Electronic Supplementary Information

Oriented Mesoporous g-C$_3$N$_4$ Nanorods as Multifunctional Supports of Ultrafine Metal Nanoparticles: Hydrogen Generation from Water and Reduction of Nitrophenol with Tandem Catalysis in One Step

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Chemicals: Tetraethylorthosilicate (TEOS) were purchased from Acros, and other chemicals were purchased from Sigma-Aldrich. All chemicals were used as received.

Synthesis of SBA-15 nanorods: SBA-15 nanorods were prepared according to a modified method reported previously.[ref5] Briefly, 4.0 g of triblock copolymer Pluronic P123 was added into 150 g of 1.8 M HCl aqueous solution, which was stirred at 35 °C overnight. Then, 8.50 g of TEOS was added to this solution under vigorous stirring within 3 min. And then the mixture solution was kept under static conditions at 35 °C for 48 h. The solid products were collected by filtration, washed with water and ethanol, and calcined at 550 °C for 4 h in air.

Synthesis of m-CNR: 1 g of SBA-15 nanorods was homogeneously dispersed into 50 mL of water via sonication and stirring over night. 0.5 g of cyanamide was added into the dispersion, which was further heated at a temperature of 80 °C for 24 h to remove the water. The resulting white powder was heated at a temperature of 600 °C for 4 h (ramp: 2.5 °C min^{-1}) under the protection of N_2. The as-obtained yellow powder was dispersed into 50 mL of water via sonication and stirring over night, followed by the addition of the 50 mL of 4 M NH_4HF_2 solution. The mixture was stirred for 24 h. m-CNR were recovered via centrifugation, washed thoroughly with water several times, and redispersed into 100 mL of water via bath-sonication (100 W, 30 min). The suspension was kept still for 24 h. After that, the supernatant with a concentration of about 3 mg/ml was collected for further use. The solid powders for further characterization were separated via centrifugation and washed thoroughly with a certain amount of ethanol, followed by the removal of solvent in vacuum at 60 °C overnight,

Impregnation of noble metal NPs (3 wt%): Aqueous solution of H_2PtCl_6 and $HAuCl_4$, and a mixed solution of $PdCl_2$ with 1 M HCl were used as precursor for the impregnation of Pt, Au and Pd NPs inside the mesochannels of m-CNR. Briefly, 5 mL of m-CNR dispersion (15 mg of m-CNR) and a known amount of metallic salts solution containing 0.45 mg of corresponding metal component were added into 15 mL of water, and were stirred overnight. And then, 5 mL of 0.1 M $NaBH_4$ were added dropwise to this suspension. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and finally redispersed into 13.5 mL of water for further use and characterization. The solid powders for further characterization were separated via centrifugation and washed thoroughly with a certain amount of ethanol, followed by the removal of solvent in vacuum at 60 °C overnight,

Photodeposition of Au NPs (3 wt%): 5 mL of m-CNR dispersion (15 mg of m-CNR), and a known amount of solution of $HAuCl_4$ solution containing 0.45 mg of gold were added into 15 mL of water and were stirred overnight. Afterwards, 2 mL of TEA were added to this suspension, followed by irradiated under a 300 W Xe lamp for 30 min under magnetic stirring. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and finally redispersed into 13.5 mL of water for further use and characterization. The solid powders for further characterization were separated via

centrifugation and washed thoroughly with a certain amount of ethanol, followed by the removal of solvent in vacuum at 60 °C overnight,

Catalytic reduction of 4-nitrophenol: In a typical reaction, 4.5 mL of catalyst dispersion, 0.3 mL of 1 mM 4-nitrophenol solution was mixed under stirring. 0.2 mL of freshly prepared aqueous solution of NaBH$_4$ (0.15 M) was then added. This reaction was usually completed within 10 min. The conversions were demonstrated by monitoring the change in UV/Vis absorption and GC-MS spectra. Without the presence of either catalyst, reductant, or the noble metal NPs, the reaction does not proceed.

