Supplementary Information (SI) for Chemical Science.

Supporting Information for

Electrochemical Hydrogenative Coupling of Nitrobenzene for Sustainable Azobenzene Electrosynthesis over Mesoporous Palladium-Sulfur Cathode

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Materials and Methods

Materials and Chemicals

Dimethyl distearylammonium chloride (DODAC), Palladium (II) chloride ($PdCl_2$, 99.9 wt%), sodium thiosulfate ($Na_2S_2O_3$, 99%), borane dimethylamine complex (DMAB, 96%), urea (99%), oleylamine (80%-90%), N, N-Dimethylformamide (DMF, 99%) were purchased from Aladdin. Sodium hypophosphite (NaH_2PO_2, ≥ 99.0%) and polyvinylpyrrolidone (PVP, M_w = 55000) were purchased from Sigma-Aldrich. Nafion solution (5 wt.% in alcohol and H_2O) and L-ascorbic acid (AA, ≥99%), Ammonium fluoride (NH_4F), Ammonium fluoride (H_3BO_3) were obtained from Alfa Aesar. sodium borohydride ($NaBH_4$), hydrochloric acid (HCl, 36.0%-38.0%), ethanol (CH_3CH_2OH, ≥ 99.7%), and potassium hydroxide (KOH, ≥ 85.0%), aqueous ammoniawere ($NH_3\cdot H_2O$) obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). 10 mM (mmol/L) H_2PdCl_4 solution was prepared by dissolving 0.1773 g of $PdCl_2$ with 10 mL of 0.20 M HCl solution in a 100 mL volumetric flask and further bringing to volume by deionized H_2O. Deionized H_2O used in this work has a resistivity of 18.25 mΩ. All the reagents were of analytical reagent grade and used without further purification.

Synthesis details of PdS MNSs and other counterpart samples

Synthesis of PdS MNSs. In a typical synthesis, 30 mg of DODAC and 80 mL of H_2O were placed in a 75 °C for 30 min until a uniform solution was formed. After cooling to room temperature, 20 mL of CH_3CH_2OH and 2 mL of 0.10 M NaOH were successively injected into above solution. After 5 min, 4.8 mL of 10 mM H_2PdCl_4 was added to above solution and kept at room temperature for 30 min. Subsequently, 10 mL of freshly prepared AA (0.053 g mL^{-1}) was injected into above solution under gentle shaking. After being reacted for 2 h, 3.8 mg of $Na_2S_2O_3$ was added and stirred for 2 h at room temperature. Then, 3.8 mg of $NaBH_4$ was added to the above system. After being reacted for 2 h, PdS MNSs were collected by being centrifugated and washed with H_2O/ethanol for six times.

Synthesis of PdS NPs. In a typical synthesis, 4.8 mL of 10 mM H_2PdCl_4 was dissolved into 80 mL of H_2O to form a uniform solution. Subsequently, 10 mL of freshly prepared AA (0.053 g mL^{-1}) was injected into above solution under gentle shaking. After being reacted for 2 h, 3.8 mg of $Na_2S_2O_3$ was added and stirred for 2 h at room temperature. Then, 3.8 mg of $NaBH_4$ was added dropwise to the above system. After being reacted for 2 h, PdS NPs were collected by being centrifugated and washed with H_2O/ethanol for six times.

Synthesis of Pd NPs. In a typical synthesis, 4.8 mL of 10 mM H_2PdCl_4 was dissolved into 80 mL of H_2O to form a uniform solution. Subsequently, 10 mL of freshly prepared AA (0.053 g mL^{-1}) was rapidly injected into above solution under gentle shaking. After being reacted for 2.0 h, Pd NPs were collected by being centrifugated and washed with H_2O/ethanol for six times.

Synthesis of Pd MNSs. 30 mg of DODAC and 80 mL of H_2O were placed in a 75 °C for 30 min until a uniform solution was formed. After cooling to room temperature, 20 mL of CH_3CH_2OH and 2.0 mL of 0.10 M NaOH were successively injected into above solution. After 5 min, 4.8 mL of 10 mM H_2PdCl_4 was added to above solution and kept at room temperature for 30 min. Subsequently, 10 mL of freshly prepared AA (0.053 g mL^{-1}) was rapidly injected into above solution under gentle shaking. After being reacted for 2.0 h, Pd MNSs were collected by being centrifugated and washed with H_2O/ethanol for six times.

Synthesis of PdH MNSs. As-synthesized Pd MNSs were dispersed in 15 mL of THF and further sonicated for 20 min. Then, the solution was transferred to a 20 mL of reaction kettle and further solvothermally treated at 160 °C for 2 h. After cooling down to room temperature, PdH MNSs were collected by being centrifugated and washed several times with ethanol/H_2O.

Synthesis of PdB MNSs. 30 mg of DODAC was dissolved into 10 mL of H_2O to obtain a homogeneous solution. Subsequently, 1.0 mL of NH_4F (0.337 mol L^{-1}), 1.0 mL H_3BO_3 (0.101 mol L^{-1}) and 0.8 mL H_2PdCl_4 (10 mmol L^{-1}) were added into above solution. After 40 min, 0.4 mL of $NH_3 \cdot H_2O$ (2.5 wt%) was injected into above solution and further placed at 75 °C for 30 min. Then, 1.0 mL of DMAB (0.10 mol L^{-1}) was added and reacted for 2 h at 75 °C. Finally, PdB MNSs were collected by being centrifugated and washed several times with ethanol/H_2O.

