

## Electronic Supplementary Information

(ESI)

### **g-C<sub>3</sub>N<sub>4</sub> supported metal (Pd, Ag, Pt) catalysts for hydrogen- production from formic acid**

Xiaotong Liu <sup>a</sup>, Penghe Su <sup>a</sup>, Ya Chen <sup>a</sup>, Baolin Zhu <sup>a,c</sup>, Shoumin Zhang <sup>a,c</sup>, Weiping Huang <sup>a,b,c\*</sup>

<sup>a</sup> *College of Chemistry, Nankai University, Tianjin 300071, China;*

<sup>b</sup> *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, China;*

<sup>c</sup> *The Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China*

## S I. Raman spectra

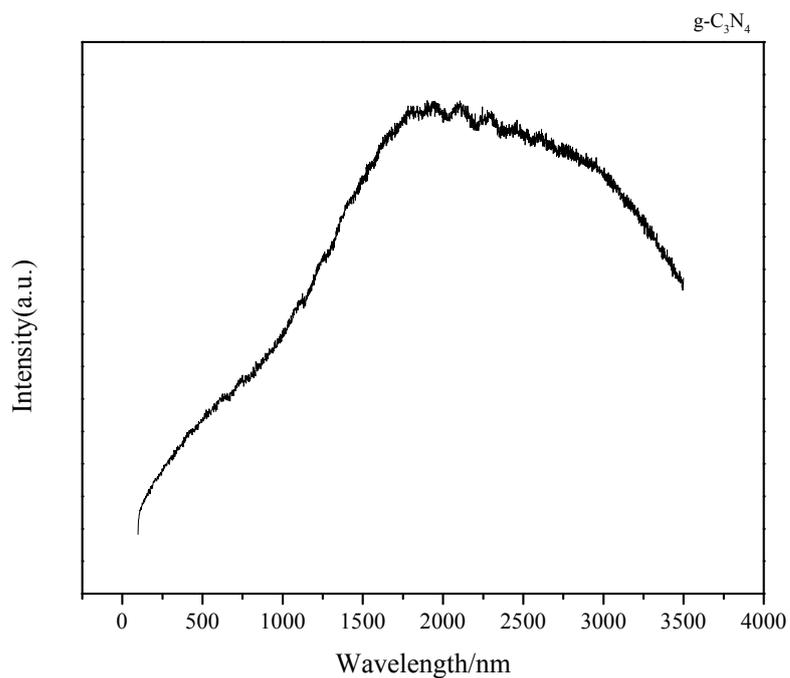


Figure S1. Raman spectrum of g-C<sub>3</sub>N<sub>4</sub> (532nm laser source)

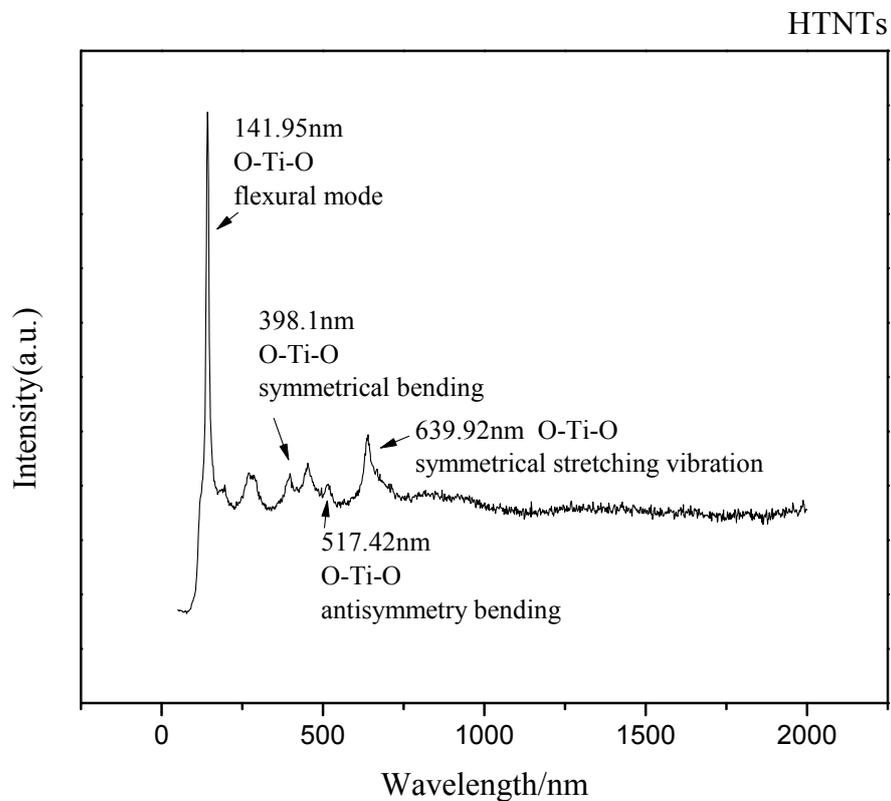


Figure S2. Raman spectrum of HTNTs (532nm laser source)