Photocatalytic reduction of 4-nitrophenol: In a typical reaction, 4.5 mL of m-CNR-Pt-2nm dispersion, 0.3 mL of 1 mM 4-nitrophenol solution and 0.5 mL of TEA was mixed with constant magnetic stirring. The mixture was irradiated under a 300 W Xe lamp and a water filter for 4 h under magnetic stir. The wavelength of the incident light was controlled by using an appropriate cut-off filter. The temperature of the reactand solution was maintained at room temperature by a water bath during the reaction. The conversions were demonstrated by monitoring the change in UV/Vis absorption and GC-MS spectra.

Characterization: XRD measurements were performed on a Bruker D8 diffractometer operating at the Cu K$_{\alpha 1}$ radiation. UV-vis spectra were recorded using a Varian Cary 500 Scan UV-vis system equipped with a Labsphere diffuse reflectance accessory. FTIR spectra were recorded on a BioRad FTS 6000 spectrometer. Transmission electron microscopy (TEM) was recorded on a Zeiss 920 microscope and Scanning electron microscopy (SEM) was performed on a LEO 1550-Gemini instrument.
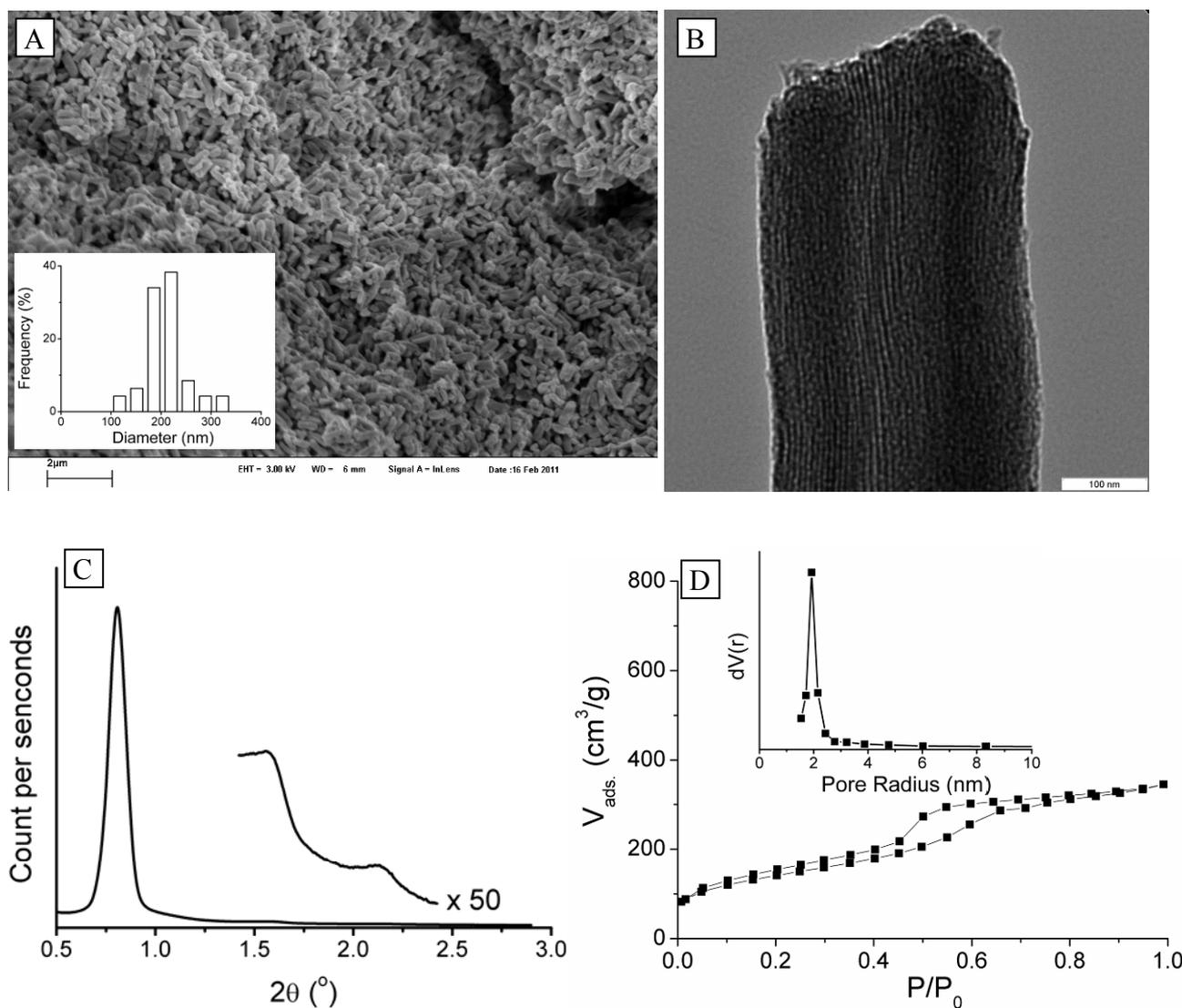
Figure S1 SEM (A) and TEM (B) images, Small-angle X-ray scattering (SAXS) pattern (C) and nitrogen adsorption-desorption isotherm (D) of SBA-15 nanorods used as templates in present work. Insets: diameter distribution (A) and pore size distribution of SBA-15 nanorods.