Synthesis of PdN MNSs. 50 mg of urea and 70 mg of PVP were dispersed in 4 mL of H_2O containing as-synthesized Pd MNSs and further sonicated for 20 min. Then, the mixture was transferred to a 20 mL of reaction kettle and further solvothermally treated at 180 °C for 1.5 h. After cooling down to room temperature, PdN MNSs were collected by being centrifugated and washed several times with ethanol/H_2O.

Synthesis of PdP MNSs. As-synthesized Pd MNSs and 4.2 mg of NaH_2PO_4 were mixed and stirred for 2 h at room temperature. Then, 4.0 mg of $NaBH_4$ was added to the above system. After being reacted for 2 h, PdP MNSs were collected by being centrifugated and washed with H_2O/ethanol for six times.

Electrocatalytic Measurements

Electrochemical nitrobenzene hydrogenation coupling reaction (NBHR)

All electrochemical measurements were carried out using a CHI 660E electrochemical workstation (Chenhua, Shanghai) at 25 °C. The three electrodes system consists of Ag/AgCl (reference electrode), Pt sheet (counter electrode), and working electrode with catalysts ink. To prepare catalysts ink, 1.0 mg of catalyst was dispersed into a mixture containing 124 μL of ethanol, 60 μL of H_2O and 16 μL of Nafion. After thoroughly sonicating the above mixture for 30 min, the catalyst ink was dropped onto carbon paper and dried at room temperature before use. Cyclic voltammetry (CV) curves and linear sweep voltammetry (LSV) curves were obtained at a rate of 50 mV s^{-1} from -0.4 V to -1.4 V. The products were analyzed in the high-performance Liquid Chromatography (HPLC) with a 4.6 mm × 250 mm C_{18} column (Sinochrom ODS-BP 5 μm filler) and a UV detector at 25 °C.

In-situ FTIR measurements

The *in-situ* electrochemical attenuated total-reflection infrared absorption spectral (ATR-FTIR) measurements were carried on the Thermo ScientificNicolet 6700 FTIR equipped with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. All the data were collected in 1.0 M KOH containing 1.5 mmol L^{-1} NB at -1.2 V.

Electrocatalytic CO stripping experiment

Electrochemical CO stripping curves were carried out using a three electrodes system in an electrochemical station (CHI 660E). Before the test, the samples were first saturated with CO by bubbling the gas at 0.15 V in 1.0 M KOH solution for 30 min. Afterwards, CVs were recorded at 0.05 V s^{-1} in a potential range of -0.2 V–-0.9 V.

Characterizations

SEM images were collected using a field emission scanning electron microscope (JEOL JSM-7600F, JEOL Ltd., Japan). SEM samples were prepared by dropcasting a suspension of the sample powder onto a silicon wafer. TEM and HAADF-STEM studies were carried out using a field emission transmission electron microscope (JEM-F200, JEOL Ltd., Japan) with an accelerating voltage of 200 kV. TEM and HAADF-STEM samples were prepared by dropcasting a diluted suspension of the sample powder (samples were suspended in ethanol) onto a carbon coated copper grid (300 mesh). XRD patterns were recorded on powder samples using a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite-monochromatized Cu Kα radiation in 2θ ranging from 20° to 80°. High-resolution XPS spectra were performed on a scanning X-ray microprobe (Thermo ESCALAB 250Xi) that uses Al Kα radiation. The binding energy of the C 1s peak (284.8 eV) was employed as a standard to calibrate the binding energies of other elements (Pd and S). The FT-IR tests were performed on the Thermo Fisher Is50 spectrometer in the spectral range from 4000 cm^{-1} to 400 cm^{-1}.

Calculation method

Energy calculations were conducted using the Vienna ab initio simulation package (VASP). The projector augmented wave (PAW) method was employed to describe the ionic potential, while the Perdew-Burke-Ernzerhof (PBE) functional was utilized for exchange-correlation interactions. A plane-wave kinetic energy cutoff of 500 eV was applied, ensuring energy convergence. Van der Waals interactions were incorporated through the Grimme (DFT+D3) method. Brillouin zone sampling was performed using a 3×2×1 Monkhorst-Pack k-point mesh. Structural relaxation was carried out with an electronic energy convergence criterion of 1×10-5 eV, and ionic relaxation continued until all forces were below 0.03 eV/Å.

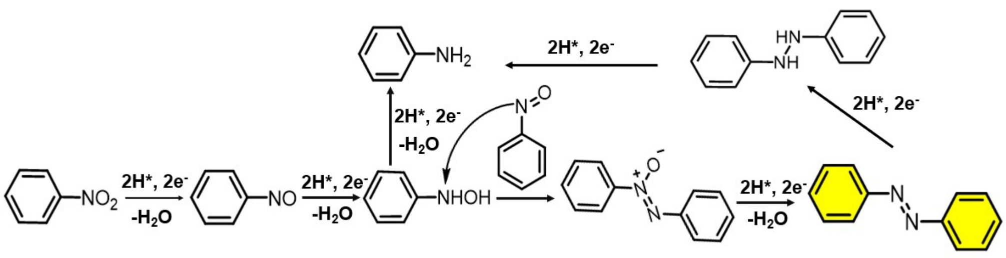

Figure S1. Proposed pathways of NBHR electrocatalysis.