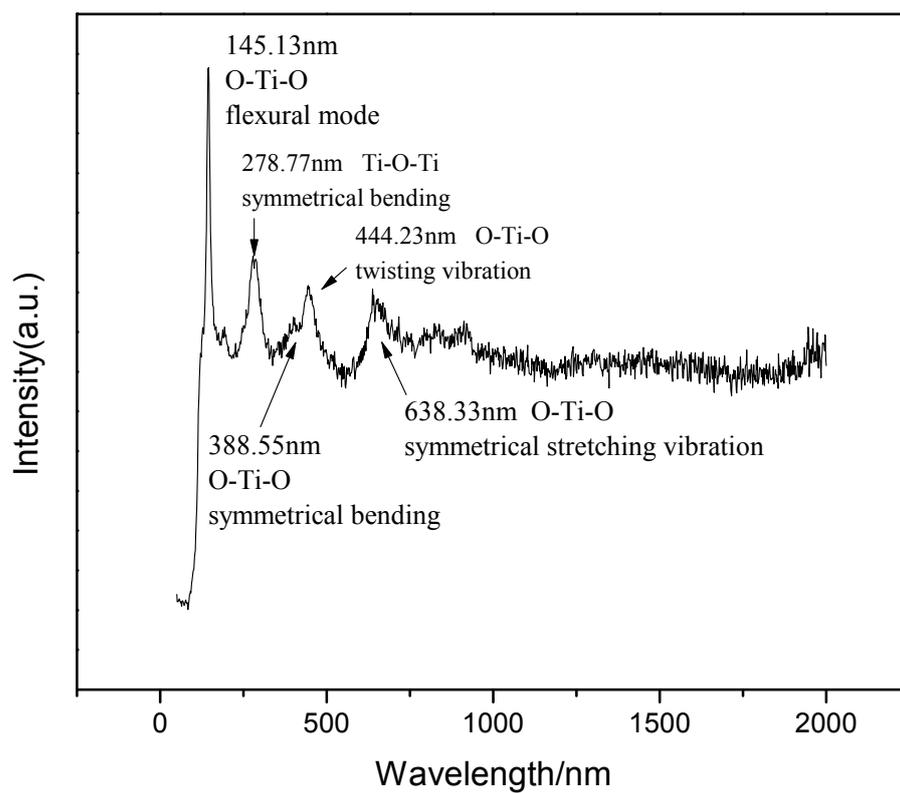


Figure S3. Raman spectrum of Pd/HTNTs (532nm laser source)

## S II. Metal content

Table S1. Metal contents of catalysts after catalytic reaction.

Sample	Contents (%)		
	Pd	Pt	Ag
Pd/g-C <sub>3</sub> N <sub>4</sub>	1.08	—	—
Pt/g-C <sub>3</sub> N <sub>4</sub>	—	0.66	—
Pt-Pd/g-C <sub>3</sub> N <sub>4</sub>	1.03	0.51	—
Ag/g-C <sub>3</sub> N <sub>4</sub>	—	—	0.39
Ag-Pd/g-C <sub>3</sub> N <sub>4</sub>	1.01	—	0.59
Pd/HTNTs	0.93	—	—
Pt-Pd /HTNTs	0.91	1.28	—
Ag-Pd /HTNTs	0.97	—	0.59

### S III. XPS spectra

The Pd 3d spectra exhibits two contributions. Major part is Pd<sup>0</sup>, located at 334.4-335.35 eV (3d<sub>5/2</sub>) and 339.6-340.6 eV (3d<sub>3/2</sub>), which can be assigned to be Pd NPs. And minor part is Pd<sup>2+</sup>, located at 336.35-338.15 eV (3d<sub>5/2</sub>)<sup>1,2</sup> and 341.75-343.30 eV (3d<sub>3/2</sub>)<sup>3</sup>, which has no catalytic activity.

