms of Ni/CM-C_3N_4 composites.

Table S1. The mass ratios of Ni to (Ni+CM-C_3N_4)

	1	2	3
Feed ratio	3%	10%	20%
ICP	0.8%	3.24%	5.61%

Table S2 Carbon nitride-based photocatalysts for hydrogen generation comparison

Photocatalyst	Light Source	Sacrifical reagent	H_2 generation (μmolh^{-1}g^{-1})	Ref (year)
10 wt% Ni/CM-C_3N_4 50 mg	500 W	10 vol% triethanolamine	313.2	This work
Zn10/g-C_3N_4 0.5 wt% Pt 200 mg	200 W λ > 420 nm	18.5 vol% methanol	297.5	S[1] (2011)
CNIC 3 wt% Pt 100 mg	λ > 420 nm	10 vol% triethanolamine	3460	S[2] (2013)
K10/g-C_3N_4 0.5 wt% Pt 100 mg	300 W λ > 420 nm	10 vol% triethanolamine	1020.8	S[3](2014)
C_3N_4 NTs 2 wt% Pt 100 mg	300 W λ > 420 nm	10 vol% methanol	135	S[4] (2015)
2 wt% Ni/g-C_3N_4 50 mg	300 W λ > 420 nm	10 vol% triethanolamine	100	S[5] (2015)
10 wt% Ni/g-C_3N_4 50 mg	500 W	10 vol% triethanolamine	168.2	S[6] (2015)

Table S3 The BET specific surface area of CM-C_3N_4 and Ni/CM-C_3N_4 composites.

Samples	CM-C_3N_4	CM-Ni3	CM-Ni5	CM-Ni10	CM-Ni15	CM-Ni20
BET surface area(m^2/g)	31.21	43.57	36.19	35.28	37.24	41.09

The quantum efficiency

The apparent quantum efficiency (QE) was measured according to the previous literature.[7,8] A 300 W mercury lamp were used as light source to trigger the photocatalytic reaction, and the number of photons of the light source at 365 nm were measured by UV−Visible spectrophotometry. Typically, 100 mL (0.01M) $K_3Fe(C2O4)_3.3H_2O$ solution (V_0) were placed in photocatalytic reactor under stirring, and then the solution were irradiated 20s using 365 nm light, 5 mL samples (V_1) were taken and added into a 50 mL brown volumetric flask; 10 mL of (0.01M) 1,10-Phenanthroline monohydrate solution and 10 mL of acetic acid-sodium acetate buffer solution (pH 4.6) were added, then diluted to 50 mL (V_2), and placed flask in the dark for 30 min. Three parallel samples of each samples were taken for measuring, and the absorbance was measured at 510 nm (A_t). The QE was finally calculated by the Eq1.1 and Eq1.2:

$$\Phi^{H_2} = 2nNo/n' \times 100\% \quad (1.1)$$

Where n is the amount of hydrogen generated in t time (mol/3600 s); N, Avogadro's constant; n′, the number of light source emitted photon in per unit time (s^{-1}).

$$n' = \frac{(A_t - A_0)\ N_0 V_0 V_2}{\varepsilon L V_1 \Phi Fe^{2+} t} \quad (1.2)$$

Where A_0 is the absorbance of zero irradiation time; ε, the molar extinction coefficient of Fe^{2+} ($\varepsilon_{max}=1.11\times10^4$ L/mol·cm); L, the thickness of the cuvette; t is the irradiation time of the light source, $\Phi_{Fe}{}^{2+}$ is 1.21 (the quantum efficiency of 300 W mercury lamp at λmax = 365nm).

According to the calculated results above, the QE of CM-Ni10 is about 0.4% at 365 nm.

References

1 B. Yue, Q. Li, H. Iwai, T. Kako and J. Ye, *Sci Technol Adv Mat.* 2011, **12**, 3.

2 H. Gao, S. Yan, J. Wang, Y. A. Huang, P. Wang, Z. Li and Z. Zou, *Phys. Chem. Chem. Phys.,* 2013, **15**, 18077-18084.

3 M. Wu, J. M. Yan, X. N. Tang, M. Zhao and Q. Jiang, *ChemSusChem.,* 2014, **7**, 2654-2658.

4 K. Li, Z. Zeng, L. Yan, S. Luo, X. Luo, M. Huo and Y. Guo, *Appl. Catal. B-Environ.,* 2015, **165**, 428-437.

5 G. Zhang, G. Li and X. Wang, *Chemcatchem*. 2015, **7**, 2864-2870.

6 L. L. Bi, D. D. Xu, L. J. Zhang, Y. H. Lin, D. J. Wang and T. F. Xie, *Phys. Chem. Chem. Phys.* 2015, **17**, 29899-29905.

7 张耀君，郭烈锦，延卫，赵亮，杨鸿辉，李明涛，许云波．太阳能学报, 2006, **27**(11):1113— 1116.

8 J. Zhang, P. Wang, J. Sun, and Y. D. Jin, *ACS Appl Mater & Inter.,* 2014, **6**, 19905−19913.