

Supplementary information

Magnetic boron nitride adorned with Pd nanoparticles: Efficient catalyst for the reduction of nitroarenes in aqueous media

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Experimental

Materials and characterization

All chemicals used for the synthesis and reactions are commercially procured from commercial companies and used without further purification. Hexagonal boron nitride (h-BN), potassium ferricyanide (III) ($K_3[Fe(CN)_6]$), and potassium palladium(II) chloride (K_2PdCl_4) were purchased from Sigma-Aldrich. All other chemicals used in this study were purchased from the Daejung and Samchun chemical companies. The crystallinity of as-prepared h-BN/Pd/Fe₂O₃ nanocatalyst was characterized using X-ray diffraction (XRD, D8-Advance) using D8-Advance in 2 θ range of 10-90° with a scan rate of 5°/min. Fourier transform infrared spectroscopy (FT-IR, Nicolet iS50) was obtained in the range of 4000-400 cm⁻¹. The morphology of the catalyst was examined using a transmission electron microscope (TEM), a high-resolution TEM (HRTEM) and selected area electron diffraction (SAED, JEOL JEM-2100F) instrument coupled with an energy dispersive spectrometer (EDS).

The surface area of the h-BN/Pd/Fe₂O₃ catalyst was analyzed using a Brunauer-Emmett-Teller device (BET, Micromeritics 3Flex) with the Barrett-Joyner-Halenda (BJH) method to study the pore size. Inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian 730ES) was used to determine the concentrations of the various metal species. The chemical state of the nanocatalyst was identified using an X-Ray photoelectron spectroscope (XPS, AXIS-His) with the Al K α X-ray source. The magnetic property was investigated using a vibrating-sample magnetometer (VSM-7410). Finally, the results of the catalytic reactions were analyzed using a gas chromatography mass spectrometer (GC-MS) with Agilent technologies 7693 autosampler and ultraviolet-visible spectroscopy (UV-vis).

Preparation of h-BN/Pd/Fe₂O₃ catalyst

The h-BN/Pd/Fe₂O₃ catalyst was prepared using a facile and green method. First, 1 g of h-BN was dispersed in 50 mL of deionized (DI) water and subsequently added to K₂PdCl₄ (50 mg) and K₃Fe(CN)₆ (50 mg); In next step, the obtained solution was treated for sonication for 15 min. Subsequently, the mixture was vigorously stirred for 12 h at room temperature. After stirring, the product was obtained by centrifugation and washed with DI water. Finally, the product was dried in an oven and annealed at 900 °C for 4 h under Ar and H₂ mixture gas flow to produce the h-BN supported Pd and Fe₂O₃ NPs catalyst.

Catalytic reduction

In a typical reaction, 20 mL of deionized water was used to dissolve 0.15 mmol NaBH₄, and 0.1 mmol nitroaromatics was prepared. Next, the h-BN/Pd/Fe₂O₃ catalyst was directly added to the above system and the ensuing mixture was kept for 20 minutes under an air atmosphere. After the reaction, the h-BN/Pd/Fe₂O₃ catalyst was separated using a small magnet. GC-MS was applied to measure the yield of the amino aromatic groups. UV-vis was used to recorded the concentration of 4-NP at a wavelength of 400 nm and 4-AP at 300 nm.

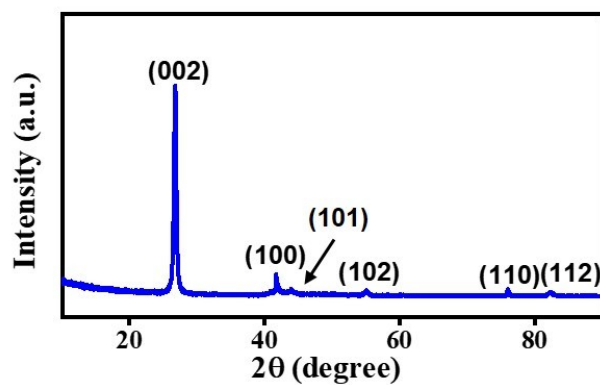


Figure S1. XRD pattern of h-BN/Pd/Fe₂O₃ catalyst.

