Electronic Supporting Information for

Palladium Particles Dispersed on the Hollow Structural Support Improves the CO_2 Conversion

Changsong Shi, Ruiming Xu, Ting Suo, and Ruirui Yun*

The key laboratory of functional molecular solids Ministry of Education, Anhui Carbon Neutrality Engineering Center, College of chemistry and Materials Science, Anhui Normal University, Wuhu 214001, P. R. China.

S1. Materials and Instrumentation

Tetraethyl silicate, TEOS (adddin, ≥ 99%), dopamine hydrochloride (adddin, 98%), palladium dichloride (adddin, Pd ≥ 59.8%), phenyl ethylene oxide (Shanghai Acme Biochemical Co., Ltd, 98%), tetrabutylammonium bromide (TBAB, adddin, AR, 99%), hydrofluoric acid (ACMEC, AR, ≥ 40%), Ethyl acetate (Sinopharm Chemical Reagent Co., Ltd., AR, 99.5%), ammonia (Sinopharm Chemical Reagent Co., Ltd., AR, 25.0%~28.0%), ethanol (Sinopharm Chemical Reagent Co., Ltd., AR, ≥ 99.7%), deionized water (resistance 18.25 M Ω · cm) from Millipore system.

Powder X-ray diffraction (PXRD) data were collected at room temperature using Cu Kα radiation (λ = 1.5418 Å) with a Smart Lab X-ray diffractometer. Transmission electron microscopy (TEM) observations were obtained on a Hitachi HT7700 instrument at an electron accelerating voltage of 100 kV. Scanning electron microscopy (SEM) was carried out with Hitachi 8100, operating voltage: 5 kV. JEOL-2011 was subjected to high-resolution transmission electron microscopy (HR-TEM) and EDS measurement. Raman experiments were performed using an argon laser (λ = 532 nm) of the LABRAMHR spectrometer (France) as the excitation source. The Pd content in the catalyst was determined on an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). Meanwhile, the BET adsorption isotherms of the samples at 77 K were determined with a Micrometrics ASAP 2020. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a thermal high-performance electron spectrometer ESCALAB 250. The excitation source was monochromate Al Ka (hν = 1486.6 eV). The post-reaction products were analyzed and identified by Thermo

gas-mass spectrometer (GC-MS).

S2. Preparation of samples

Synthesis of SiO_2 templates: Silica microspheres have been prepared using the traditional Stöber method. Typically, 100 ml of ethanol, 6 ml of deionized water and 6 ml of ammonia were thoroughly mixed. Then gradually add 3 ml of tetraethyl silicate. At 40 ° C, mix and stir 5 h, The resulting suspension centrifugal, with ethanol and water washing several times, 60 ° C vacuum drying, to get even size, well dispersion of silica microspheres.

Synthesis of SiO_2@Pd-DA: Firstly, the ultrasound was evenly dispersed in a 300 mg mixture of SiO_2 75 ml ethanol, 25 ml deionized water and 2 ml ammonia to form solution A; Then, 44 mg of dopamine hydrochloride is dissolved in 15 ml of deionized water to formulate solution C, and 10 ml of palladium dichloride is dissolved in the same amount of water to create solution B. Stirring at room temperature for 30 minutes while adding the C solution gradually to the B solution. Add the aforementioned mixture to solution A, stir for 24 hours at room temperature, and subsequently centrifugally collect precipitate using ethanol. Deionized water = 1:1 mixed solvent, numerous rounds of washing, and several hours of drying in a 70 ° C vacuum oven. The brownish-black powder is produced after grinding.

Synthesis of Pd/NS: Typically, the 300 mg SiO_2@Pd-DA sample was placed in a ceramic boat dish and placed in a tube furnace. Under argon atmosphere, the flow rate was 60 mL/min, the heating speed was 5 °C/min, heated to 900 °C, and after 2 h, annealed to room temperature under Ar atmosphere to obtain black powdered Pd/NS.

Synthesis of Pd/NHS: 100 mg of Pd/NS was placed in a certain amount of preconfigured 15% HF for 24 h, and the silicon template was removed to obtain Pd/NHS.

Synthesis of NHS: NHS was synthesized using the same procedure as Pd/NHS, with the exception that palladium dichloride was not employed.

S3. Procedure for the Catalytic Cycloaddition Reaction of Carbon Dioxide with Epoxides

Typically, an autoclave was filled with 5 mg of catalyst, 0.1 mmol TBAB, 3 mL of MeCN, and 0.22 mmol of substrate. By aerating CO_2 three times, the reaction can be carried out in a pure CO_2 environment. 100 ℃ and 5 bars of pressure were present for five hours. Following the reaction, the combined solution was centrifuged, the reaction product was extracted, 2 mL of the supernatant was added to 2 mL of ethyl acetate, and the mixture was thoroughly shaken. The above ethanol was then used to extract a 150 μL sample via a syringe. Finally, GC-MS came to a conclusion.

