EXPERIMENTAL PROCEDURES

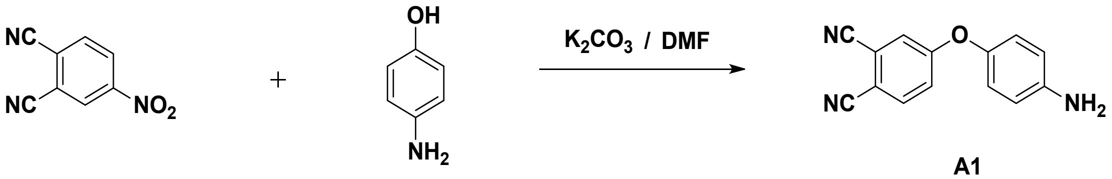
Reagents and Chemicals. The graphene oxide (GO) was purchased from Nanjing XFNANO Materials Tech Co. Ltd. (Nanjing, China). Dimethyl formamide (DMF) was purchased from Sigma-Aldrich and used as received. The 4-nitrophthalonitrile was obtained from Shanghai Yuanhe Chemical Co., Ltd. The p-hydroxyaniline was purchased from Sinopharm Chemical Reagent Co., Ltd. The triphenylmethyl chloride and DBU were obtained from Aladdin Reagent Co., Ltd. 1-Pentanol was purchased from Shanghai LingFeng Chemical Reagent Co., Ltd. Trifluoroacetic acid was provided by China Pharmaceutical Shanghai Chemical Reagents Co., Ltd. Sodium sulfate anhydrous was obtained from Shanghai Xinbao Fine Chemical Plant. Palladium acetate was obtained from Shanghai De Bai Chemical Technology Co., Ltd. Commercial Pd/C was purchased from Johnson Matthey, U.S. All the reagents were of analytical reagent grades and directly used without further purification.

Synthesis of Pd ISAs/GNS

1. Synthesis of palladium tetra-(aminophenoxy) phthalocyanine (PdPc-TAP)

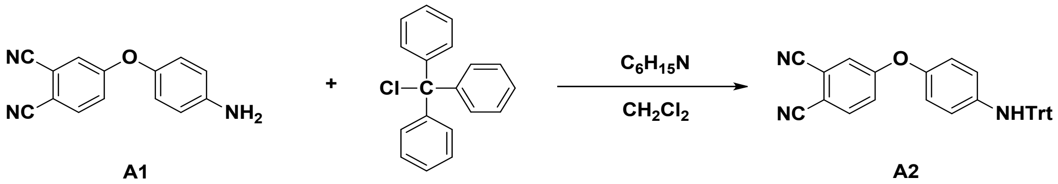
A DBU liquid phase catalysis was used for the synthesis of PdPc-TAP by employing n-pentanol as solvent, phthalonitrile derivative as reagent, and DBU as catalyst under the reflux condition.[1]

1.1 Synthesis of 4-(aminophenoxy) phthalonitrile (A1)



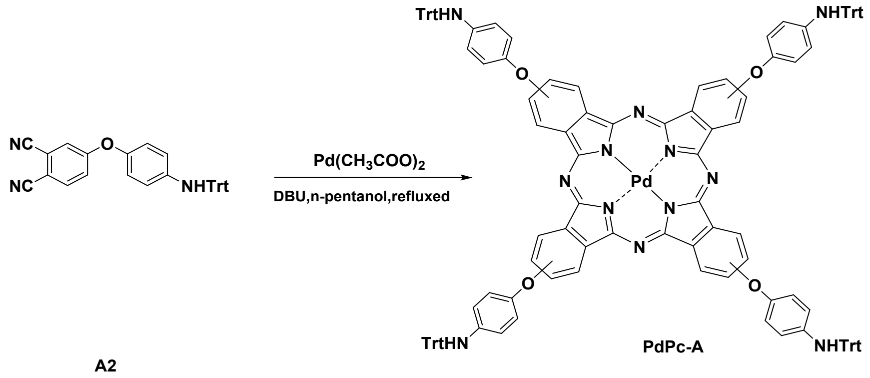
Typically, 1.50 g of 4-nitrophthalonitrile and 0.96 g of p-hydroxyaniline were dissolved in 20 mL of DMF solution and stirred under a protective nitrogen atmosphere. Afterwards, 3.00 g of ground K_2CO_3 was added and the reaction mixture was stirred continuously for 1.5 h at 40 ^{o}C. After the reaction cooling down to room temperature, the mixture was added to 30 mL of saturated NaCl solution and stirred for another 30 min. The organic phase was filtered, washed with DI water, NaCl solution, and ethyl acetate for several times and then dried using anhydrous Na_2SO_4. Finally, the yellow product, namely 4-(aminophenoxy) phthalonitrile (A1), was obtained from column chromatography by using petroleum ether and ethyl acetate (1:1). 1H NMR (400 MHz, DMSO) δ (ppm) 8.03 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 2.6 Hz, 1H), 7.25 (d, J = 8.8, J = 2.6 Hz, 1H), 6.86-6.84 (m, 2H), 6.64-6.62 (m, 2H), 5.20 (s, 2H).