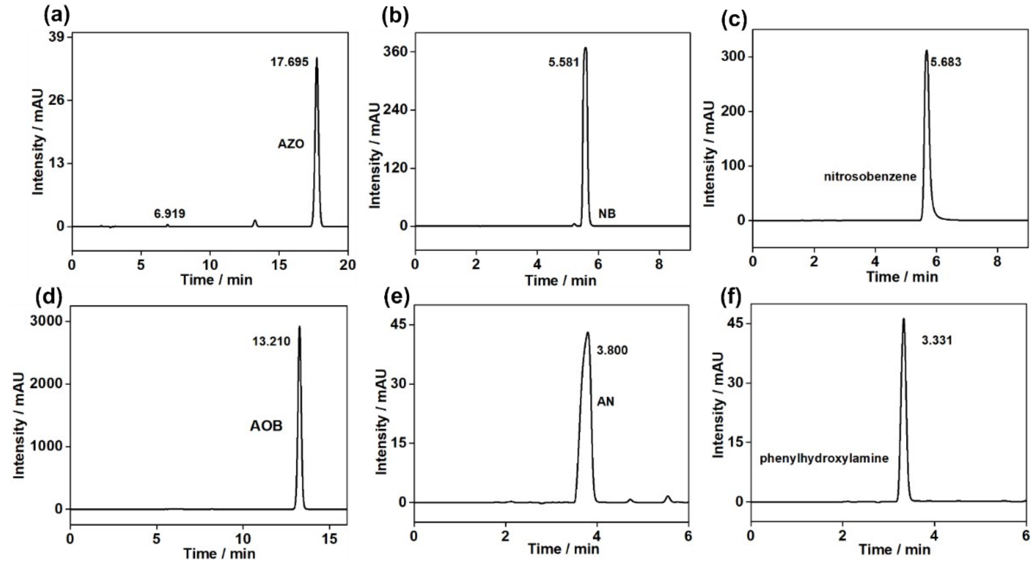

Figure S2. HPLC standard retention time peaks of (a) AZO, (b) NB, (c) nitrosobenzene, (d) AOB, (e) AN, and (f) phenylhydroxylamine.

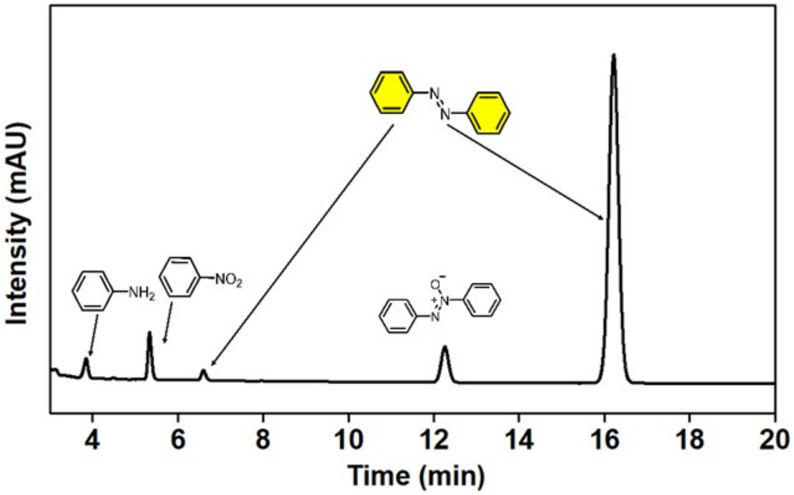

Figure S3. HPLC peaks of product mixture after NBHR electrocatalysis at -0.9 V for 6 h.

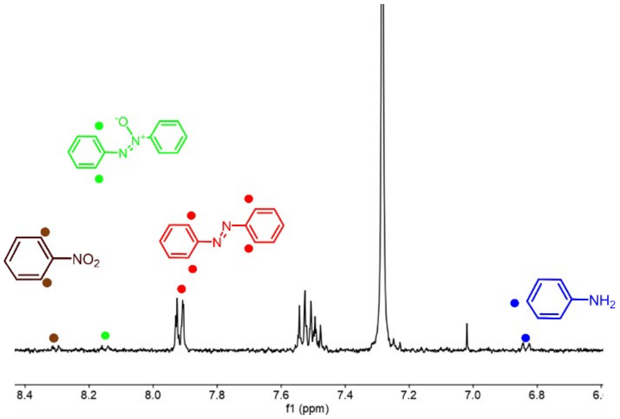

Figure S4. ^{1}H NMR of product mixture after NBHR electrocatalysis at -0.9 V for 6 h.

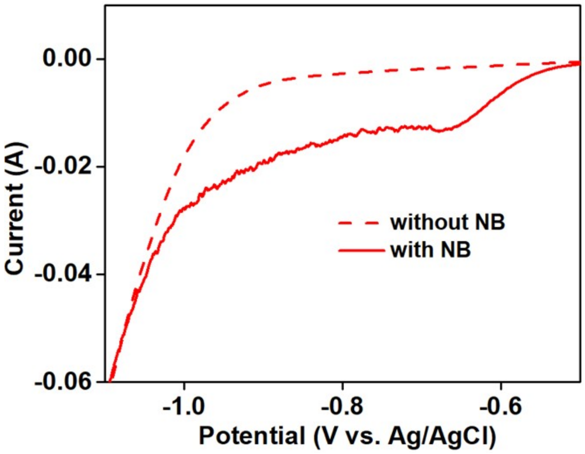

Figure S5. Linear sweep voltammetry (LSV) curves of PdS MNSs required in 1.0 M KOH with and without NB.