S4. Turnover Frequency Calculation（TOF）

Loading capacity：1.6 %

Particle Average: 7.36 nm

Dispersion: D=1/d=1/7.36=0.136

Catalyst amount：5 mg

Substrate amount：0.22 mmol

Catalysis time：20 minutes

Conversion percent：33 %

M: Amount of palladium on the catalyst surface

N: Total conversion rate of substrate in 20 minutes

M= (5/1000) *0.016*0.136/106=1.026*10^{-7}

N= (0.22/1000) *0.33=0.73*10^{-4}

TOF=N/(M*Time) =0.73*10^{-4}/ (1.026*10^{-7}*20) =35.575 min^{-1}=2134.5 h^{-1}

S5. Characterization of the samples

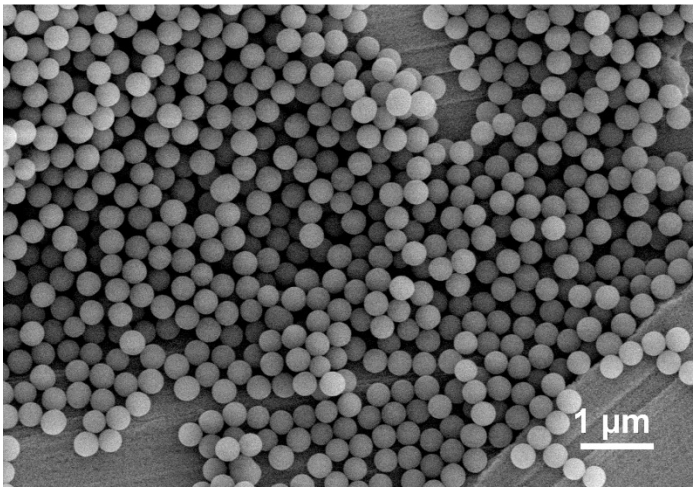

Figure S1. The SEM image of SiO_2.

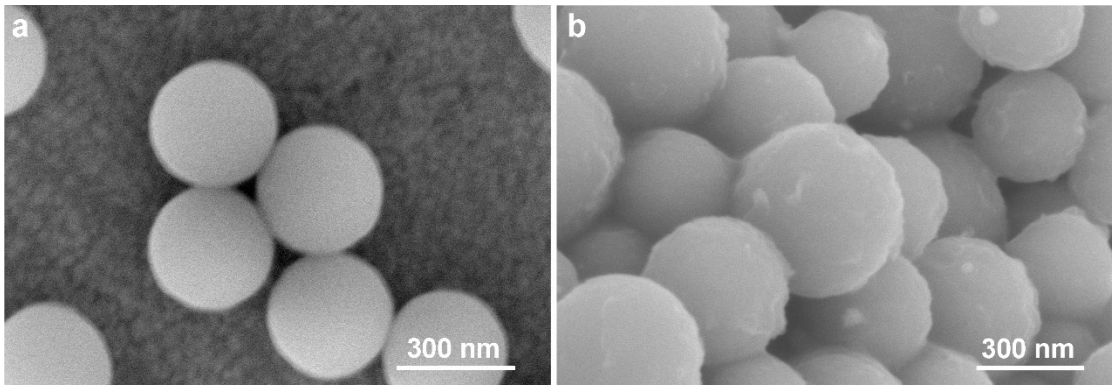

Figure S2. The SEM images of SiO_2 and SiO_2@Pd-DA, respectively.