1.2 Synthesis of 4-(4-(triphenylmethylamino)phenoxy) phthalonitrile (A2)



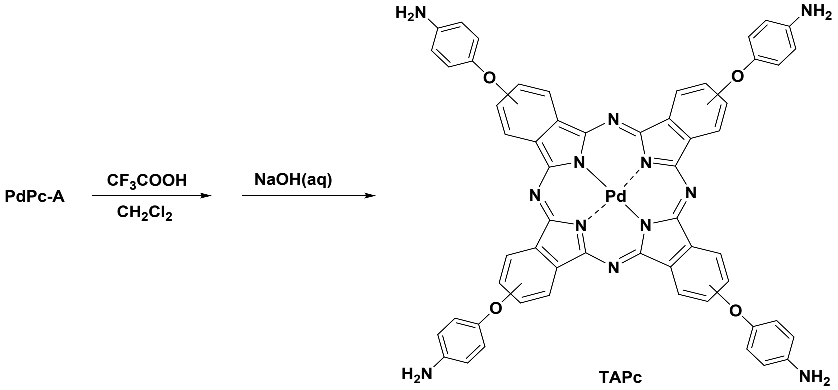
Typically, 1.00 g of A1, 1.12 mL of triethylamine, and 40 mL of dichloromethane were added in a 100-mL flask and mixed uniformly. Meanwhile, 1.42 g of triphenylchloromethane was resolved in 40 mL of dichloromethane, then the mixture solution was dropped slowly into the above-mentioned 100-mL flask and stirred continuously for another 2 h. Afterwards, the products were filtered, washed with DI water for several times and then dried using anhydrous Na2SO4. Finally, the 4-(4-(triphenylmethylamino)phenoxy) phthalonitrile, called A2 for short, was obtained from column chromatography by using petroleum ether and ethyl acetate (1:3). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.67 (d, J = 8.7 Hz, 1H), 7.40-7.27 (m, 15H), 7.14 (d, J = 8.7 Hz, J = 2.6 Hz, 1H), 7.09 (d, J = 2.5 Hz, 1H), 6.64-6.61 (m, 2H), 6.45-6.41 (m, 2H), 5.12 (s, 1H).

1.3 Synthesis of palladium tetra-((triphenylmethylamino)phenoxy) phthalocyanine (PdPc-A)



Typically, a mixture of 0.5 g of A2, 400 mg of palladium acetate, 400 μL of DBU, and 10 mL of n-pentanol was added in a 50-mL three-necked flask. The mixture was gradually heated and maintained at 140 ^{o}C for 10 h with continuously stirring under a protective nitrogen atmosphere. After cooling down to room temperature, the mixture was stirred with 60 mL of methanol for 30 min, then obtained by suction filtration. Finally, the deep green product, called PdPc-A for short, was obtained from column chromatography by using methanol and dichloromethane (1:5).