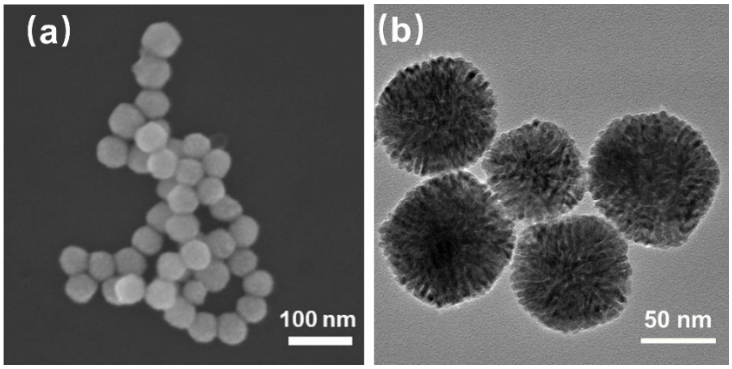

Figure S6. (a) SEM and (b) TEM images of Pd MNSs.

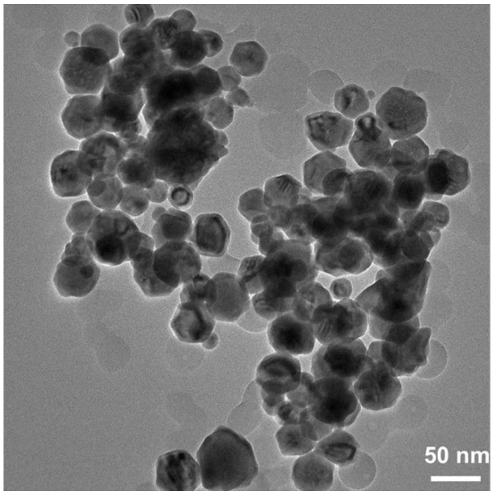

Figure S7. TEM image of Pd NPs.

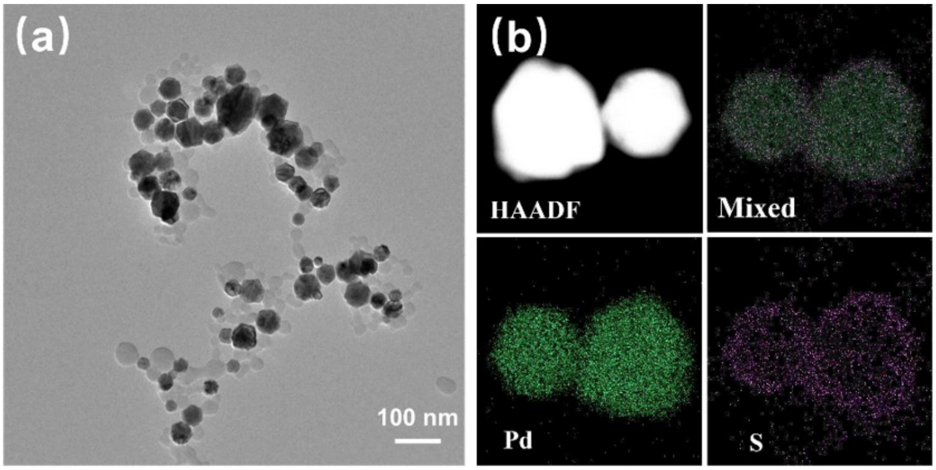

Figure S8. (a) TEM and (b) HAADF-STEM EDX mapping images of PdS NPs.

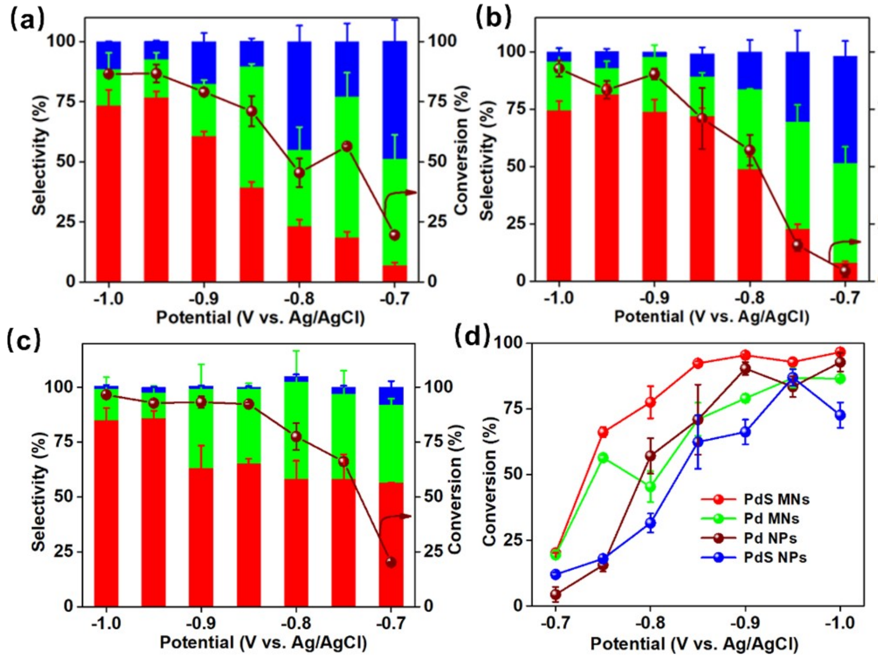

Figure S9. Electrochemical selectivity and conversion of NBHR under different potentials (for 6 h) over (a) Pd MNSs, (b) Pd NPs, and (c) PdS NPs. (d) Summarized NB conversion of NBHR of catalysts collected at different potentials.

