

**Pt NPs immobilized on N-doped graphene@Al<sub>2</sub>O<sub>3</sub> hybrid support as  
robust catalysts for low temperature CO oxidation**

Zhimin Jia,<sup>ab</sup> Fei Huang,<sup>ab</sup> Jiangyong Diao,<sup>a</sup> Jiayun Zhang,<sup>ab</sup> Jia Wang,<sup>c</sup> Dang Sheng Su,<sup>a</sup> Hongyang Liu<sup>a\*</sup>

<sup>a</sup> Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

<sup>b</sup> School of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China

<sup>c</sup> Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000, China

\*Corresponding author: *E-mail:* [liuhy@imr.ac.cn](mailto:liuhy@imr.ac.cn) (*Hongyang Liu*); *Fax:* +86 2483970019; *Tel:* +86 2423971577

## 1. Experimental part

### 1.1 Synthesis of N-doped graphene@Al<sub>2</sub>O<sub>3</sub> nanocomposite (Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub>)

The Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub> powder was prepared by chemical vapor deposition using acetonitrile as a precursor and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder as a template.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder and acetonitrile was placed in a quartz boat and then put in the high-temperature and low-temperature zones of the furnace, respectively. Then the high-temperature and low-temperature zones were heated to 800 and 90°C, respectively, under Ar flow at ambient pressure. The samples were then held at this temperature for 20 min under argon for graphene growth.

### 1.2 Synthesis of Pt/Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub> catalyst

The Pt/Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub> catalyst was prepared by a deposition–precipitation method by introducing aqueous H<sub>2</sub>PtCl<sub>6</sub>. Typically, the as-prepared Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub> powder (200 mg) was dispersed in deionized water, and the mixture was heated to 100°C under reflux conditions with stirring, and this was followed by the addition of sodium formate. Then an aqueous solution containing H<sub>2</sub>PtCl<sub>6</sub> (1mg Pt) was added, and the mixture was stirred for one hour at the same temperature. Subsequently, the resulting product was filtered and washed with deionized water several times. After dried, the catalyst was further treated in H<sub>2</sub> atmosphere at 200°C for 2 h and the final sample was denoted as Pt/Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub>. The theoretical Pt weight loading was 1 wt%.

### 1.3 Synthesis of Pt/Al<sub>2</sub>O<sub>3</sub>-800 catalyst

The Pt/Al<sub>2</sub>O<sub>3</sub>-800 catalyst was prepared by the process as above mentioned. The Al<sub>2</sub>O<sub>3</sub>-800 was calcined at 800°C using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder under Ar. The Pt loading of the Pt/Al<sub>2</sub>O<sub>3</sub>-800 catalyst was 1 wt% for comparison.

### 1.4 Catalytic CO oxidation reaction

CO oxidation was carried out at ambient pressure in a temperature programmed mode with a rate of 2 K min<sup>-1</sup>. Before the reaction, the catalysts were reduced in H<sub>2</sub> at 200°C for 1 h. Typically, the gas reactant contained 1 vol% CO and 0.5 vol% O<sub>2</sub> with a balance of He. The catalyst loading is 50 mg. The reactants and products were analyzed by an online gas chromatography (Agilent 7890) using a HP-5 capillary column connected to FID and a Carbo Plot capillary column connected to TCD.

### 1.5 Direct dehydrogenation reaction of n-butane

The catalytic performance for the DDH reaction of n-butane was evaluated in a fixed-bed stainless steel micro-reactor with a quartz lining under ambient pressure at 450°C using 50 mg catalyst plugged in with quartz wool at the center of the reactor. The catalysts were heated to 450°C and fed with the gas reactant contained 2% H<sub>2</sub>, 2% n-C<sub>4</sub>H<sub>10</sub> and a balance of He (total flow rate of 15 mL min<sup>-1</sup>). The effluent mixture gas was analyzed by on-line gas chromatography (Agilent 7890 with a FID and a TCD detector).