1.4 Synthesis of palladium tetra-(aminophenoxy) phthalocyanine (PdPc-TAP)



Typically, the newly-formed PdPc-A and 0.5 mL of trifluoroacetic acid were dissolved in 20 mL of dichloromethane and stirred for 3h. Then the crude product was filtered and sequentially washed with dichloromethane for several times. Subsequently, a repetitive acid and alkaline reconciliation method was used to purify the dark green solid, using acid aqueous solution as the eluting solvent firstly, and then alkaline aqueous solution was served as eluting solvent for next round. At last, the pure PdPc-TAP were obtained from evaporation of the solvent.

2. Synthesis of Pd ISAs/GNS

For the synthesis of Pd ISAs/GNS, 5 mg of hunter green PdPc-TAP powder was uniformly dispersed in 20 mL of DMF solution. Meanwhile, 20 mg of GO was dispersed into 20 mL of DI water with continuously stirring. Then the PdPc-TAP/DMF solution was added into the above GO suspension and kept stirring for 1 h, forming PdPc-TAP/GO solution. Subsequently, the resultant PdPc-TAP/GO was separated and dried, then annealed at 300 ^{o}C for 3 h under a flow of Ar/H2 atmosphere, transforming PdPc-TAP molecules into atomically dispersed Pd-Nx species. Meanwhile, GO transformed to reduced graphene oxide, leading to the formation of Pd ISAs/GNS.

Catalytic RhB hydrogenation by $NaBH_4$

The catalytic reaction was carried out in a quartz cuvette with an optical path length of 1 cm at room temperature. Typically, 0.5 mL of 0.1 M $NaBH_4$ solution was mixed with 1 mL of 1.0×10^{-5} M RhB solution. Then 40 μL of the as-prepared Pd ISAs/GNS aqueous solution (0.4 g L^{-1}) was added into the mixture solution. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) indicates that the weight fraction of Pd in the Pd ISAs/GNS is 1.9 wt%. The reduction progress of RhB was monitored by the time-dependent absorption UV-vis spectroscopy at a regular time interval of 2 min. The maximum absorption was observed at 554 nm and used for evaluating the concentration of RhB. Commercial Pd/C (20 wt%) was employed as heterogeneous catalyst to make a comparison under the same experimental conditions. For normalization of the mass activity of Pd, 3.8 μL of 0.4 g

L^{-1} Pd/C (20 wt%) aqueous solution was added into the catalytic solution. The reaction rate constant (k) was calculated by the following equations: $ln\ (C_t / C_0) = -kt$. Where Ct noted as the concentration of RhB at reaction time t, C_0 was the initial concentration of RhB.[2] A twenty-run recycling experiment was performed to test the stability of the catalyst. After each reaction, 50 μL of 2×10^{-4} M RhB solution was directly added into the mixture solution from the second to the twentieth runs.

Characterization

Nuclear Magnetic Resonance (NMR) spectrum was performed on Bruker Avance 400, Agilent 400 (400 MHz). High-resolution Transmission electron microscopy (HRTEM) images were recorded on JEOL JEM-2010 instrument at an accelerating voltage of 200 kV. The aberration corrected high-angle annular dark-field scanning transmission electron microscope (AC-HAADF-STEM) images were observed on JEOL JEM-ARM 200F. ICP measurements were carried out on an IRIS Intrepid instrument (Thermo Fisher, USA). X-ray diffraction (XRD) analyses were performed on a Model D/max-rC X-ray diffractometer employing Kα radiation ($\lambda = 0.15406$ nm). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo VG Scientific ESCALAB 250 spectrometer with an Al Kα radiator. The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. Ultraviolet-visible spectroscopy (UV-vis) measurements were performed on a Shimadzu UV3600 spectrophotometer using a quartz cell with a breadth of 1 cm at room temperature. Fourier transform infrared (FT-IR) spectrum was performed with a Nicolet 520 SXFTIR spectrometer. The bulk component of the sample was characterized by inductively coupled plasma atomic emission spectrometer (ICP-AES, X Series 2, Thermo Scientific USA).

Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

Density functional theory (DFT) modeling

The theoretical investigation was carried out based on DFT calculations by using the Vienna ab-initio simulation package (VASP). The interactions between valence electrons and ion cores were treated by Blöchl's all-electron-like projector augmented wave (PAW) method. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) approach was adopted for the sake of consistency. The wave functions at each k-point were expanded with plane wave basis set and an energy cutoff of 400 eV was applied. The vacuum space between adjacent graphene nanosheets in the z-direction was set to the value of 15 Å, which is sufficient to avoid the layer-to-layer interactions. Brillouin zone integration was approximated by a sum over special selected k-points using the 3×3×1 Monkhorst-Pack sampling.

Figures

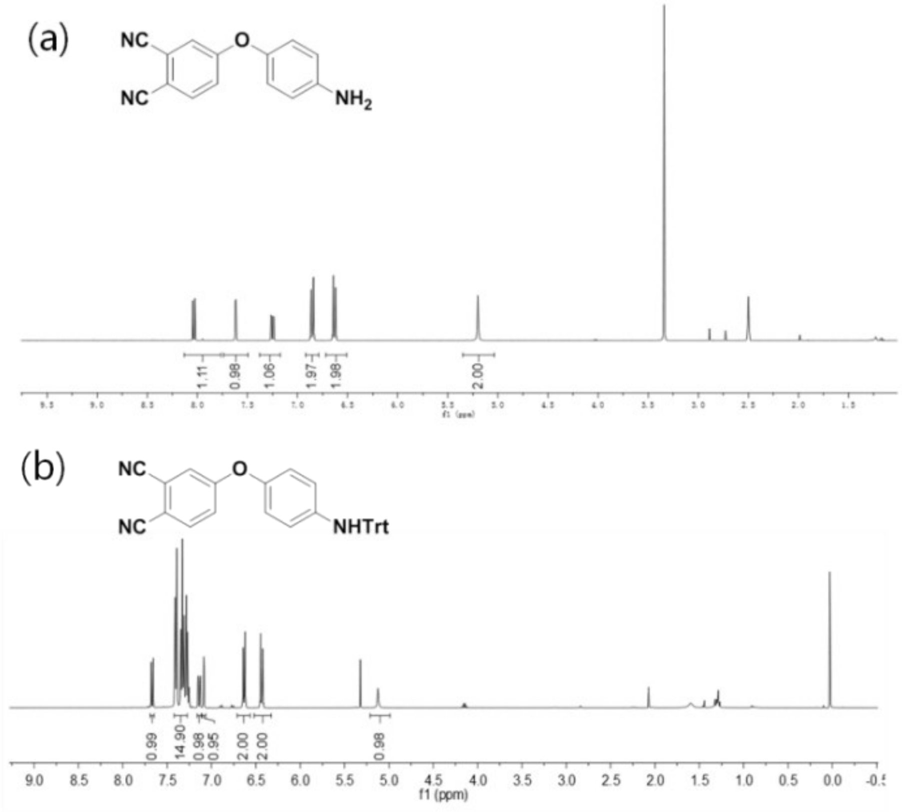


Figure S1. ^{1}H NMR Spectroscopy of the intermediate products.

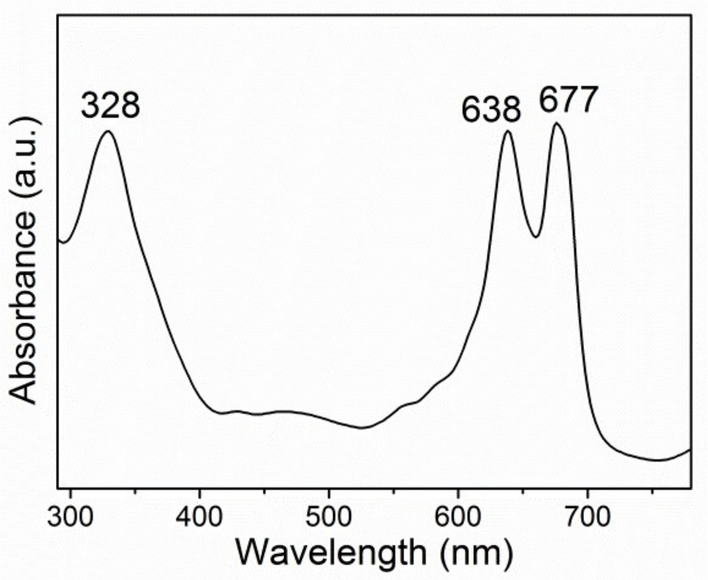


Figure S2. UV-vis absorption spectra of the as-synthesized PdPc-TAP.