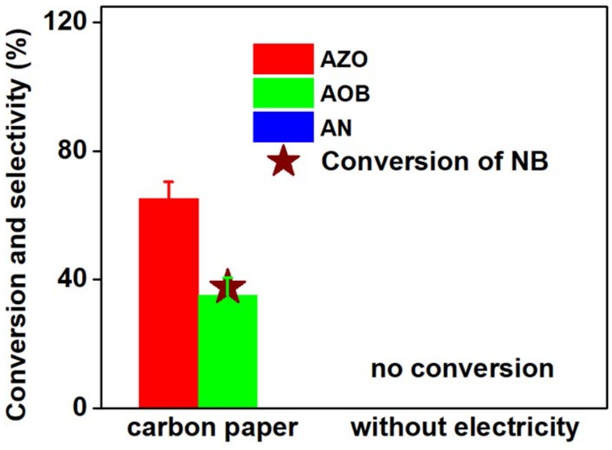

Figure S10. NBHR at open circuit potential (OCP) and conversion and selectivity of carbon paper.

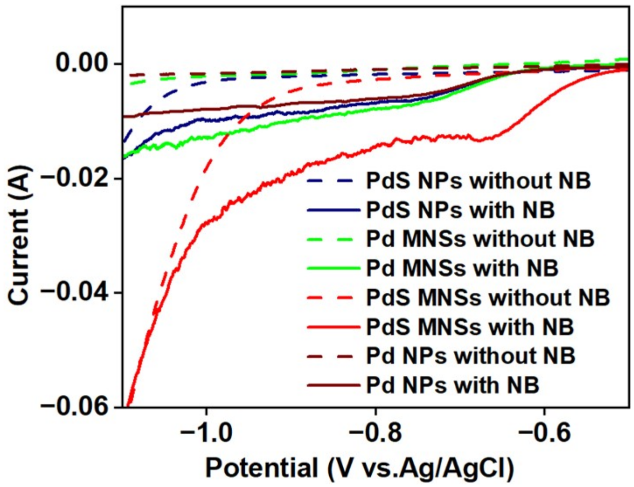

Figure S11. LSV curves of PdS MNSs, Pd MNSs, PdS NPs, and Pd NPs collected in 1.0 M KOH with or without NB.

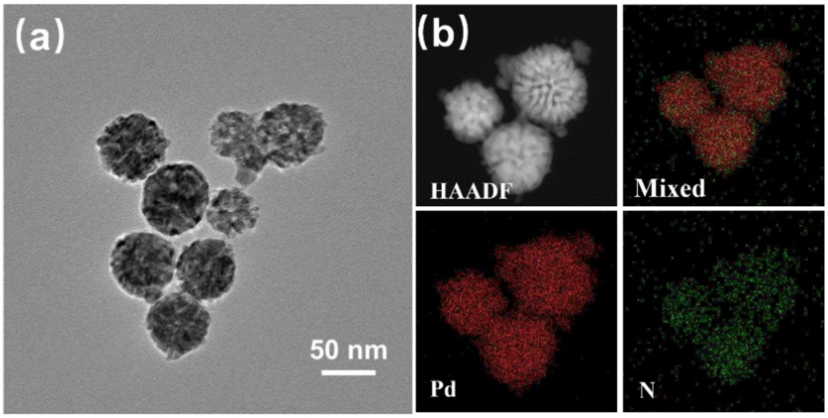

Figure S12. (a) TEM and (b) HAADF-STEM EDX mapping images of PdN MNSs.

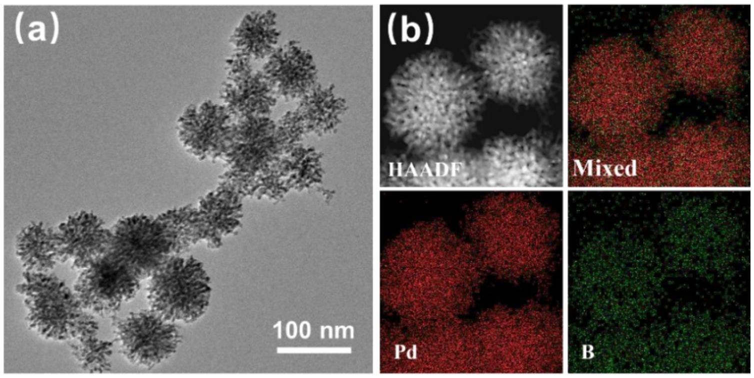

Figure S13. (a) TEM and (b) HAADF-STEM EDX mapping images of PdB MNSs.

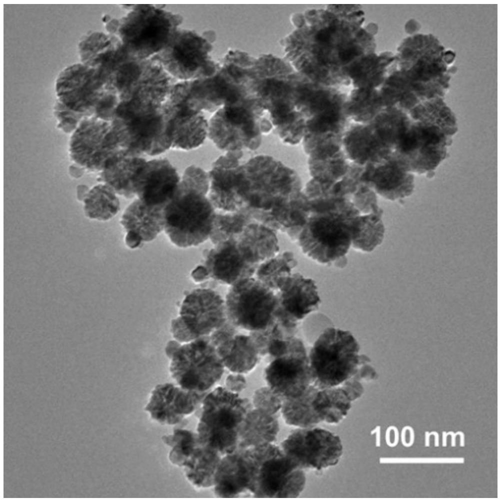

Figure S14. TEM image of PdH MNSs.

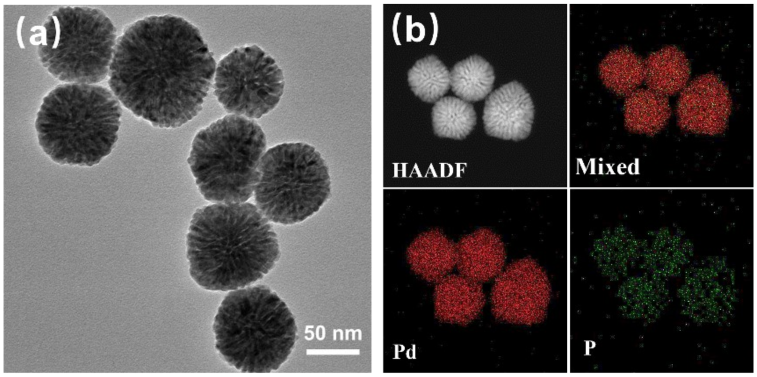

Figure S15. (a) TEM and (b) HAADF-STEM EDX mapping images of PdP MNSs.