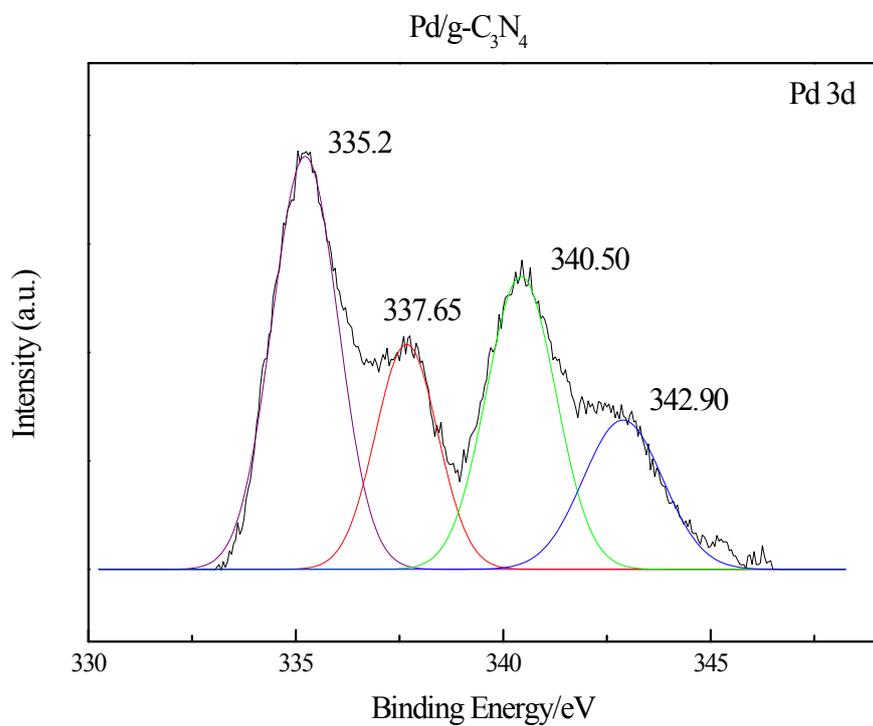


Figure S4. XPS spectrum of Pd 3d peaks of Pd/g-C<sub>3</sub>N<sub>4</sub>

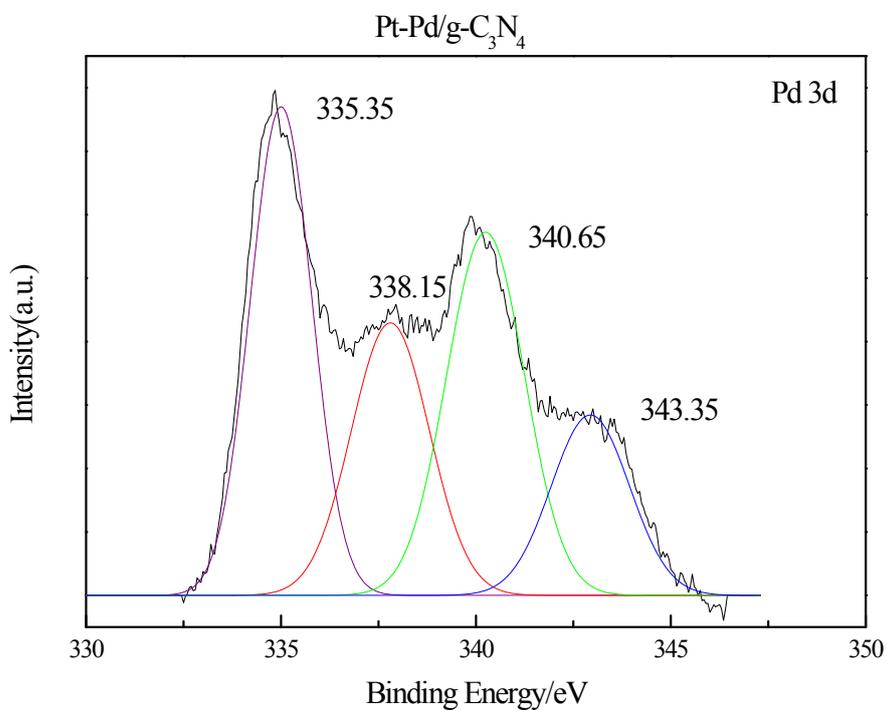


Figure S5. XPS spectrum of Pd 3d peaks of Pt-Pd/g-C<sub>3</sub>N<sub>4</sub>

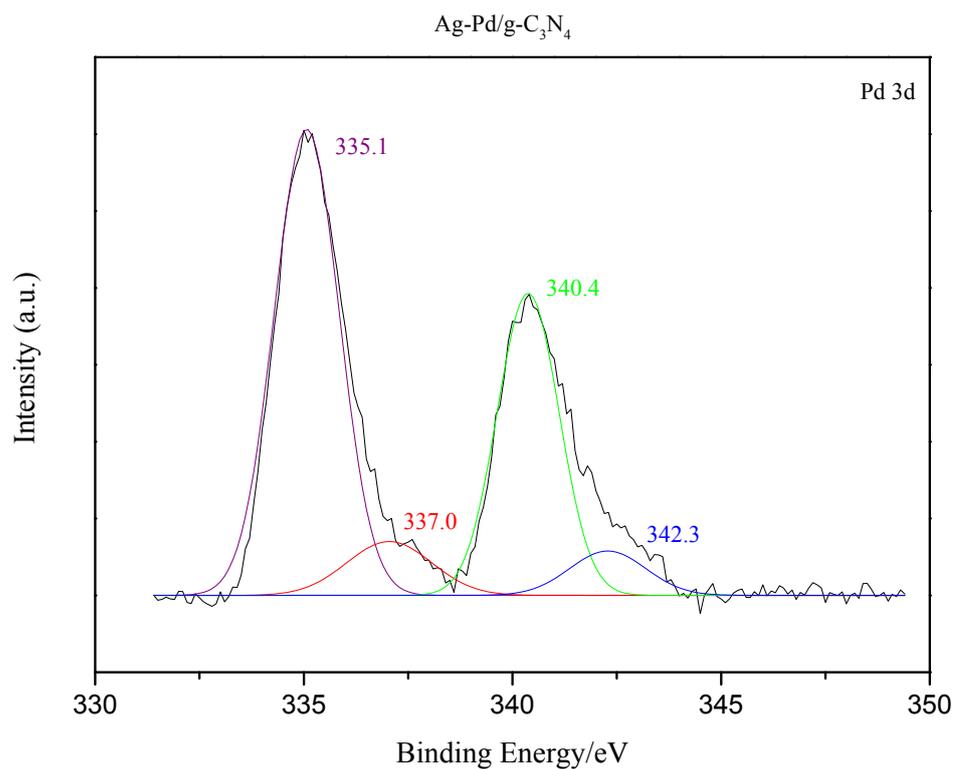