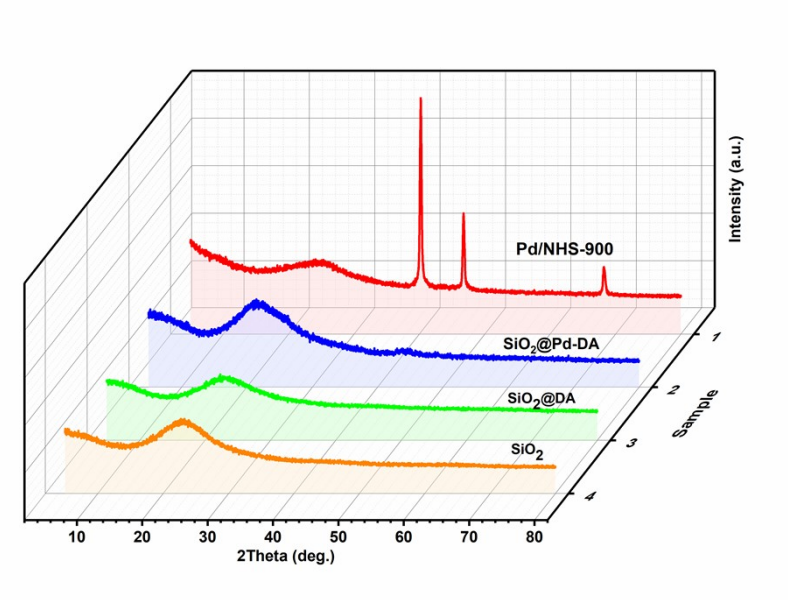

Figure S3. The PXRD patterns of the samples.

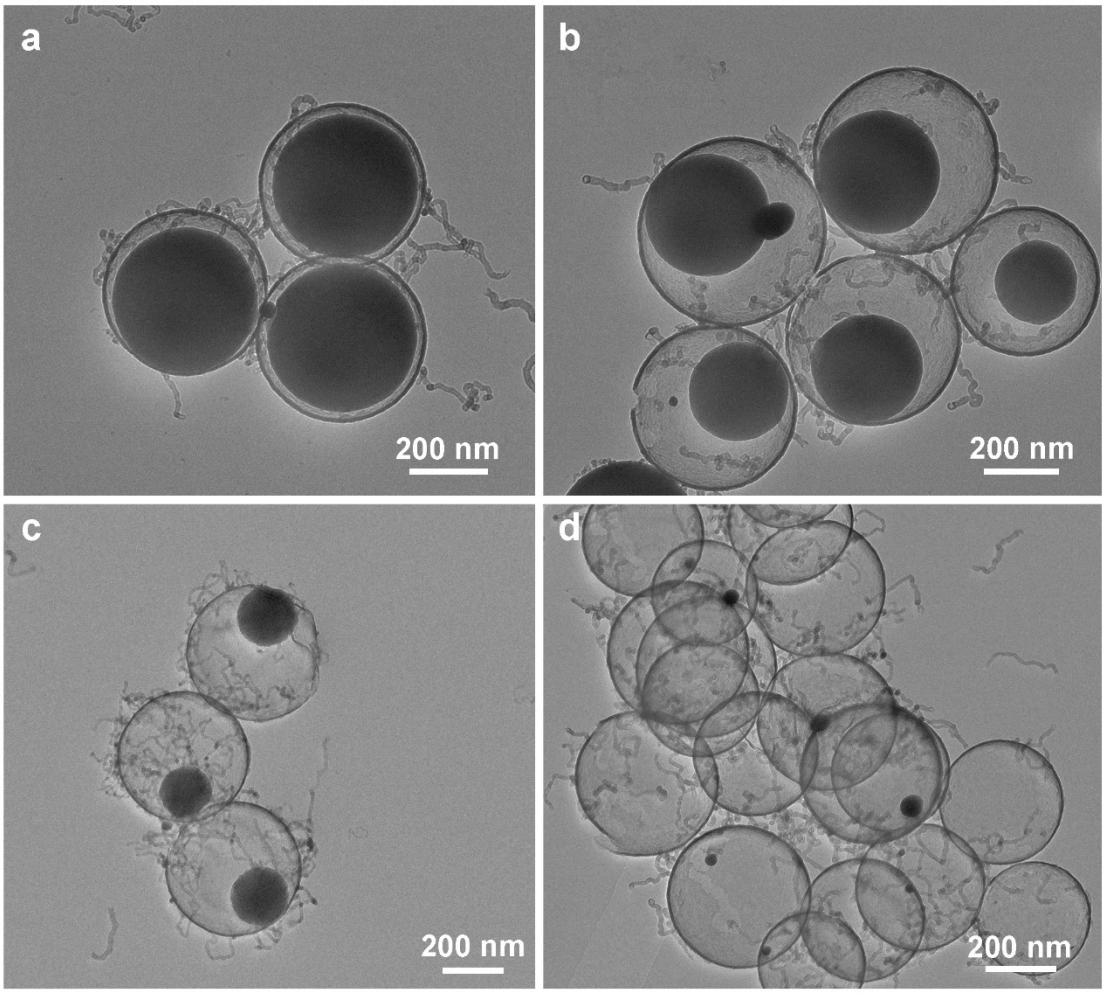

Figure S4. The TEM images schematic the forming of Pd/NHS by acid etching.