### 1.6 Characterizations

Nitrogen adsorption-desorption data were measured with a Micromeritics ASAP 2020 analyzer at 77 K. Prior to the measurements, the samples were degassed at 120°C for 12 h; The oxidation stability tests were carried out by a thermogravimetric analyzer (Netzsch 449 F3); Transmission electron microscopy (TEM) and the high-resolution transmission electron microscopy (HRTEM) images were obtained using a FEI TECNAI G2 F20 (200 kV) high-resolution transmission electron microscope; X-ray diffraction (XRD) patterns of supported Pt NPs catalysts were characterized by an X-ray diffractometer (D/MAX-2400) with Cu K $\alpha$  source at a scan rate of 2° min<sup>-1</sup>; X-ray photoelectron spectroscopy (XPS) analysis was performed with a Thermo VG Scientific ESCALab220i-XL Microprobe instrument using Al K $\alpha$  radiation as the X-ray source. The binding energy of the element was calibrated using a C 1s (284.6 eV) as a reference.

## 2. Figures

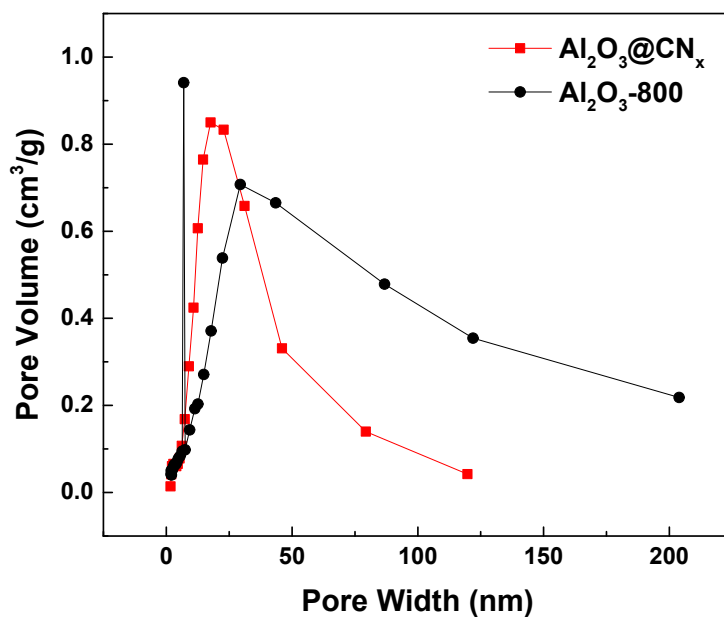


Fig. S1 Pore size distributions of the supports.

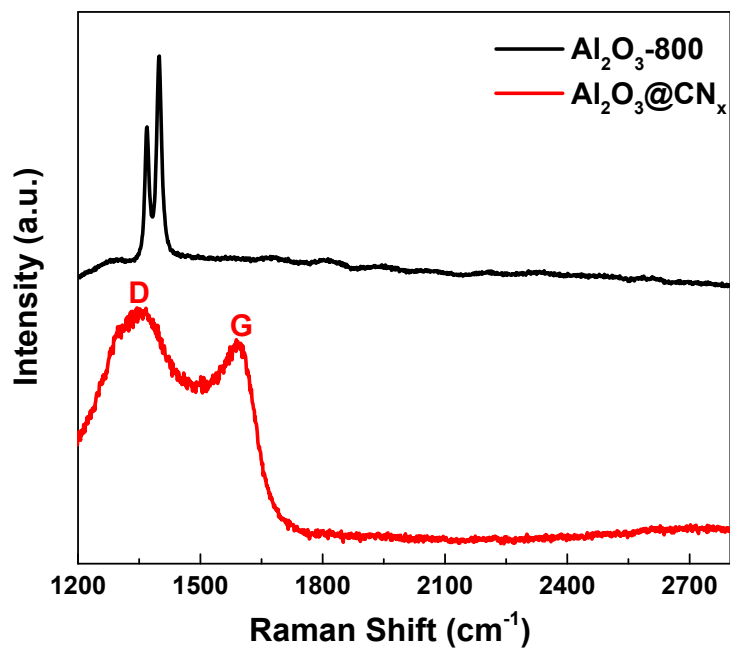


Fig. S2 Raman spectra of  $\text{Al}_2\text{O}_3\text{-800}$  and  $\text{Al}_2\text{O}_3@\text{CN}_x$ .