Figure S6. XPS spectrum of Pd 3d peaks of Ag-Pd/g-C<sub>3</sub>N<sub>4</sub>

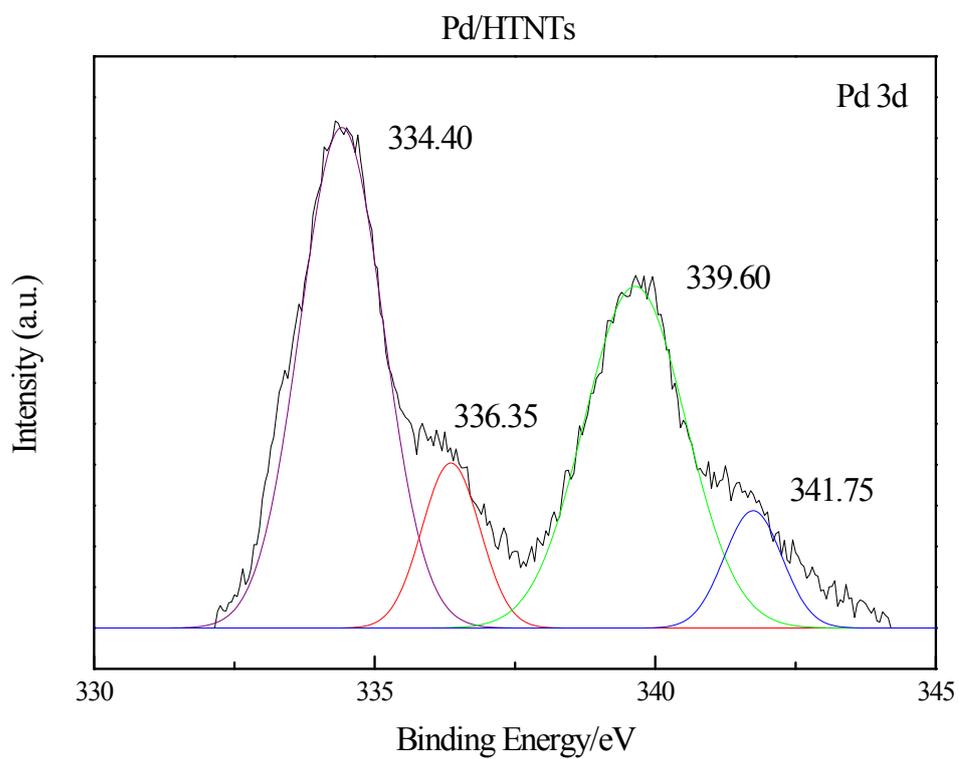


Figure S7. XPS spectrum of Pd 3d peaks of Pd/HTNTs

#### S IV. TEM images

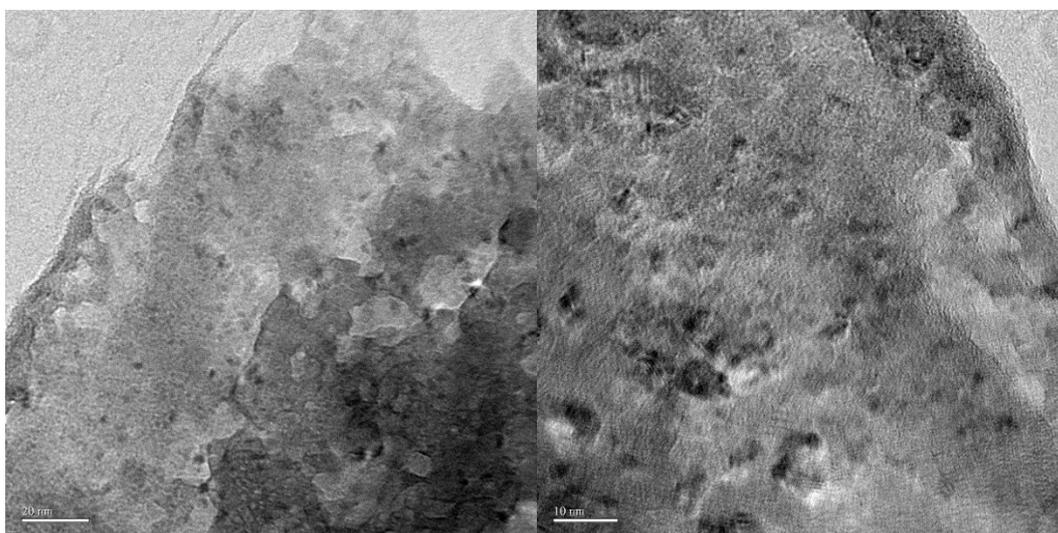
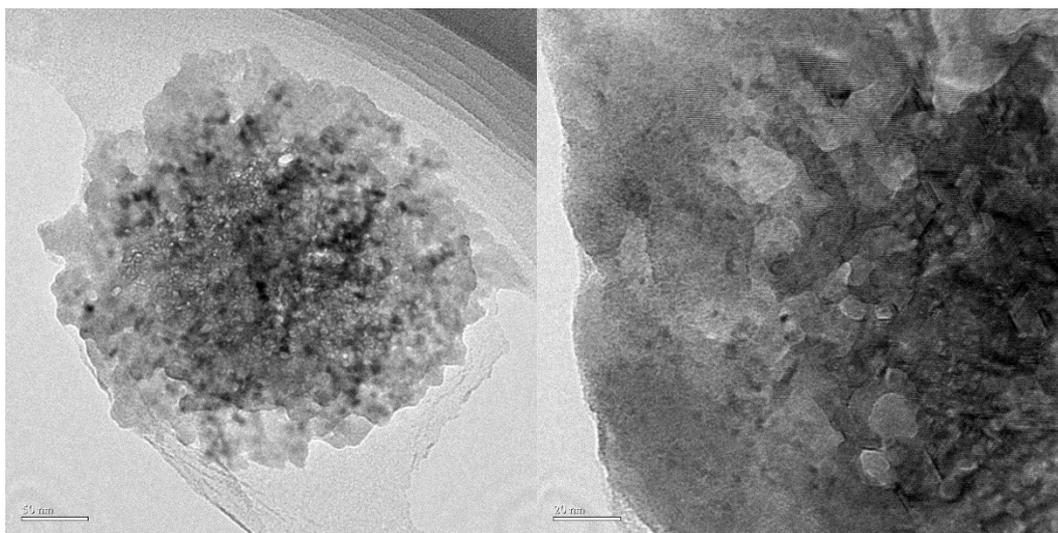