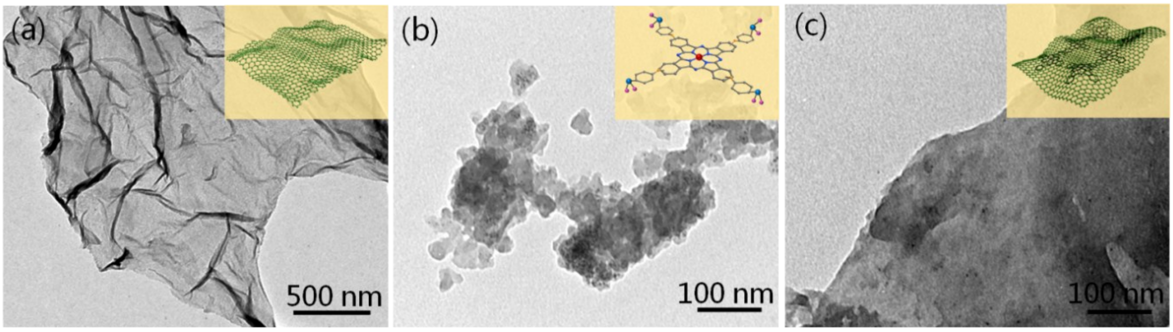


Figure S3. TEM images of intermediate products. (a) GO, (b) PdPc-TAP, and (c) PdPc-TAP/GO.

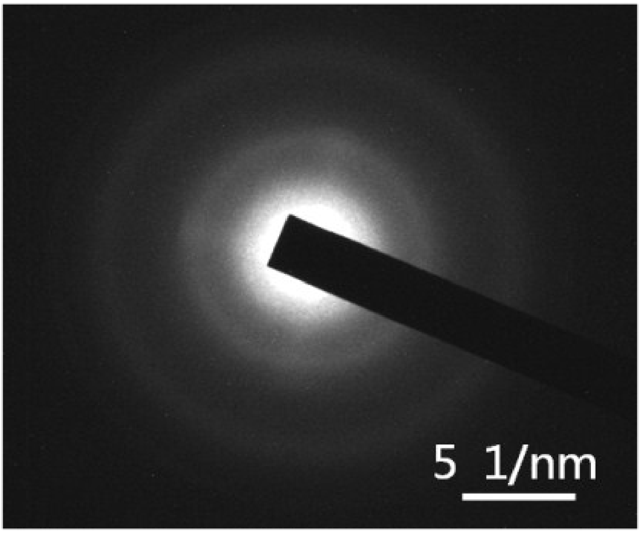


Figure S4. SAED pattern of Pd ISAs/GNS.