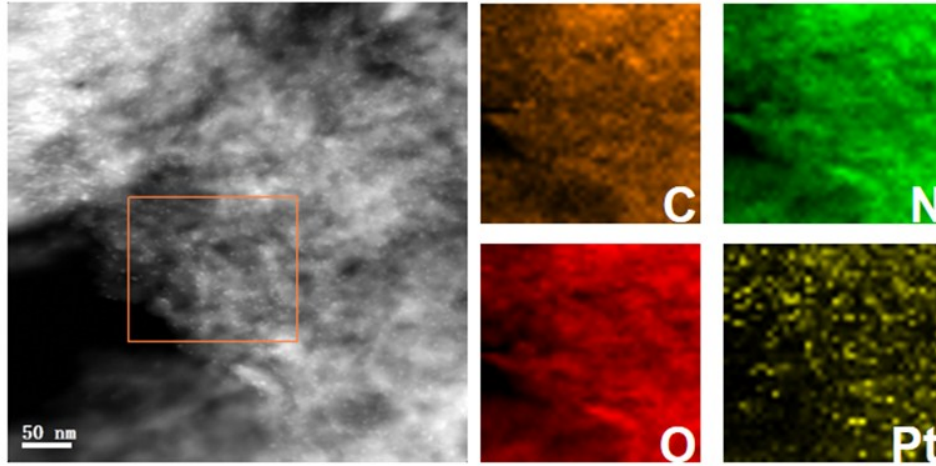


Fig. S3 EDX elemental maps of Pt/Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub>.

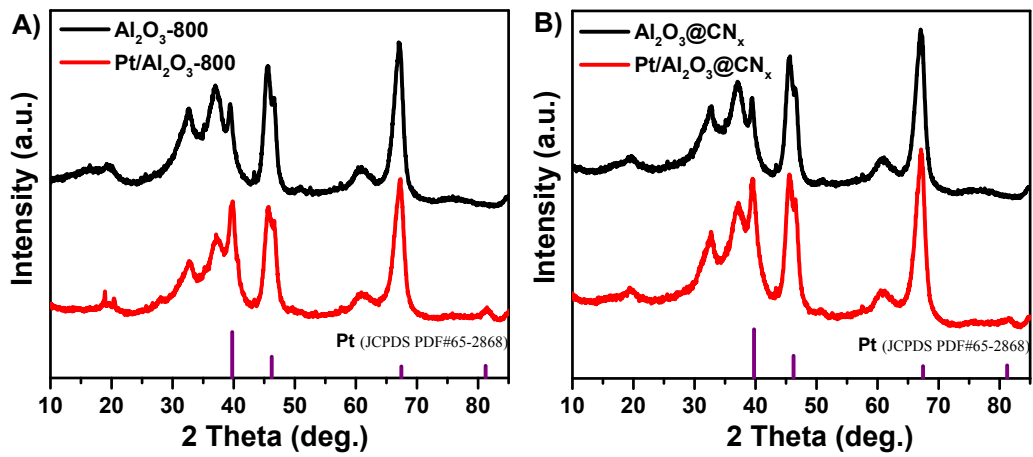


Fig. S4 XRD patterns of the fresh A) Pt/Al<sub>2</sub>O<sub>3</sub>-800 and B) Pt/Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub>.

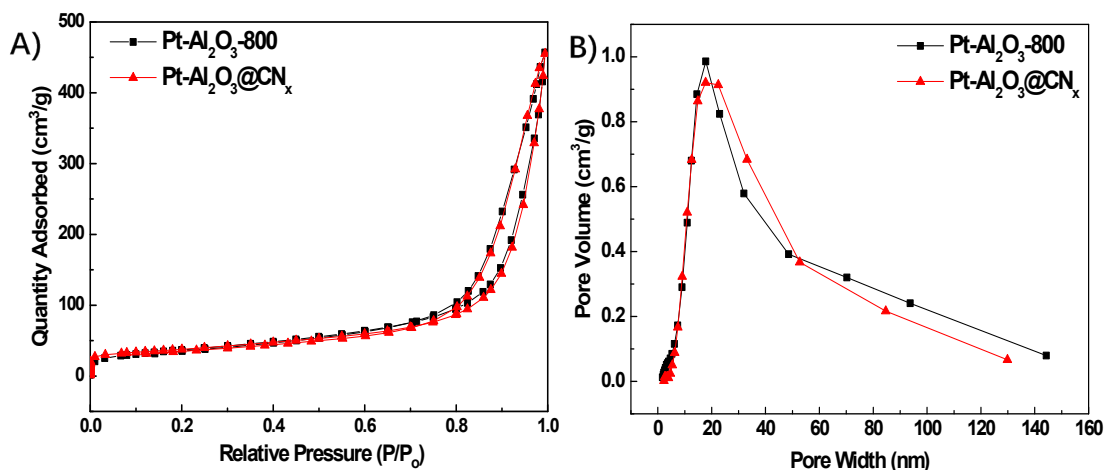


Fig. S5 Pore structure characterization of Pt/Al<sub>2</sub>O<sub>3</sub>-800 and Pt/Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub>. A) N<sub>2</sub> adsorption/desorption isotherms. B) Pore size distributions.