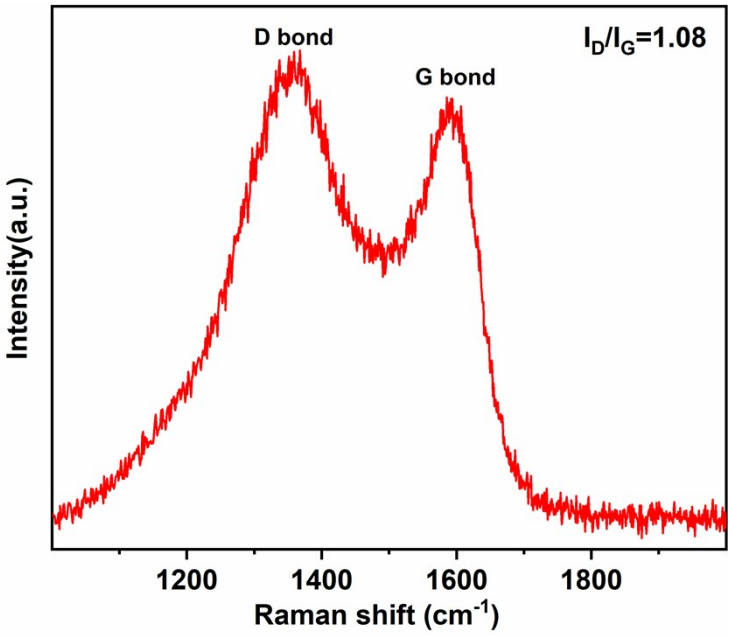

Figure S5. The Raman spectra of Pd/NHS.

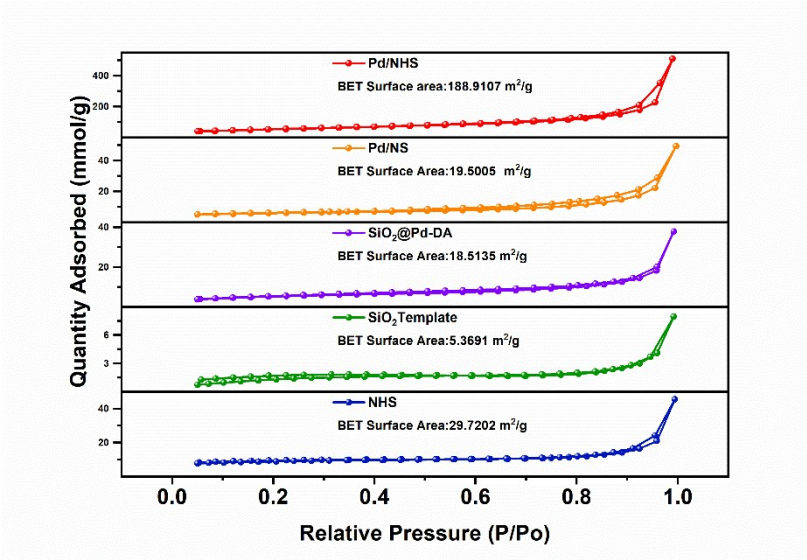

Figure S6. The Nitrogen adsorption isotherm curves of the samples.

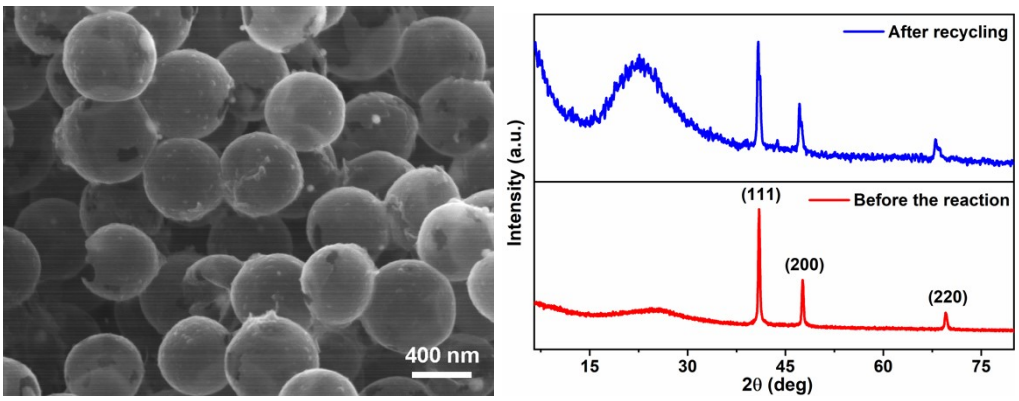

Figure S7. The SEM image and XPD patterns of catalyst after 8 times recycling.