

## Acceleration of the semi-hydrogenation of alkynes over an N-doped porous carbon sphere-confined ultrafine PdCu bimetallic nanoparticle catalyst

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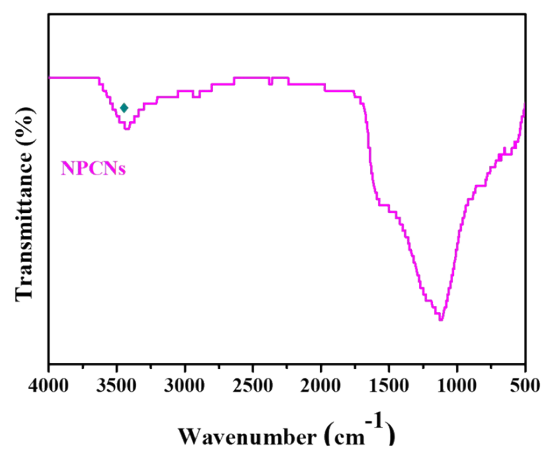
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## **Preparation of the N-doped porous carbon nanospheres**

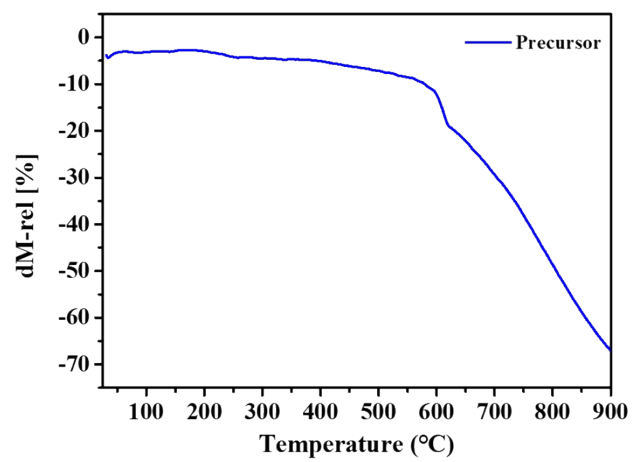
In the typical preparation of NPCNs (N-doped porous carbon nanospheres), Pluronic F127 ((EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>, M<sub>av</sub>=12600, 1.0 g) and DA (C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub>·HCl, PDA, 0.5 g) were dispersed in 100 mL solvents (water:ethanol=1:1) and stirred at 1000 rpm to gain a transparent system at 25 °C. Subsequently, 2.0 mL TMB, was added to the above solution at the stirring rate 500 rpm to form a nano emulsion system. When the above solution was stirred for another 30 min, ammonia (NH<sub>4</sub>OH, 25-28%, 5.0 mL) was added dropwise and stirred at 500 rpm for another 12 h. The formed product was filtered off and washed with water and ethanol in sequence for at least three times. The N-doped porous carbon nanospheres could be obtained after pyrolysis at 350 °C for 3 h and further heating to 800 °C for 2 h under nitrogen atmosphere with a heating rate of 1°C min<sup>-1</sup>.

## **The detail procedure of the H<sub>2</sub>-TPR experiments**

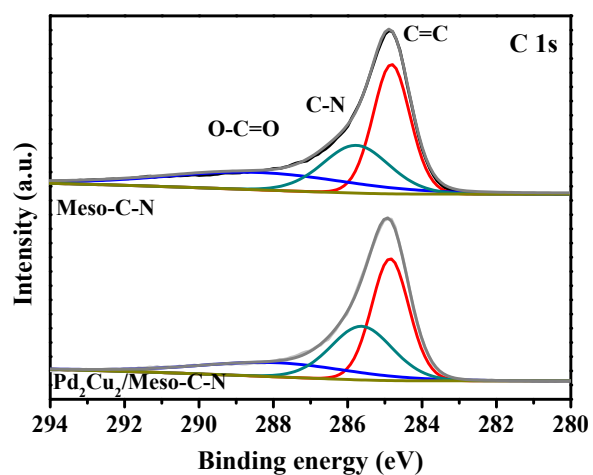
H<sub>2</sub>-TPR experiments were realized with a Micromeritics ChemiSorb 2720 instrument for investigate the redox states of the samples. Firstly, 50 mg catalyst sample were enclosed into a U-shaped quartz tube. The sample was heated to 250 °C at a rate of 10 °C·min<sup>-1</sup>, the catalyst was blown with Argon for 1h. Then the detector temperature was drop to 60 °C, the gas was converted to H<sub>2</sub> gas. Also, the temperature was raised up from 60 °C to 800 °C.