Table S1 Structural properties of template and m-CNR.

Sample	D_p (nm)[a]	d_{100} (nm)[b]	S_{BET} (m²/g)[c]	W (nm)[d]
SBA-15 nanorods	3.8	11	500	8.9
m-CNR	3.63	-	110-200	-

[a] Pore diameter. [b] (100) interplanar distance. [c] BET specific surface area. [d] Pore wall thickness: $W = d_{100}(2/3^{1/2}) - D_p$.
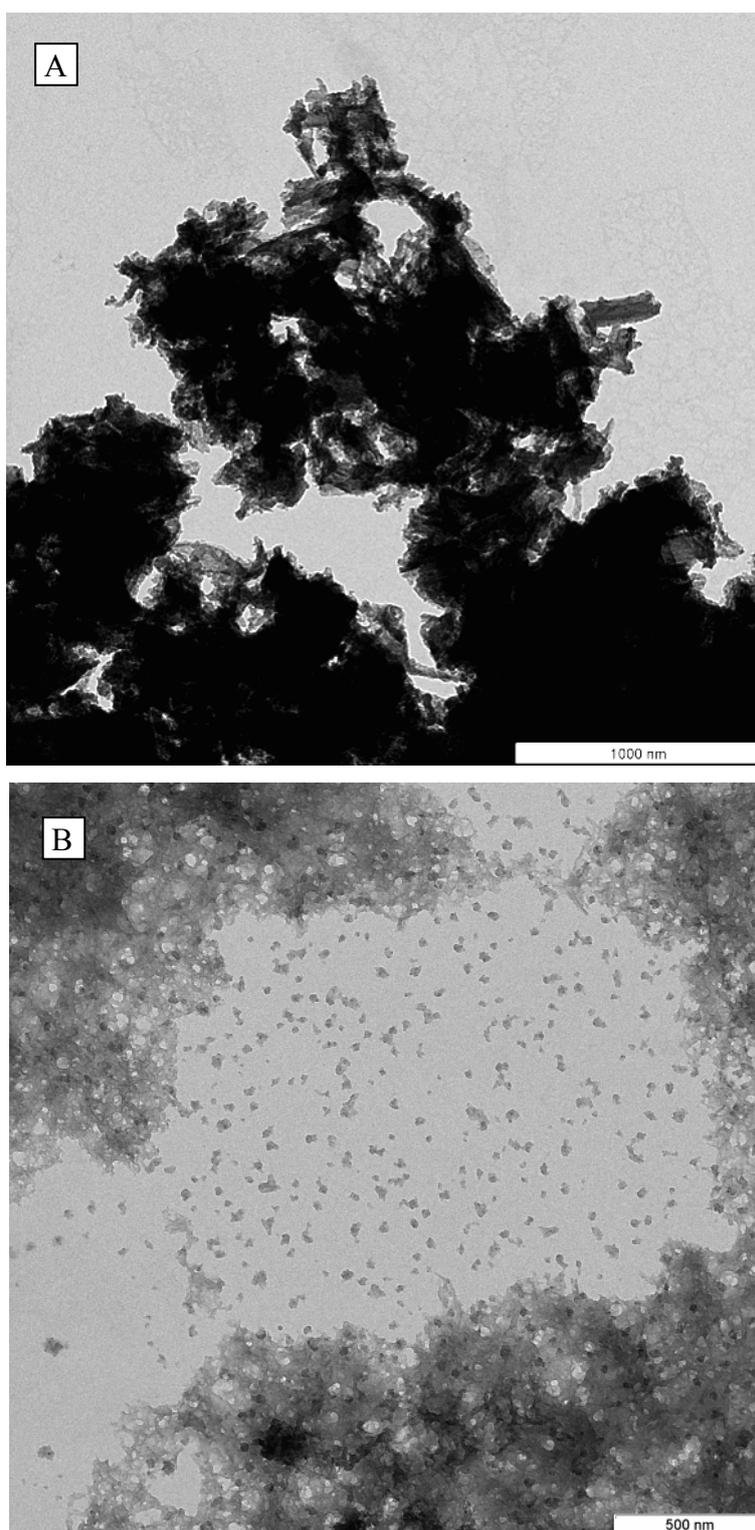
Figure S2 TEM images of the carbon nitride compounds prepared with a monomer/template weight ratio of 1 (A) and 0.2 (B), respectively.