Figure S8. TEM images of Pd/g-C<sub>3</sub>N<sub>4</sub>

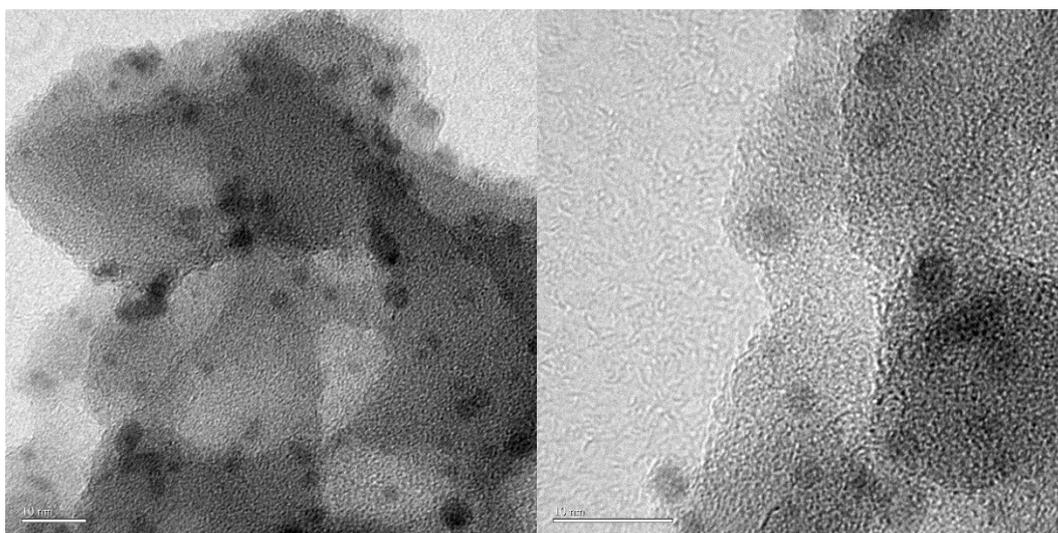


Figure S9. TEM images of Pt-Pd/g-C<sub>3</sub>N<sub>4</sub>

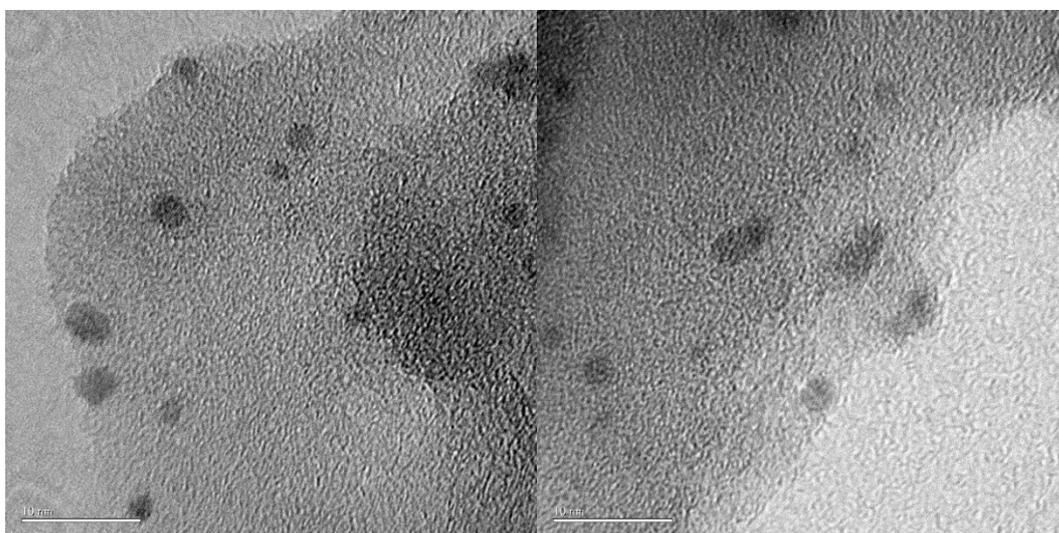
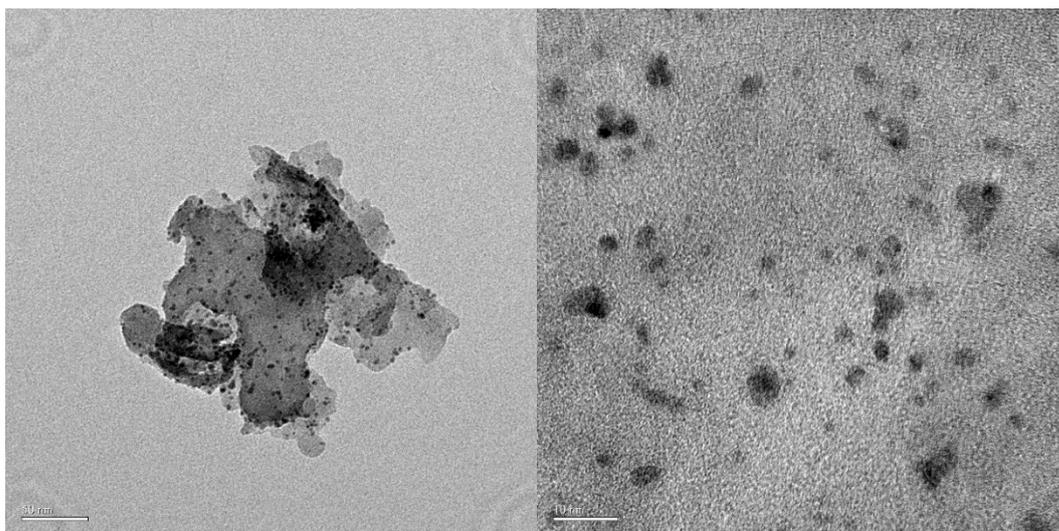