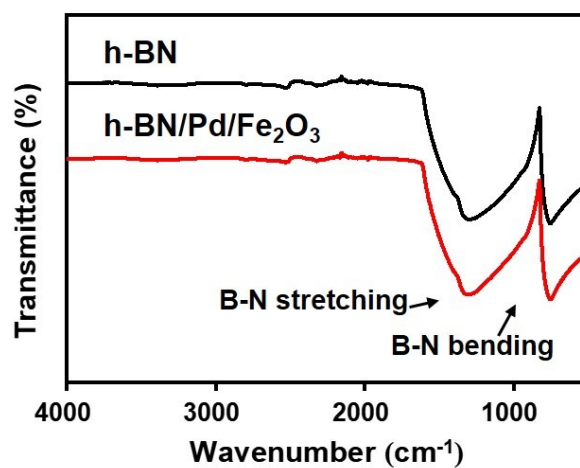


Figure S2. FT-IR spectra of h-BN and h-BN/Pd/Fe₂O₃ catalyst.

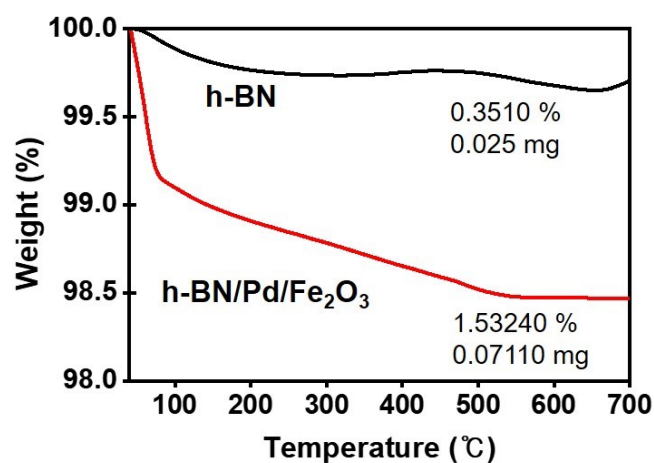


Figure S3. TGA curves of h-BN and h-BN/Pd/Fe₂O₃ catalyst.

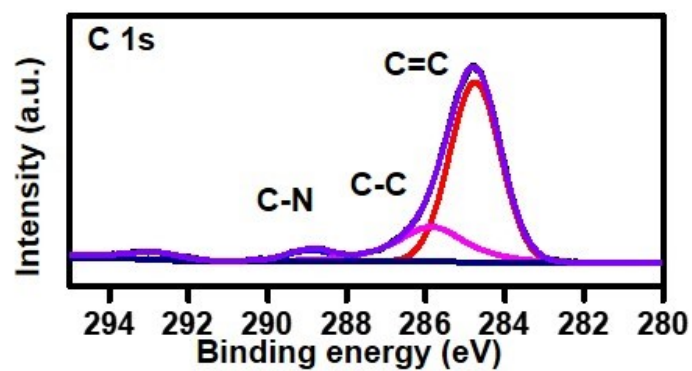


Figure S4. XPS spectrum of C 1s.

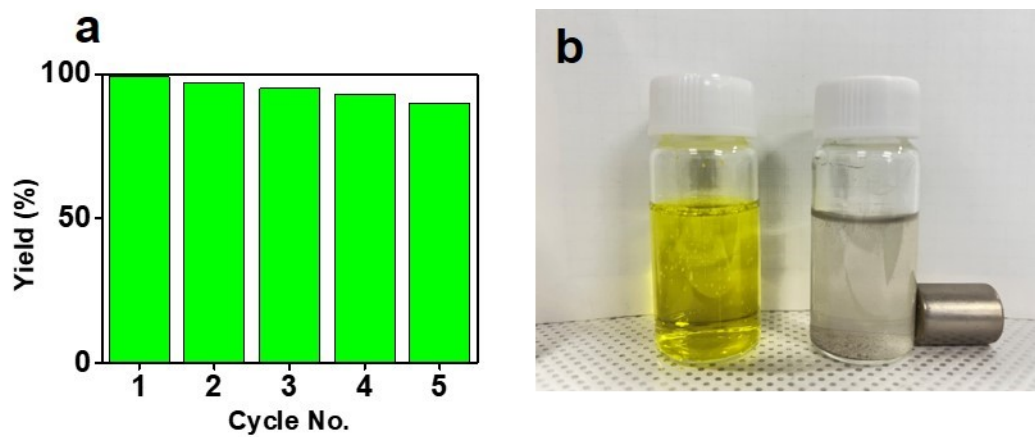


Figure S5. (a) Recycling test for the reduction of nitrobenzene to aniline by h-BN/Pd/Fe₂O₃ catalyst. (b) Digital camera image of before and after magnetic separation for h-BN/Pd/Fe₂O₃ catalyst in aqueous media.