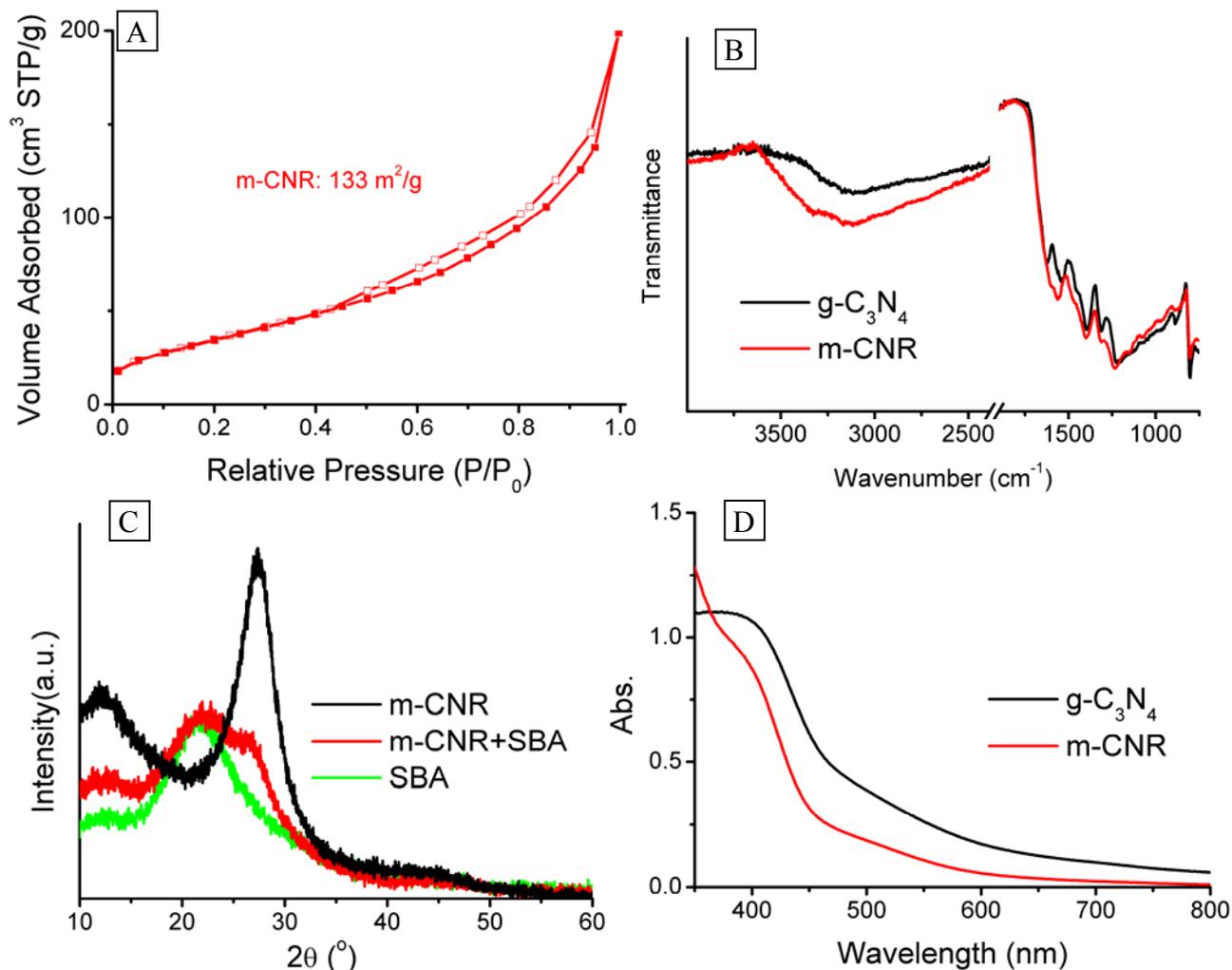
Figure S3 Typical nitrogen adsorption-desorption isotherm (A), FTIR spectra (B), XRD patterns (C) and the UV-vis spectra (D) of m-CNR and corresponding control samples. The FTIR spectrum of m-CNR displays the characteristic aromatic CN heterocycles bands between 1200 and 1600 cm^{-1}, and the band breathing mode of the triazine units at 800 cm^{-1}, revealing