Figure S10. TEM images of Ag-Pd/g-C<sub>3</sub>N<sub>4</sub>

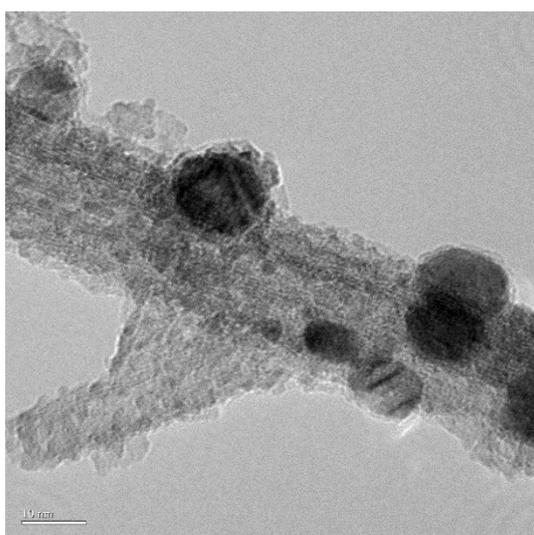


Figure S11. TEM image of Pd/HTNTs

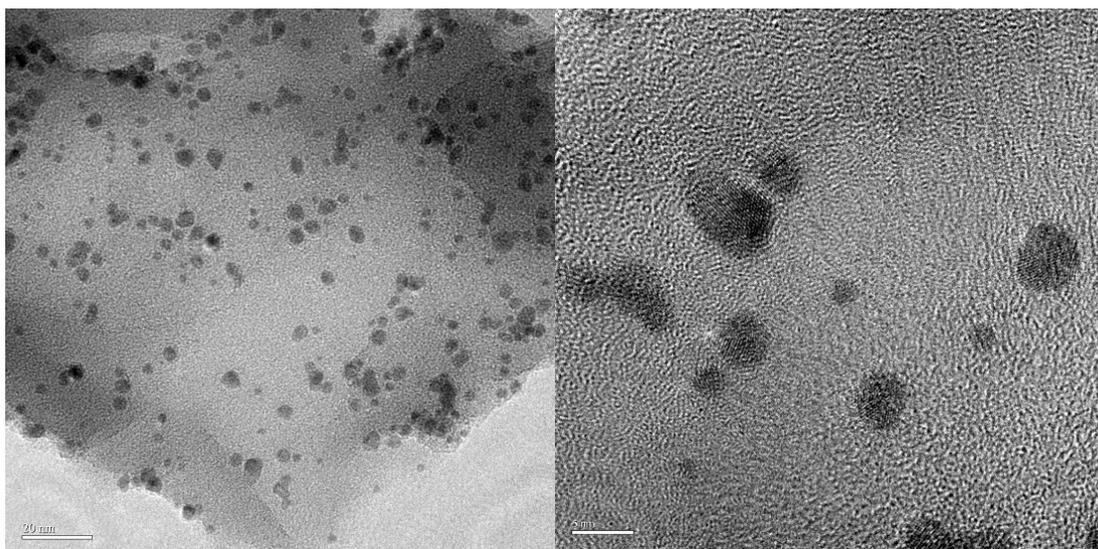


Figure S12. TEM image of Pd/g-C<sub>3</sub>N<sub>4</sub> (After catalytic reaction)

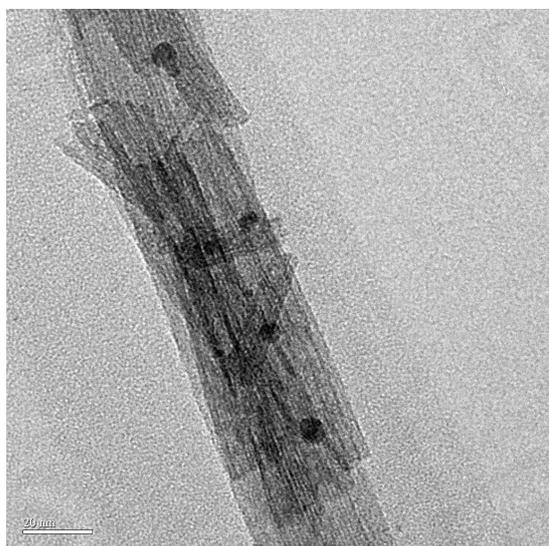


Figure S13. TEM image of Pd/HTNTs (After catalytic reaction)

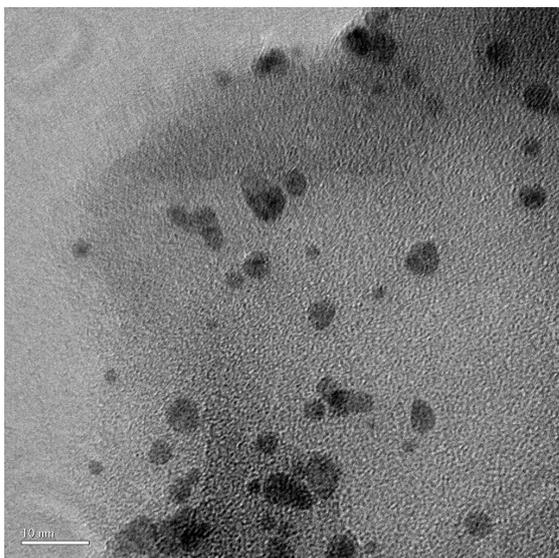


Figure S14. TEM image of Pt-Pd/HTNTs (After catalytic reaction)

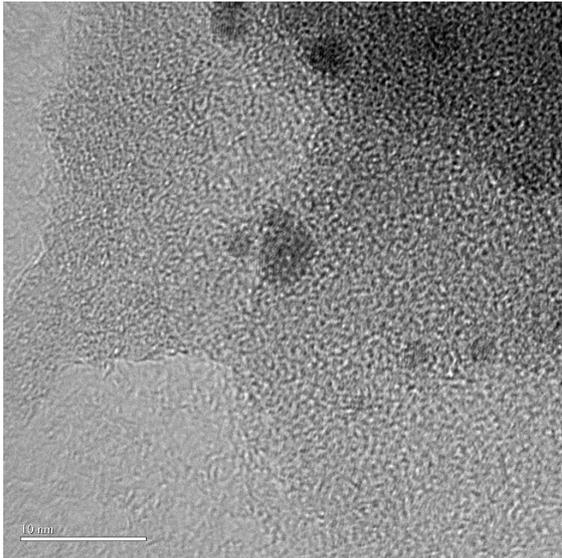


Figure S15. TEM image of Ag-Pd/HTNTs (After catalytic reaction)