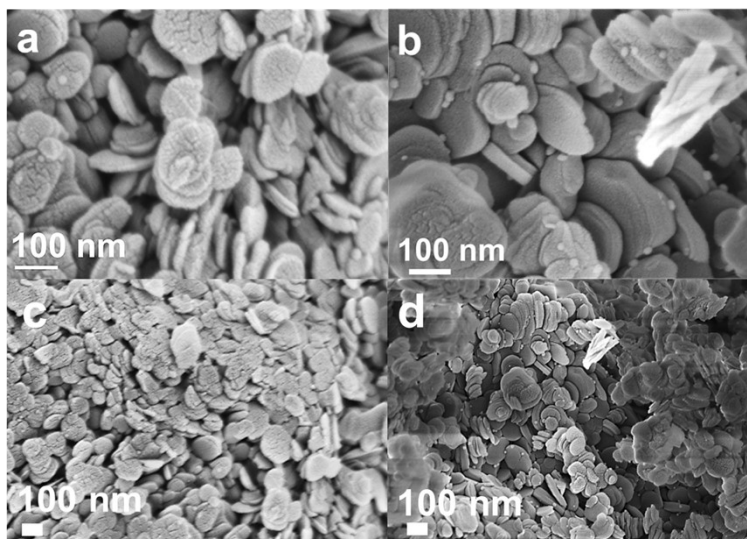


Figure S6. (a and c) FESEM images of the as-prepared h-BN/Pd/Fe₂O₃ catalyst. (b and d) FESEM images of the reused h-BN/Pd/Fe₂O₃ catalyst after 5th cycles.

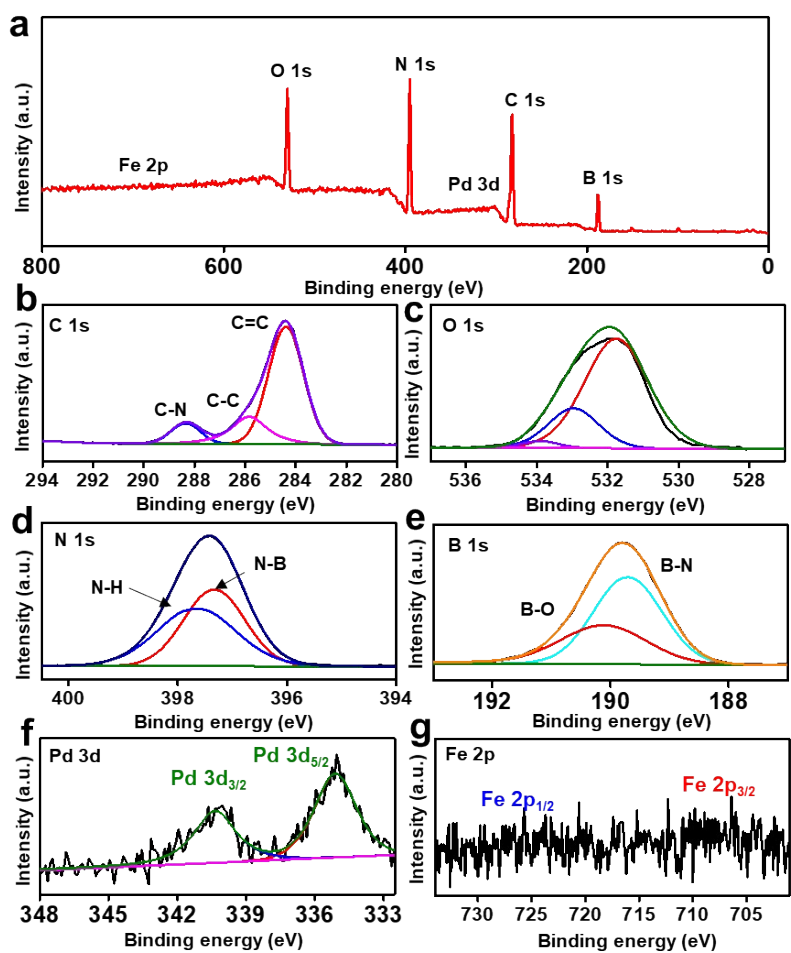
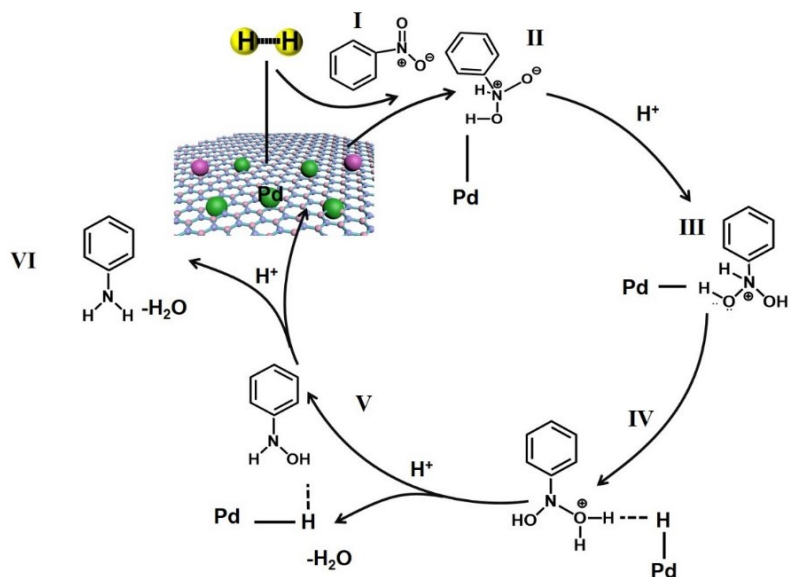