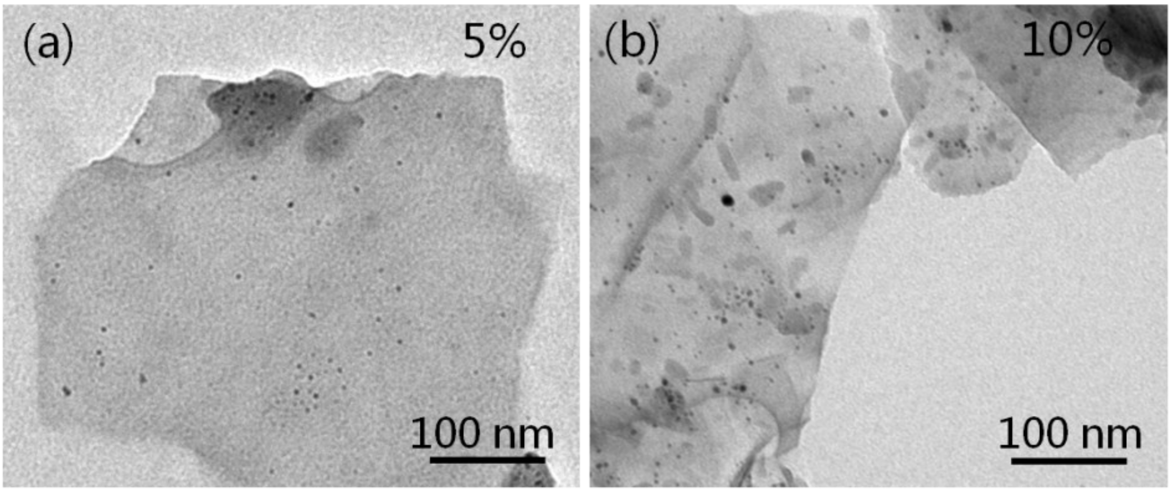


Figure S5. TEM images of the products prepared using different dosages of PdPc-TAP. (a) 5% Pd NPs/GNS, and (b) 10% Pd NPs/GNS.

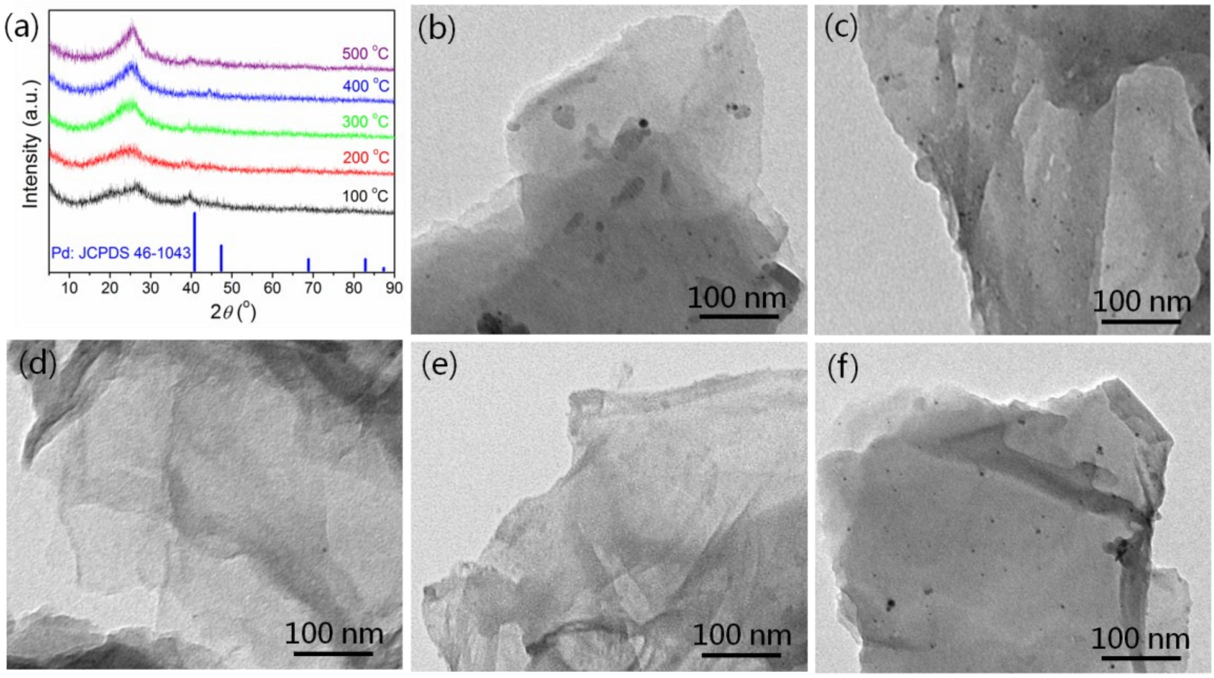


Figure S6. (a) XRD pattern. TEM images of the products prepared at different temperatures. (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, and (f) 500 °C.