## S V. Statistics researches of the size range of metal NPs

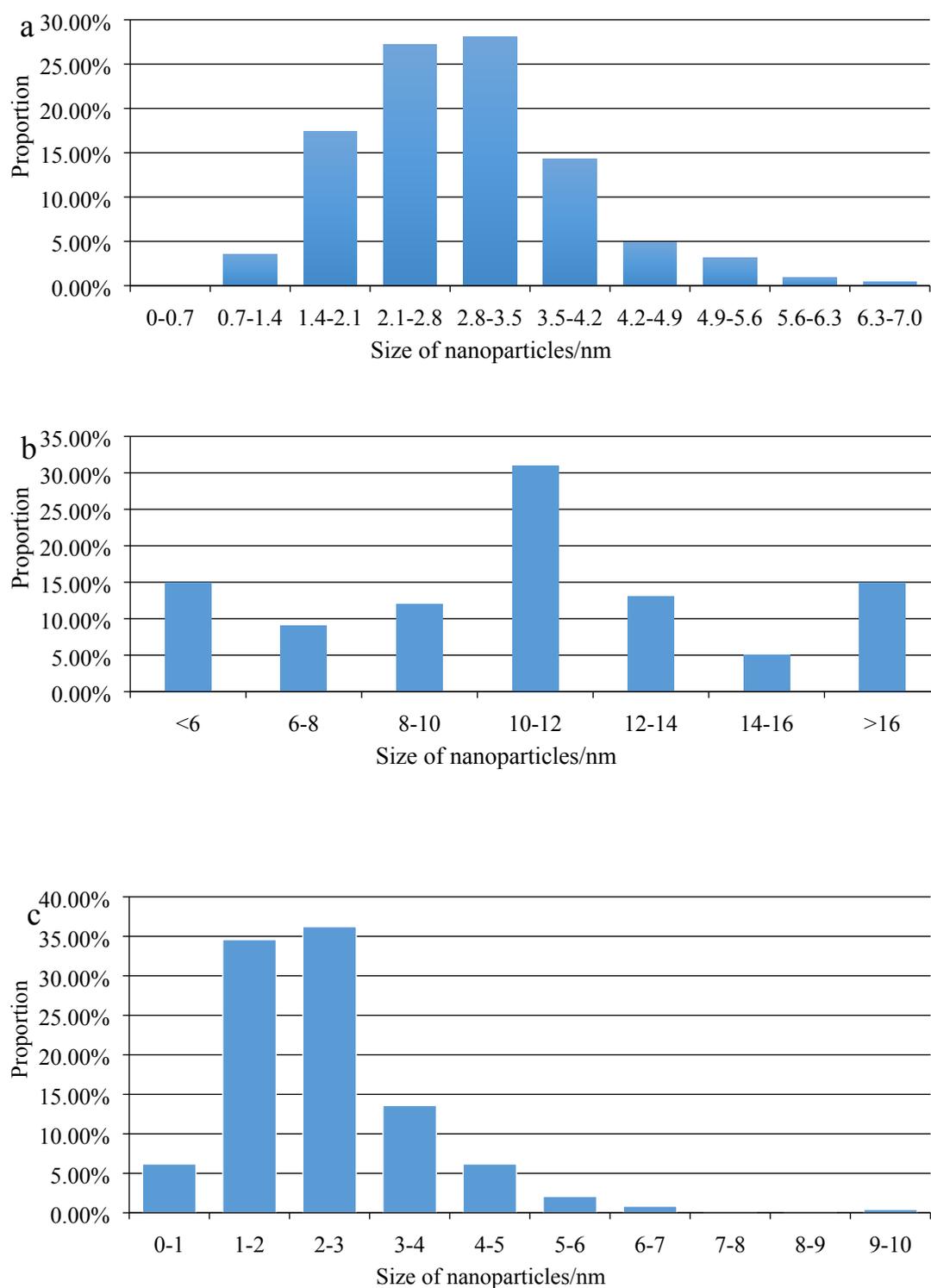


Chart S1. Statistics researches of the size range of metal NPs in Pd/g-C<sub>3</sub>N<sub>4</sub> (a), Pd/HTNTs (b) and Pt-Pd/g-C<sub>3</sub>N<sub>4</sub> (c)

## S VI Kinetic curves

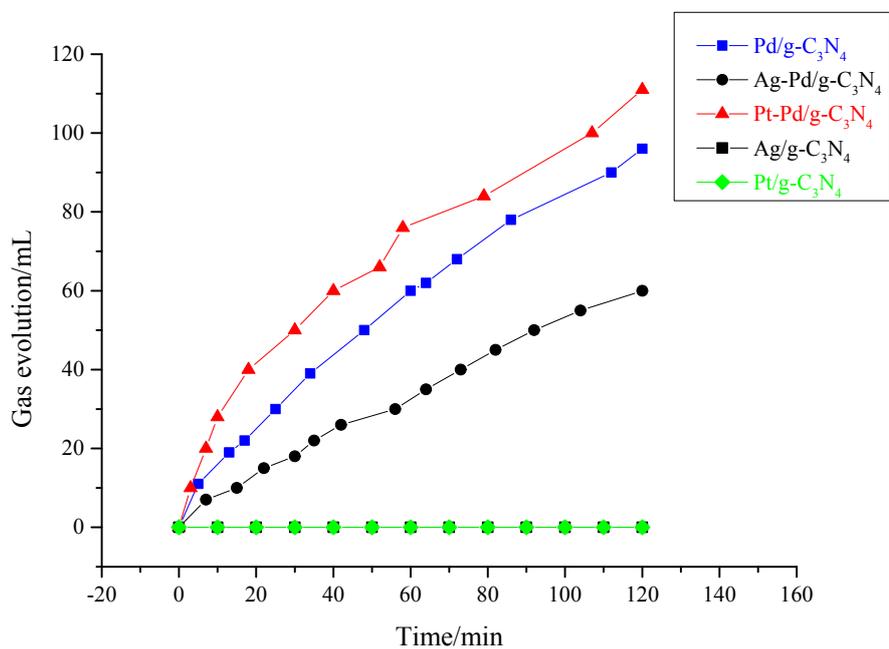


Figure S16. Gas generation of catalysts in first 2 h.