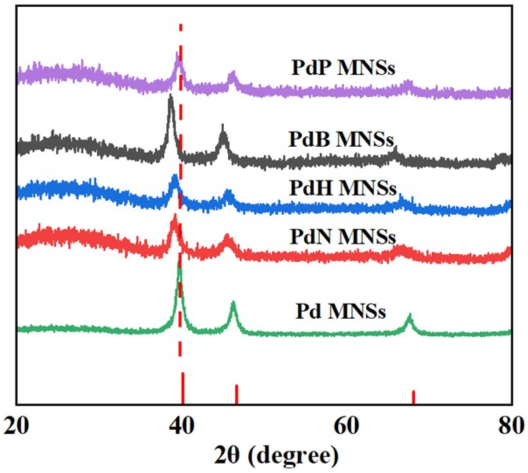

Figure S16. Powder XRD patterns of PdP MNSs, PdB MNSs, PdH MNSs, PdN MNSs, and Pd MNSs.

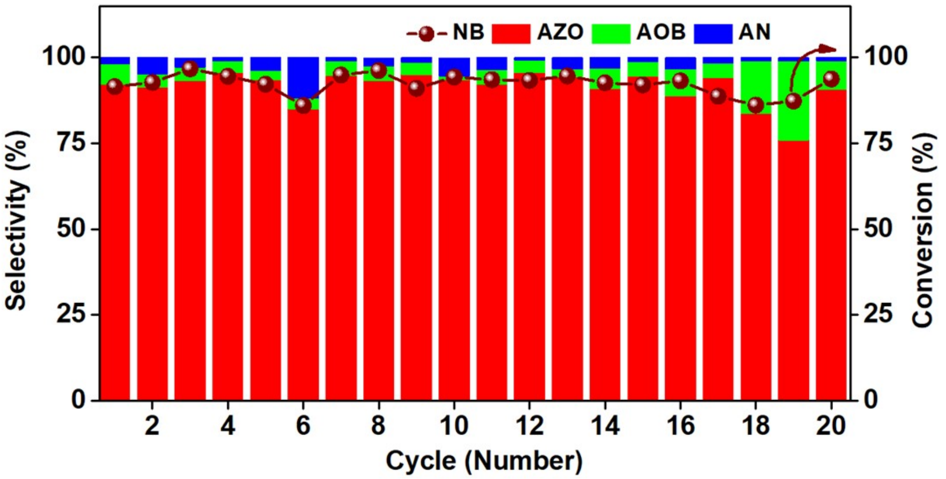

Figure S17. Electrochemical cycling stability of PdS MNSs in NBHR over 20 cycles.

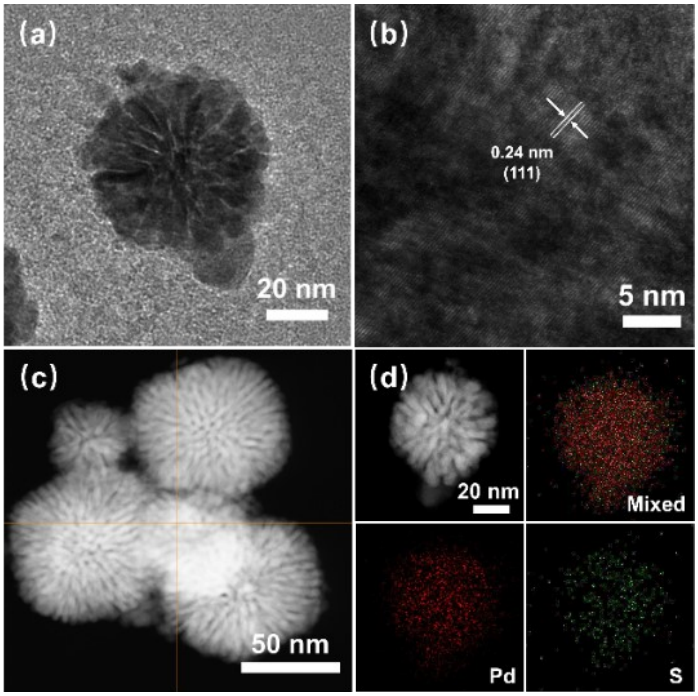

Figure S18. (a) TEM and (b) high-resolution TEM image, (c) HAADF-STEM image and (d) HAADF-STEM EDX mapping images of PdS MNSs after reaction.