Figure S7. XPS pattern (a) survey scan, (b) C 1s, (c) O 1s, (d) N 1s, (e) B 1s, (f) Pd 3d, (g) Fe 2p for the reused h-BN/Pd/Fe₂O₃ catalyst after 5th cycles.



Scheme S1. Proposed catalytic hydrogenation mechanism and possible reaction pathways for nitrobenzene reduction with NaBH₄ in the presence of h-BN/Pd/Fe₂O₃ catalyst.

Table S1. Surface area and pore volume of h-BN, BN/Pd/Fe₂O₃, h-BN/Pd, and h-BN/Fe₂O₃.

Sample	BET Surface Area/m ² g ⁻¹	Pore Volume/cm ³ g ⁻¹
h-BN	32.99	0.3225
h-BN/Pd/Fe ₂ O ₃	56.073	0.6837
h-BN/Pd	29.411	0.3754
h-BN/Fe ₂ O ₃	16.969	0.1877

Table S2. Catalytic performance comparison of selected examples of previously published heterogeneous precious metals catalysts utilized in the reduction of nitrobenzene.

Entry	Catalyst	Reaction conditions	Yield (%)	Refs.
1	Fe ₃ O ₄ @Fritillaria/Pd (0.1 mol%)	Hydrazine, EtOH:H ₂ O (2:1), 80 °C, 30 min	98	S1
2	Fe ₃ O ₄ @C/Pd (40 mg)	NaBH ₄ , EtOH, (60 ml), 60 °C, 1 h	99	S2
3	HAP-Pd (1 mol%)	NaBH ₄ , H ₂ O, r.t, 2 h	99	S3
4	TiO ₂ @Au (100 mg)	Citric acid, H ₂ O, 60 °C, 720s	93	S4
5	SBA-Pr-3AP@Pd (0.03 g)	NaBH ₄ , EtOH:H ₂ O (1:1) r.t, 4 min	95	S5
6	Au@ZP(AEP) (1 mol%)	NaBH ₄ , EtOH, 30 °C, 4 h	94	S6
7	Au@SBA15 (2 mol%)	NaBH ₄ , EtOH 30 °C, 4 h .	92	S7
8	Bento-crt@Pd (0.1 mol%)	NaBH ₄ , H ₂ O/EtOH r.t, 30 min	99	S8
9	Ru-PPT (0.15 mol%)	NaBH ₄ , H ₂ O/THF r.t, 1 h	99	S9
10	n-CeO ₂ (9 mol%)	Hydrazine, H ₂ O, 80 °C, 8 h	99	S10

Table S3. ICP analyses for the as-prepared h-BN/Pd/Fe₂O₃ and the reused h-BN/Pd/Fe₂O₃ catalyst after 5th cycle.

Element	As-prepared h-BN/Pd/Fe ₂ O ₃ (mg/L)	5th cycled h-BN/Pd/Fe ₂ O ₃ (mg/L)
Fe	96.639	38.132
Pd	114.169	86.575

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