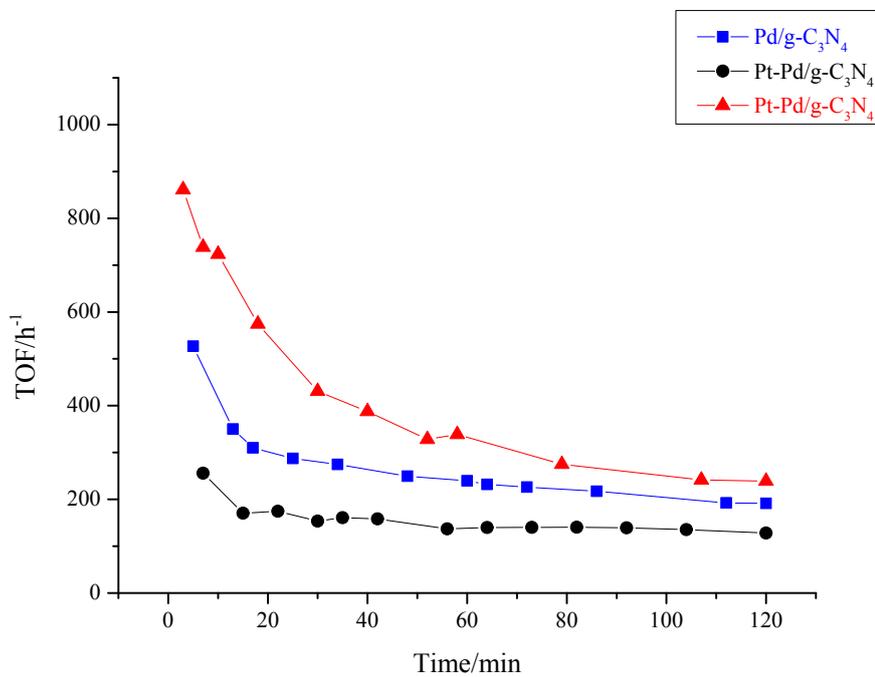


Figure S17. TOF of catalysts in first 2 h.

## S VI. Result of GC

Because the reaction system is SF: FA=9:1, in such alkaline condition,  $\text{CO}_2$  turns into  $\text{HCO}_3^-$

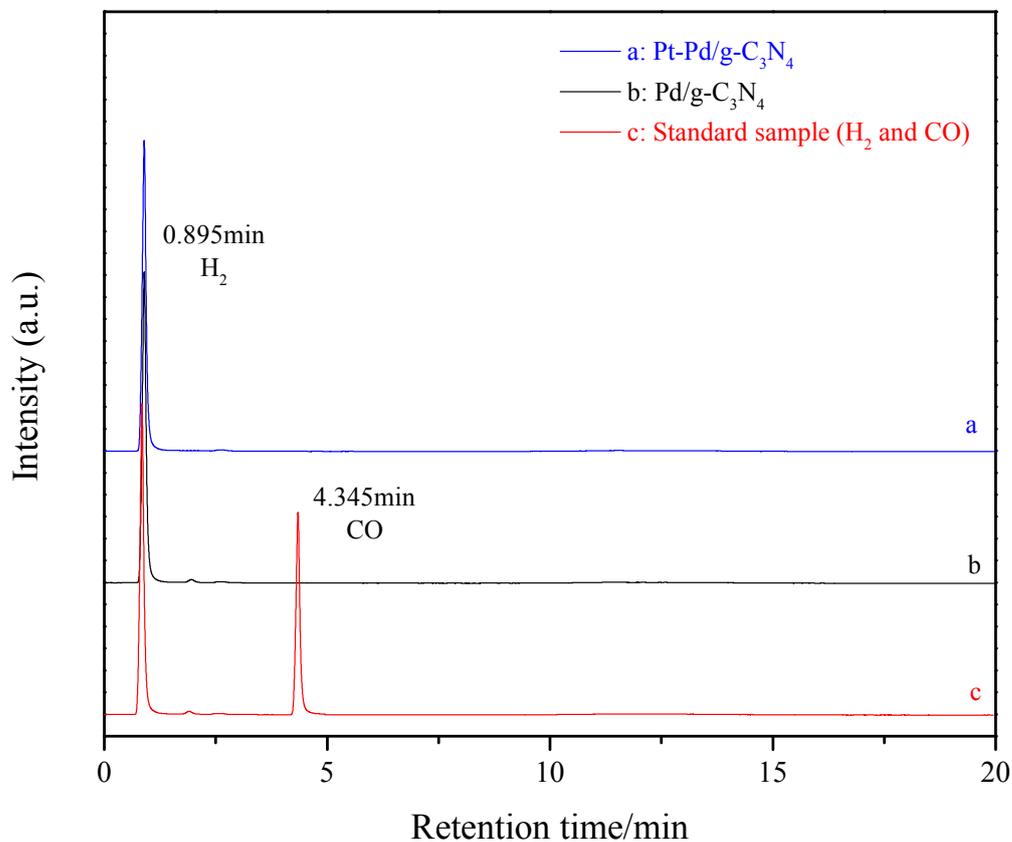


Figure S18. GC results of Pd/g-C<sub>3</sub>N<sub>4</sub> and Pt-Pd/g-C<sub>3</sub>N<sub>4</sub>

### Notes and references

- 1 Noack, K.; Zbinden, H. and Schlogl, R. *Catal. Lett.* 1990, **4**, 145.
- 2 Kumar, G.; Blackburn, J.R.; Albridge, R.G.; Moddeman, W.E. and Jones, M.M. *Inorg. Chem.* 1972, **11**, 296.
- 3 Tressaud, A.; Khairoun, S.; Touhara, H. and Watanabe, N. *Z. Anorg. Allg. Chem.* 1986, **540**, 291.