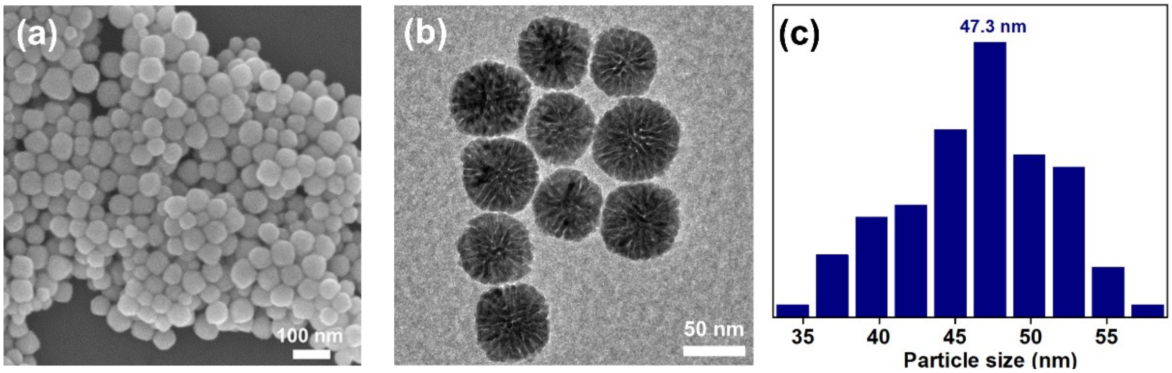

Figure S19. (a) SEM and (b) TEM images, and (c) summarized particle size distribution of PdS MNSs.

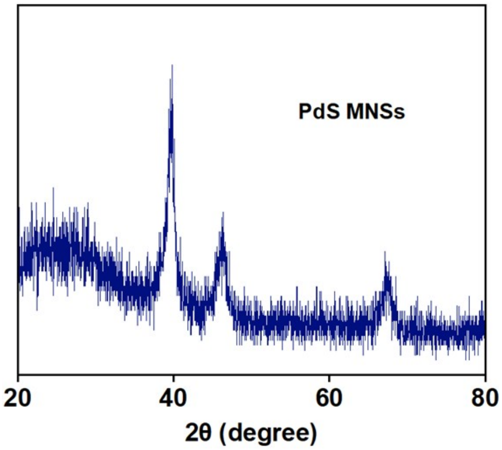

Figure S20. Powder XRD pattern of PdS MNSs.

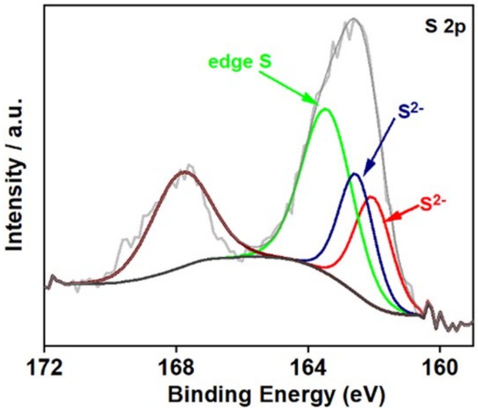

Figure S21 High-resolution XPS S 2p spectra of PdS MNSs.

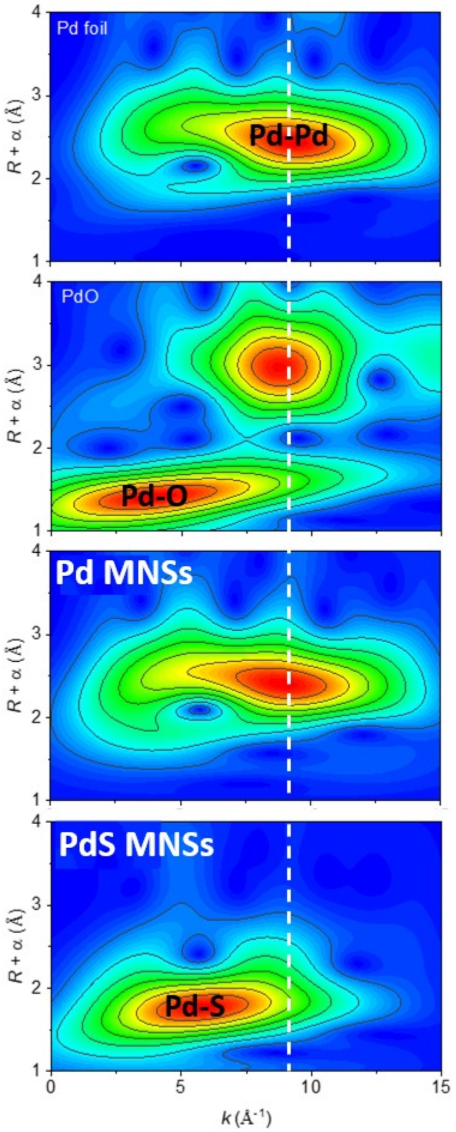

Figure S22. Two-dimensional WT contour plots of PdS MNSs, Pd MNSs, PdO, and Pd foil.

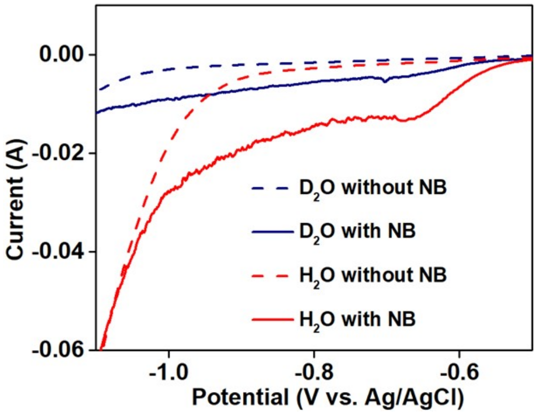

Figure S23. LSV curves of PdS MNSs collected in 1.0 M KOH with H_2O and D_2O as the solvent with/without NB.