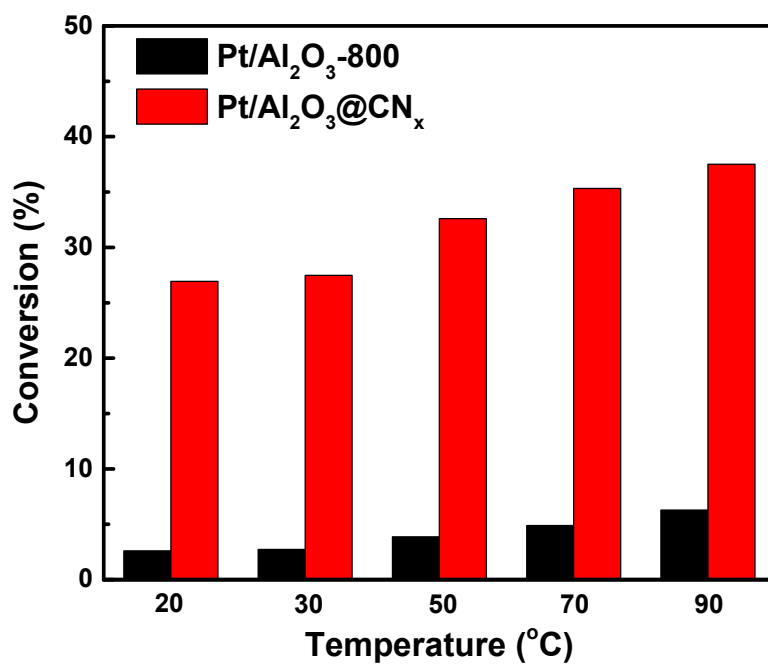


Fig. S6 Temperature dependence of the CO oxidation reaction for Pt/Al<sub>2</sub>O<sub>3</sub>-800 and Pt/Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub> catalysts.

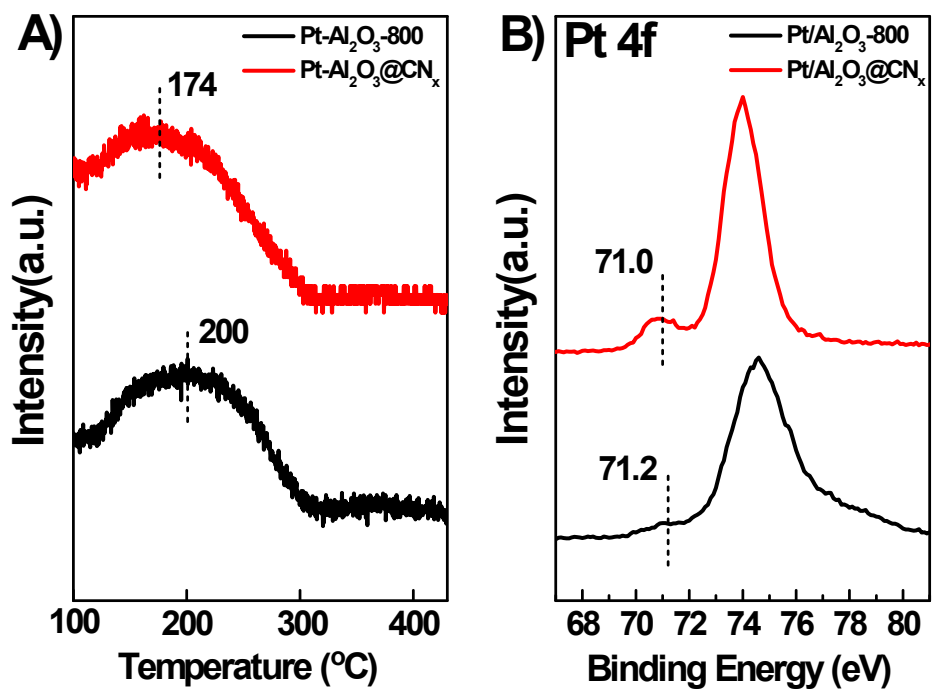


Fig.S7 A) CO TPD spectra and B) Pt 4f XPS spectra of Pt/Al<sub>2</sub>O<sub>3</sub>-800 and Pt/Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub> catalysts.