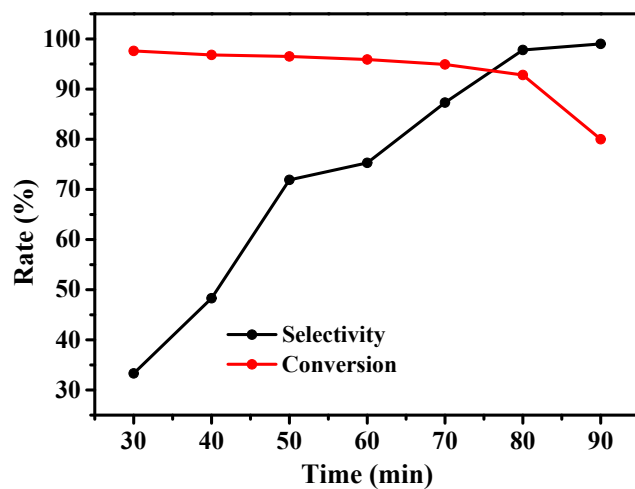
**Figure S1.** FT-IR of scale-up NPCNs.



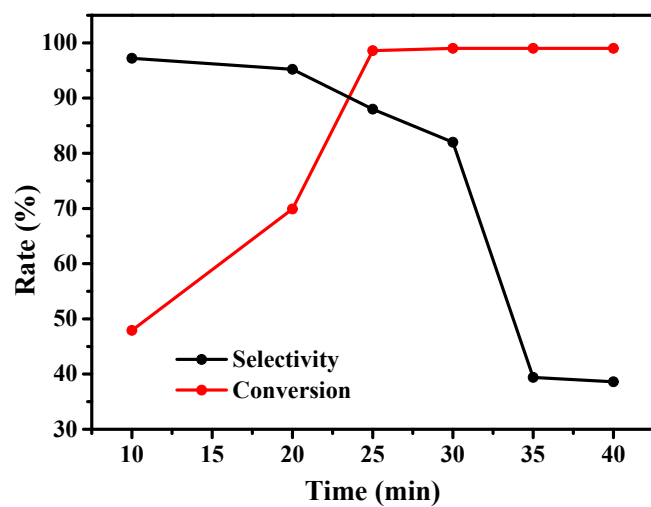
**Figure S2.** TGA of NPCNs precursor.



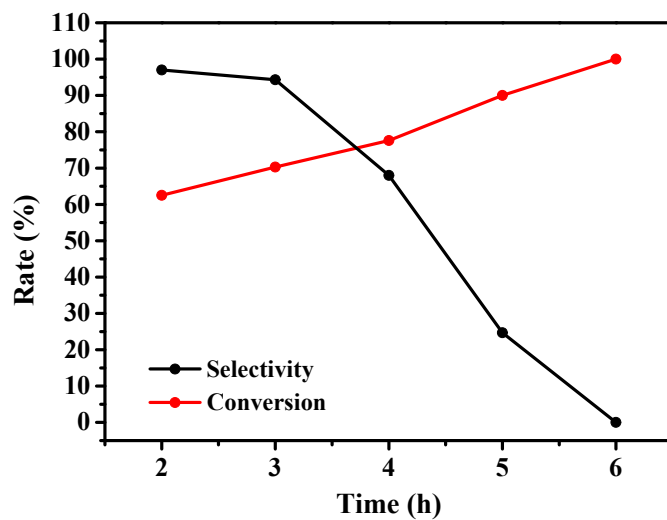
**Figure S3.** High-resolution C 1s XPS spectra of NPCNs (top) and Pd<sub>1.73</sub>Cu<sub>1.66</sub>/NPCNs (bottom).