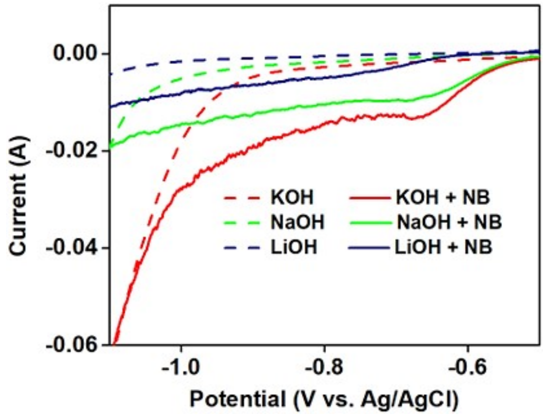

Figure S24. LSV curves of PdS MNSs collected in 1.0 M KOH, 1.0 M NaOH and 1.0 M LiOH with or without NB.

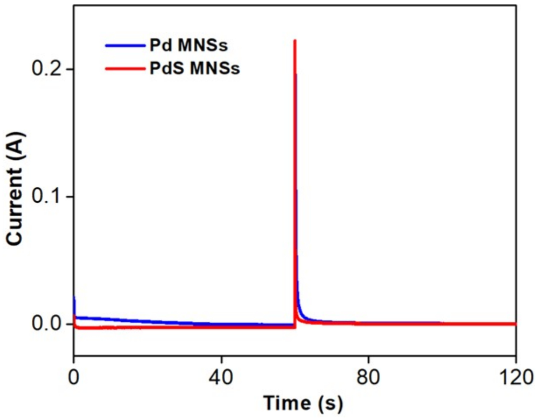

Figure S25. Chronoamperometry measurements of PdS MNSs and Pd MNSs collected at the reduction (adsorption) and oxidation (desoprtion) potentials.

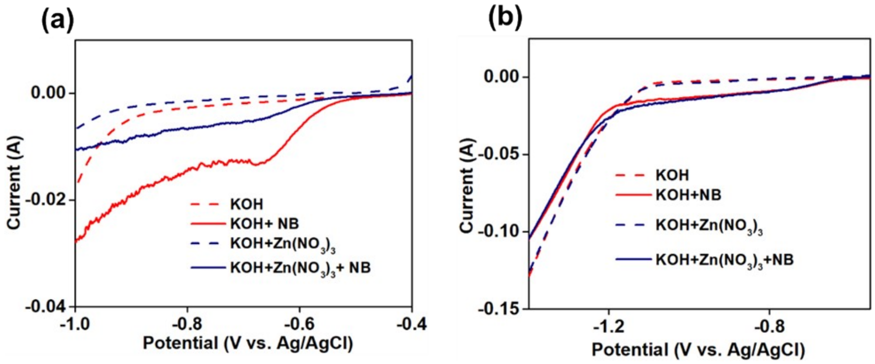

Figure S26. LSV curves collected in 1.0 M KOH with or without NB and $Zn(NO_3)_2$ over (a) PdS MNSs and (b) Pd MNSs as electrocatalysts.

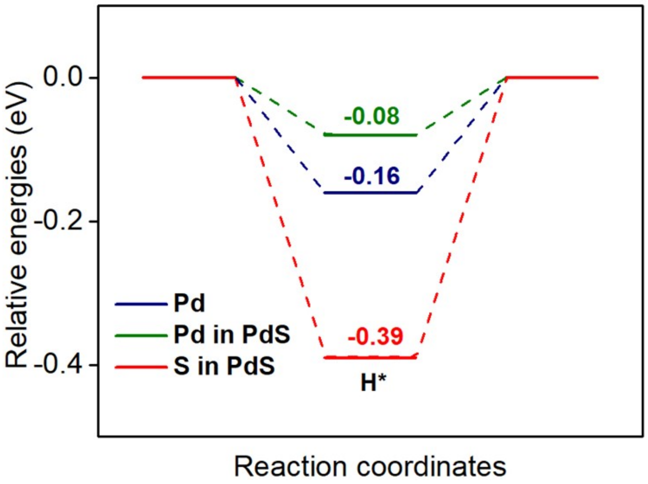

Figure S27. The adsorption energy of H* at the Pd site and S site in PdS MNSs and Pd MNSs.

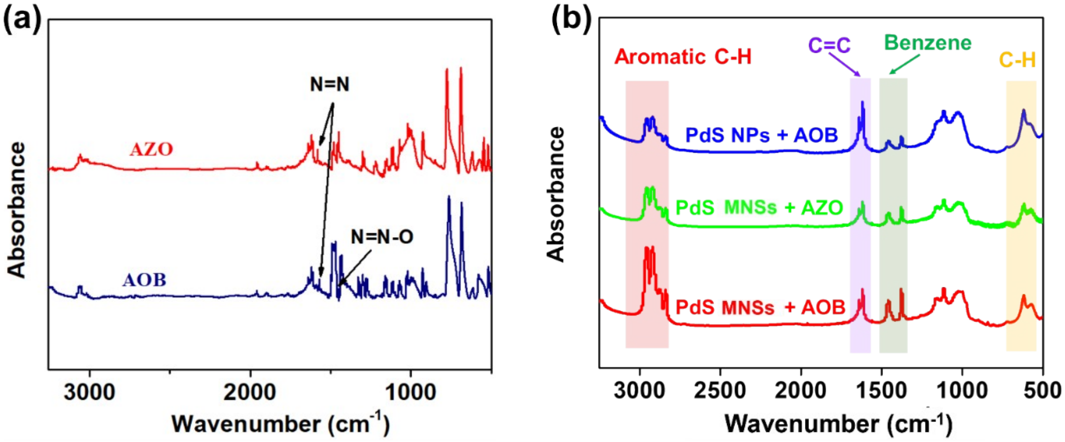

Figure S28. (a) FT-IR spectra of AZO and AOB standards. (b) ATR-IR spectra of PdS NPs and PdS MNSs in the presence of AOB or AZO.