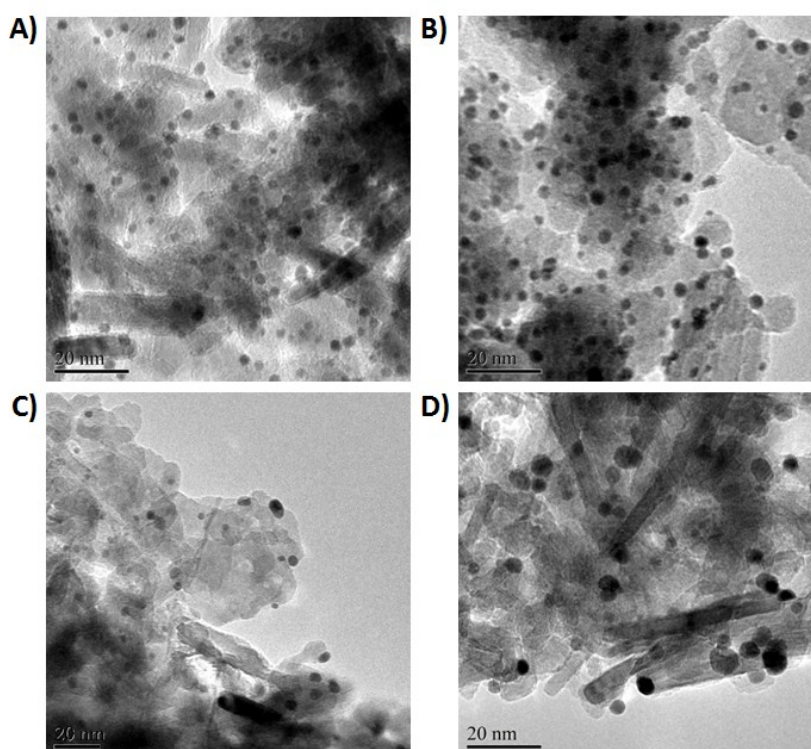


Fig. S8 TEM images of fresh and used (A&B) Pt/Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub> and (C&D) Pt/Al<sub>2</sub>O<sub>3</sub>-800 catalysts, respectively.

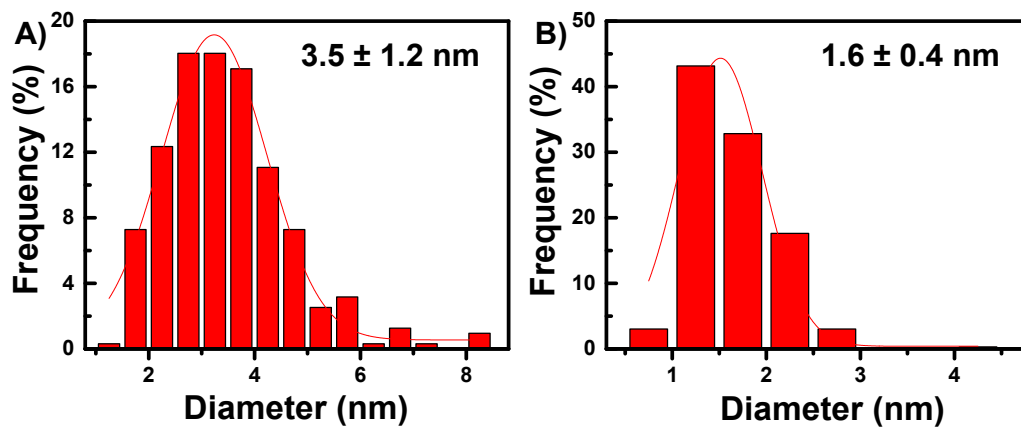


Fig. S9 The corresponding particle size distribution histograms of Pt/Al<sub>2</sub>O<sub>3</sub>-800 (A) and Pt/Al<sub>2</sub>O<sub>3</sub>@CN<sub>x</sub> (B) catalysts after the CO oxidation reaction.