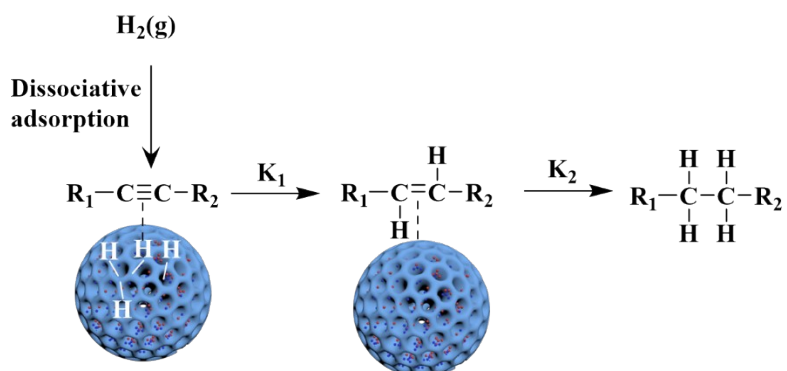
**Figure S4.** The conversion and selectivity of Pd<sub>1.73</sub>Cu<sub>1.66</sub>/NPCNs in semi-hydrogenation of phenylacetylene.



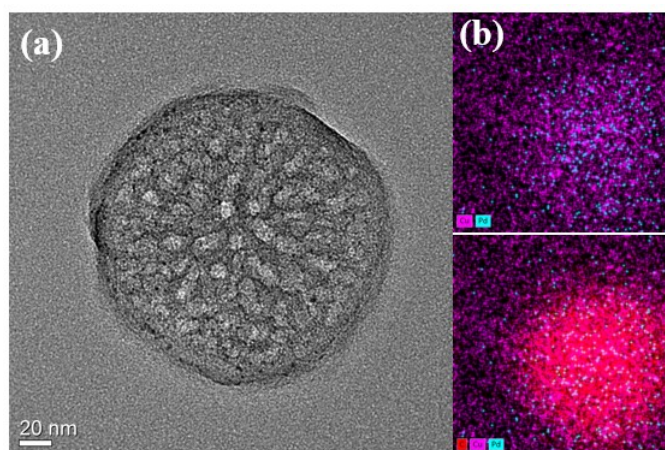
**Figure S5.** The conversion and selectivity of Pd<sub>3</sub>Cu<sub>1</sub>/NPCNs in semi-hydrogenation of phenylacetylene.



**Figure S6.** The conversion and selectivity of Pd<sub>1</sub>Cu<sub>3</sub>/NPCNs in semi-hydrogenation of phenylacetylene.



**Figure S7.** The possible mechanism of PdCu/NPCNs catalyzed hydrogenation of phenylacetylene.



**Figure S8.** TEM, and EDS elemental mapping images of recycled  $\text{Pd}_{1.73}\text{Cu}_{1.66}/\text{NPCNs}$  catalyst.

**Table S1.** Comparison of catalytic activity for the semi-hydrogenation of alkynes with Pd-based catalysts reported in literatures.

Entry	Catalyst	T (°C)	Time (h)	solvent	TOF <sup>a</sup> (h <sup>-1</sup> )	Ref.
1	Pd-NPs@ZIF-8	100	2	Ethanol	121	[1]
2	PtRu/PVP	40	1	Decane	123	[2]
3	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> (c,80)/PdZn <sub>0.6</sub>	40	1.91	Ethanol	234	[3]
4	Pd <sub>1.73</sub> Cu <sub>1.66</sub> /NPCNs	25	0.5	None	419.1	This work

### References:

- [1] Z. Li, M. Hu, B. Liu, J. Liu, P. Wang, J. Yao, X. Zhang, M. He, W. Song, Pd–Zn Alloy Nanoparticles Encapsulated into Mesoporous Silica with Confinement Effect for Highly Selective Semi-Hydrogenation of Phenylacetylene, *ChemCatChem*, 13 (2021) 868-873.
- [2] J.-Y. Ruzicka, D.P. Anderson, S. Gaw, V.B. Golovko, Platinum-Ruthenium Nanoparticles: Active and Selective Catalysts for Hydrogenation of Phenylacetylene, *Aust. J. Chem.*, 65 (2012) 1420-1425.
- [3] L. Yang, X. Chen, Z. Zhou, R. Zhang, L. Li, Z. Cheng, X. Fang, Magnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/Pd and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/Pd-M (M=Ag, Cu and Zn) Catalysts for Selective Hydrogenation of Phenylacetylene, *ChemistrySelect*, 1 (2016) 5599-5606.