the well developed polymeric network. For the final silica-free sample, the wide angle XRD pattern shows well-resolved peaks for its graphite-like structure. The strong characteristic interplanar stacking peak of aromatic systems of m-CNR at 27.3°, indexed for graphitic materials as the (002) peak, speaks for the well developed layered structure of g-C_3N_4 , but become broader as compared with that of bulk g-C_3N_4, which is due to the small size of the primary subunits of m-CNR. The absence of the broad peak at about 22° caused by amorphous silica after the removal of silica is a sign for the purity of carbon nitride, which can be confirmed by thermogravimetric analysis with a residual mass of less than 4 wt%.
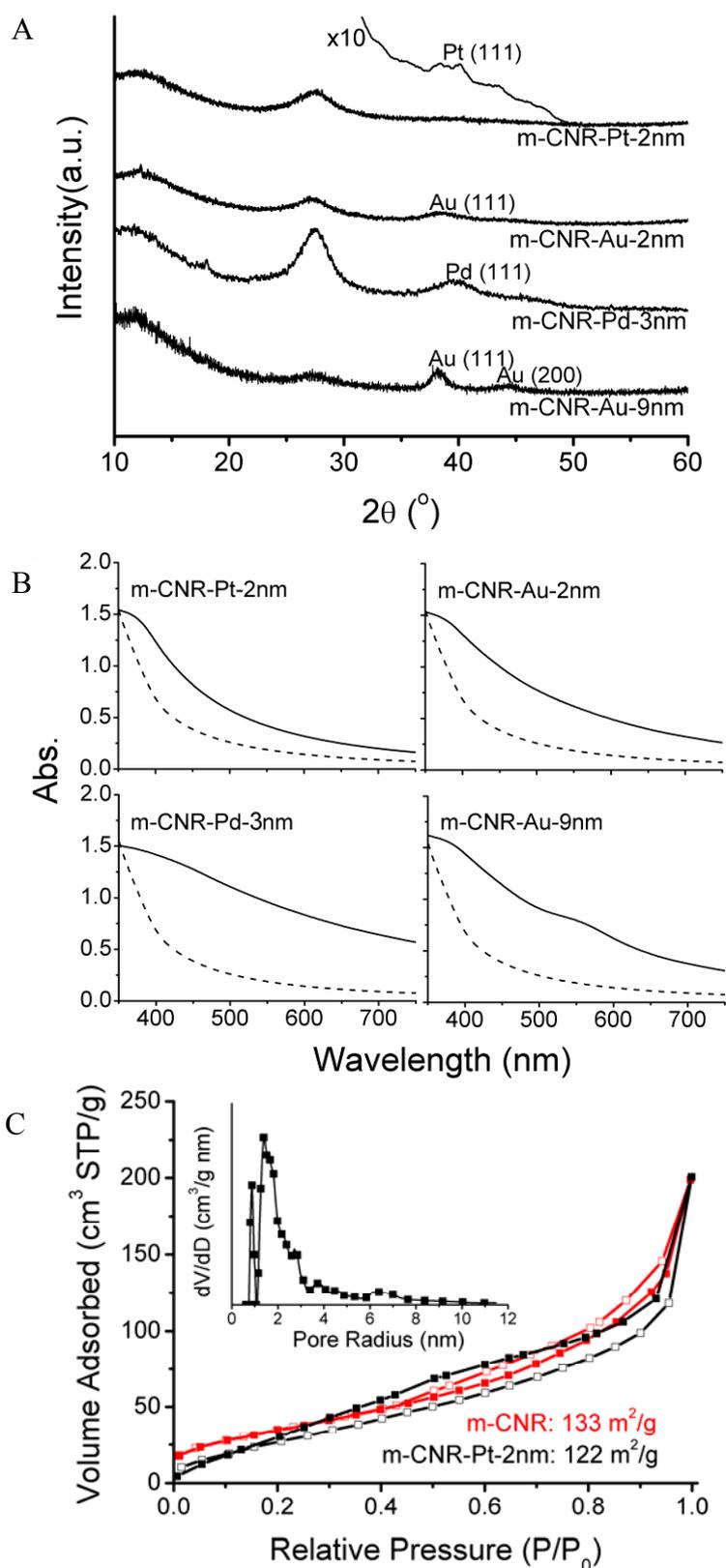
Figure S4 (A) XRD patterns of m-CNR supported noble metal NPs, (B) UV-vis spectra of corresponding aqueous dispersion (dash line: m-CNR), and (C) Nitrogen adsorption-desorption isotherms of m-CNR and m-CNR-Pt-2nm. The pore size distribution of m-CNR-Pt-2nm was slightly broadened, indicating the deposition of Pt NPs inside the mesochannels.
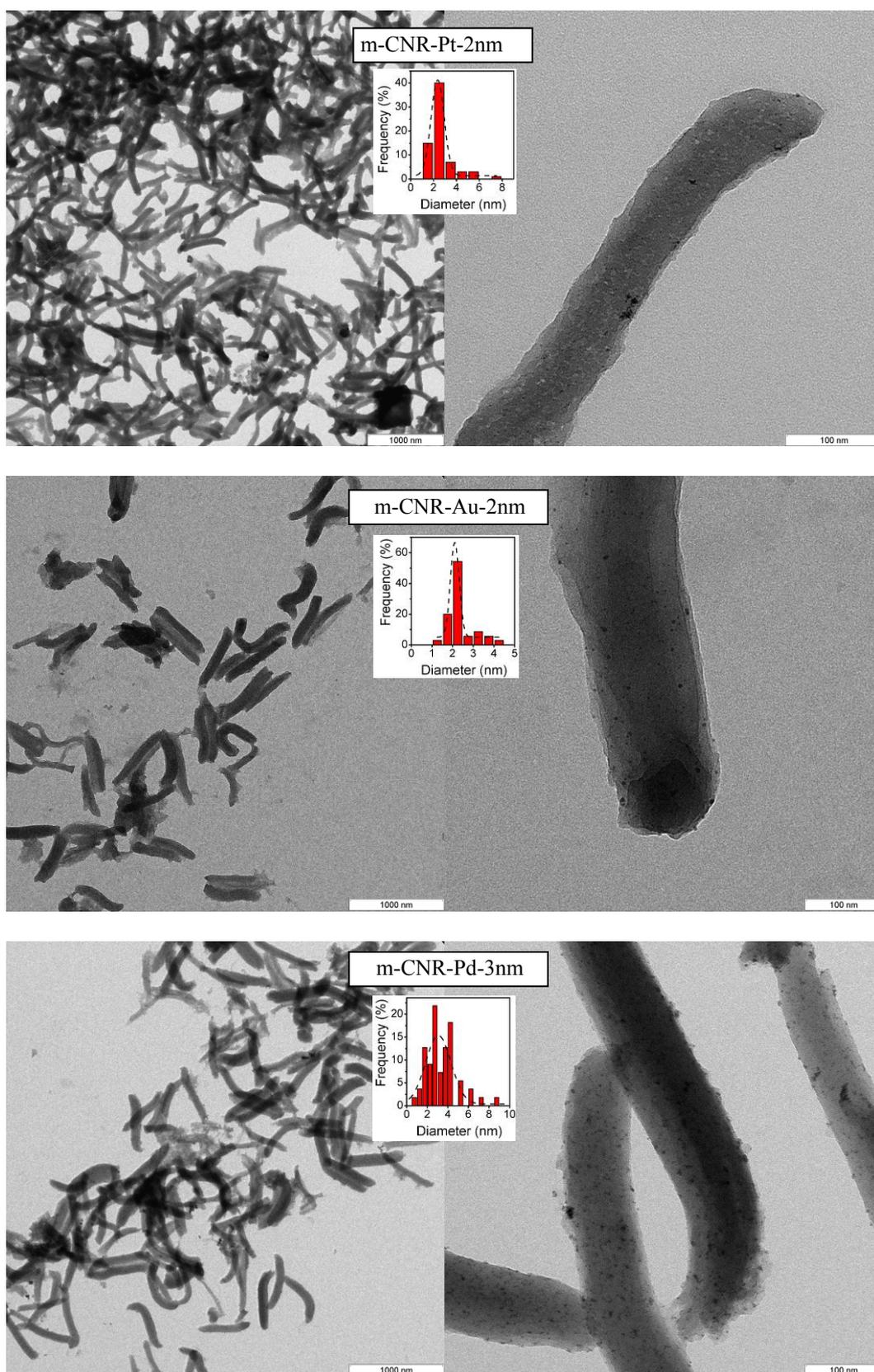
Figure S5 TEM images of m-CNR supported noble metal NPs and corresponding size distribution of the NPs (insets). Dash lines: Guass fitting.
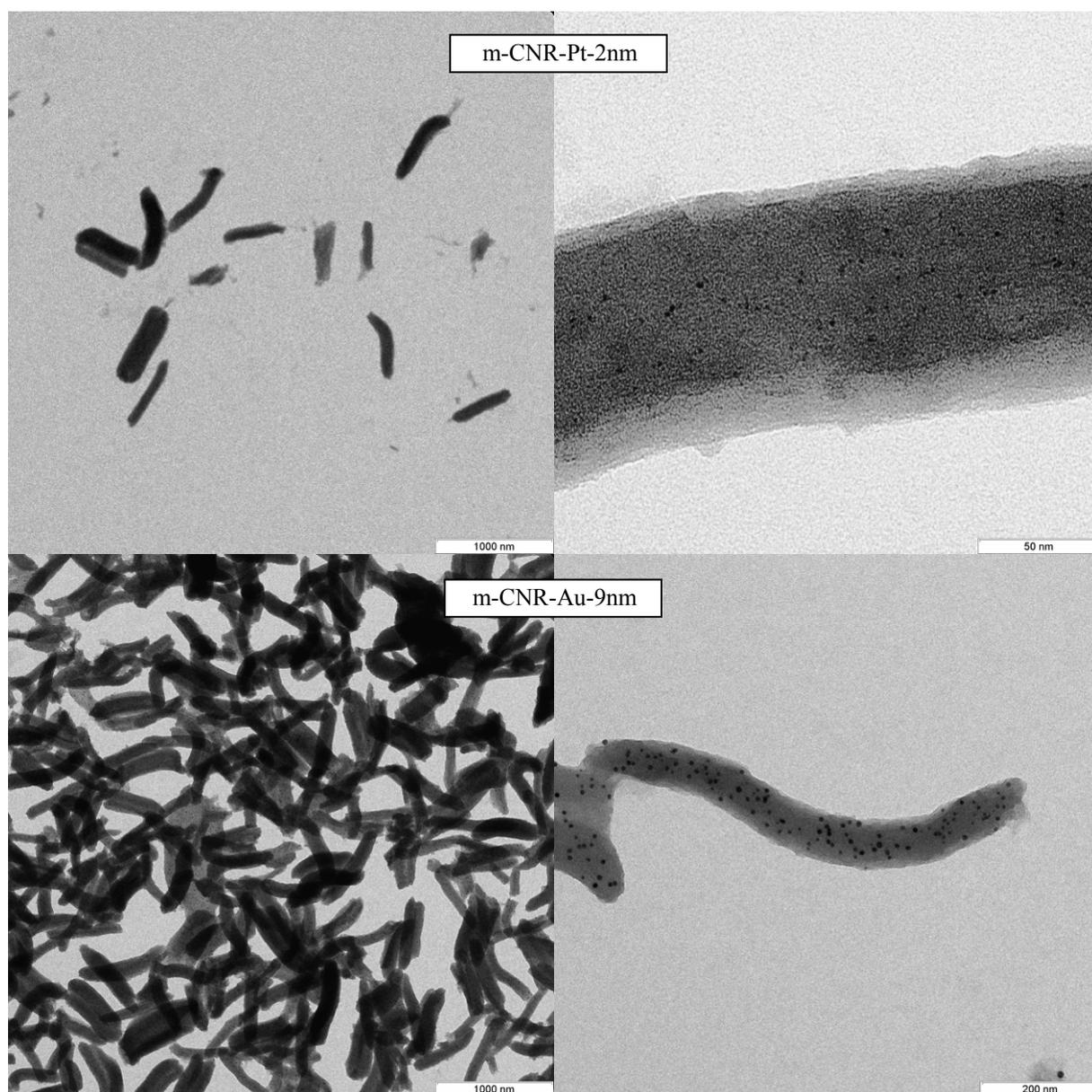
m-CNR-Pt-2nm