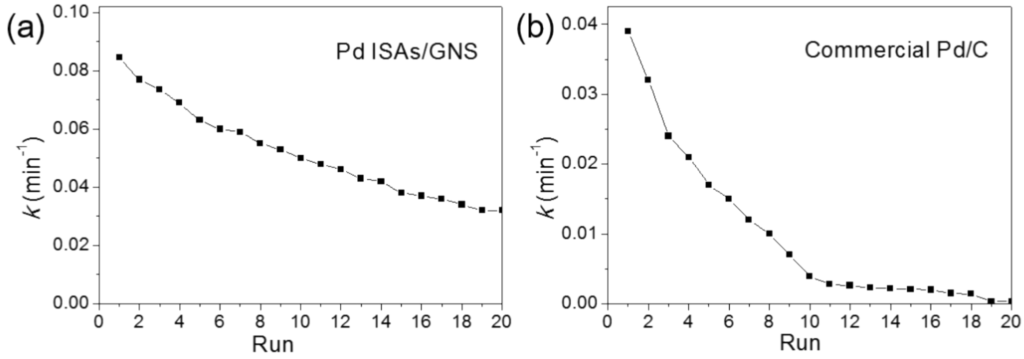


Figure S7. Recyclability tests of Pd ISAs/GNS and commercial Pd/C.

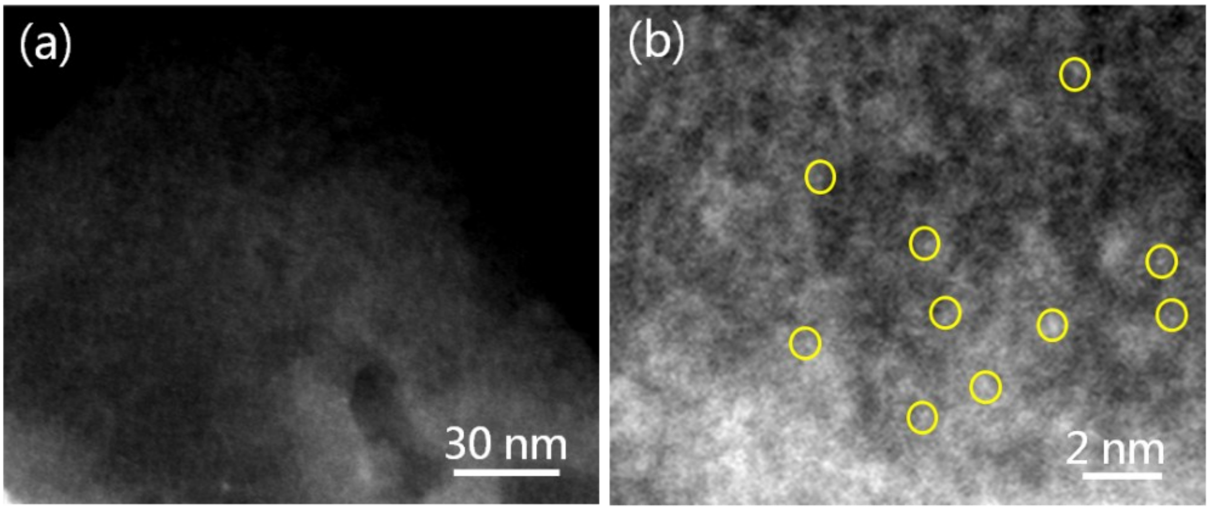


Figure S8. Aberration corrected HAADF-STEM images of the Pd ISAs/GNS after recyclability tests.

References

(1) X. Li, D. Lee, J. Huang, J. Yoon, Phthalocyanine-Assembled Nanodots as Photosensitizers for Highly Efficient Type I Photoreactions in Photodynamic Therapy, *Angew. Chem. Int. Ed*. **2018**, 57, 9885-9890.

(2) K. Gu, X. Pan, W. Wang, J. Ma, Y. Sun, H. Yang, H. Shen, Z. Huang, H. Liu, In Situ Growth of Pd Nanosheets on g-C_3N_4 Nanosheets with Well-Contacted Interface and Enhanced Catalytic Performance for 4-Nitrophenol Reduction, *Small.* **2018**, 1801812.