m-CNR-Au-9nm

Figure S6 TEM images of used m-CNR-Pt-2nm and m-CNR-Au-9nm recovered in the fifth circle of the catalytic reduction of 4-nitrophenol. Both the size and dispersion of the NPs were not changed obviously after reaction.
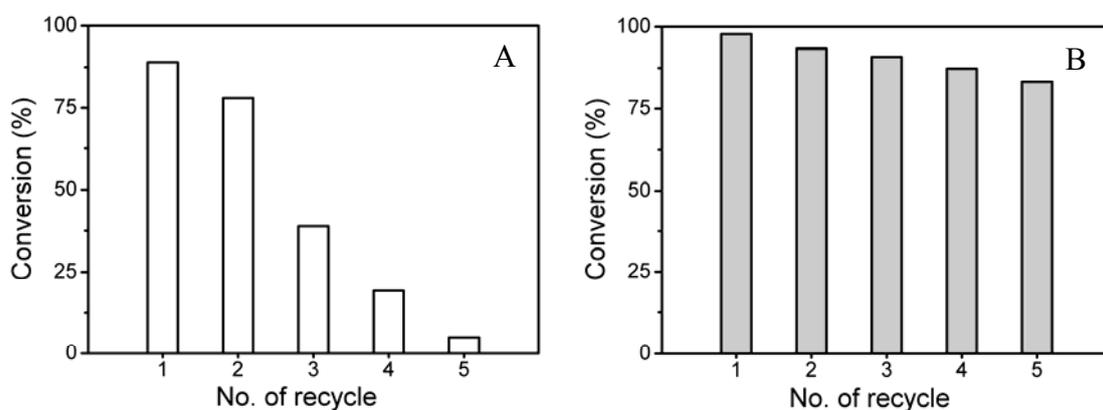

Figure S7 Conversion of 4-nitrophenol over used SBA-15-supported Pt NPs (A) and bulk g-C_3N_4-supported Pt NPs (B).