Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Surface Electronic State Mediates Concerted Electron and Proton Transfer at Metal Nanoscale Interface for Catalytic Hydride Reduction of $-NO_2$ to $-NH_2$

Bing-Qian Shan,[1] Jia-Feng Zhou,[1] Meng Ding,[1] Xiao-Dan Hu,[1]Kun Zhang[1,2,3]*

[1] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Laboratory of Interface and Water Science, College of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China;

[2] Laboratoire de chimie, Ecole Normale Supérieure de Lyon, Institut de Chimie de Lyon, Université de Lyon, 46 Allée d'italie, 69364 Lyon cedex 07, France;

[3] Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, 252059, Shandong, P. R. China.

* Correspondence: kzhang@chem.ecnu.edu.cn (K.Z.)

Table of Contents

Experiment section

Materials

(3-aminopropyl) trimethoxysilane (APTMS, 97%) were purchased from Aladdin. Cetyltrimethylammonium tosylate (CTATos) was purchased from MERK. Triethanolamine ($TEAH_3$), tetraethylorthosilicate (TEOS), sodium hydroxide (NaOH, AR), sodium borohydride ($NaBH_4$, AR), hydrochloric acid (HCI, 36%~38%), ethanol (EtOH, AR) and silver nitrate ($AgNO_3$, AR), Chloroplatinic acid (H_2PtCl_6, 37wt% Pt) were purchased from Sinopharm Chemical Reagent Co., Ltd. Potassium tetrachloroplatinate (K_2PdCl_6, 32.6 wt% Pd), Sodium borodeuteride ($NaBD_4$), Deuterium oxide (D_2O, 99% D) and Deuterium sodium hydroxide (NaOD). were achieved from Shanghai Macklin Biochemical.

Techniques

The X-ray diffraction (XRD) patterns were required using a Rigaku Ultima Discover X-Ray Diffractometer at a wavelength of Cu Kα (1.5405 Å). TEM analyses were performed by using a JEOL 2010F microscope equipped with a field-emission gun and operating at 200 kV. FTIR spectra were recorded on a Nicolet FTIR spectrometer (NEXUS 670) by diluting the sample with fine KBr powder and pressing into a pellet. Fluorescence was measured by using a FluorMax-4 fluorimeter (Horiba, Japan). Ultraviolet visible (UV–vis) spectroscopy was conducted with a Shimadzu UV-2700 UV–vis spectrophotometer and the $BaSO_4$ was used as reference. Fluorescence was measured by using a RF-6000 fluorimeter. ^1H NMR spectra were recorded on Bruker 400 MHz Spectrometer and Bruker 300 MHz Spectrometer at 298 K.

Synthesis of dendritic mesoporous silica nanospheres (DMSNs) supports

DMSNs were synthesized according to the literature report(*44*). The DMSNs were treated by HCl and then functionalized by aminopropyl before grafting metal nanoparticles. In a typical process, 2 g of DMSNs, 3.36 mL of 1 M HCl and 80 mL of EtOH were added into a round-bottom flask, the mixture was refluxed with stirring at 60 °C for 1 h. The solid was dried at 80°C after filtered. Then, 1.5 g of HCl washed DMSNs, 2.61 g of APTMS and 60 mL EtOH were introduced into a round-bottom flask and maintained at 80°C for 12 h in an oil bath with stirring under reflux condition. The solution was filtered and the solid was dried at 80°C.

Synthesis of mesoporous silica nanopaticles loaded with different metal NPs

In a 200 mL beaker, 1g of amino-functionalized DMSNs was suspended in 80 mL alcohol, subsequently add 13.27 mL of 7.72 mM $H_2PtCl_6{\cdot}6H_2O$ aqueous or 10 mL of 18.8 mM K_2PdCl_6 solution. After being stirred at room temperature for 12 h in dark, excess of $NaBH_4$ was added at once. The obtained product was filtered and washed repeatedly with deionized H_2O and dried overnight at 80°C. The products were denoted as Pt@DMSNs, Pd@DMSNs respectively. In a 200 mL beaker, 1g of amino-functionalized DMSNs was suspended in 100 mL H_2O and treated by ultrasound for 30 minutes, and subsequently 3.7 mL of 50 mM $AgNO_3$ solution was added. After being stirred at room temperature for 3 h in dark, excess of $NaBH_4$ was added at once. Then the mixture was stirred unceasingly for 30 min. The obtained product was filtered and washed repeatedly with deionized H_2O and dried overnight at 80°C. The products were denoted as Ag@DMSNs. Ag^+@DMSNs was obtained without $NaBH_4$ reduction. Ag-OH@DMSNs were prepared as according to the above method, except that after adding excess $NaBH_4$ and stirring 30 min, 10 mL of 1 M NaOH was added and stirred for 30 min. The other products which contain different concentrations of NaOH (0.01 M, 0.1 M, 2 M) were synthesized (*19*).

Synthesis of Ag loaded zeolite (Ag@LTA)

The silver loaded zeolite Ag-LTA(Na) was prepared by suspending 1 g zeolite materia (Na-LTA, Si/Al = 1~2) in 500 mL of a silver nitrate aqueous solution, the suspension was then agitated for 2 hours in the dark. The powder was recovered by filtration using a Büchner filter and washed several times with milliQ water. Then the sample was calcined at 80°C (5°C min^{-1}) (*51*). After heat treatment the sample was cooled under ambient conditions, allowing the sample to reach a fully hydrated state, and stored in the dark for further analysis.

Reduction of 4-Nitrophenol

Aqueous solutions of H_2O (2.5 mL), 4-NP (0.2 mL, 2.5 mM) and $NaBH_4$ (0.4 mL, 250 mM) were added into a quartz cuvette under stirring. Subsequently, a certain amount (30 μL) of aqueous solution of catalyst (5 mg/mL) was added. As the reaction progressed, the bright yellow solution gradually faded. The reaction was scanned by UV-vis spectrum repeatedly from 500 nm to 250 nm over the whole course to record the changes. To test the effect of hydroxide content on the reaction activity, 2.5 mL of NaOH (0.01 M, 0.1 M, 1 M, 2 M) was added instead of 2.5 mL H_2O. In the deuterium isotopic experiments, the reduction was conducted under the same conditions except for the use of $NaBD_4$ and/or D_2O. To test the reaction kinetics in different kinds of solvents, the reduction was also conducted in ethanol, and acetonitrile, respectively.

Large Scale Reduction of 4-NP.

To obtain more reduction products of 4-AP for spectroscopic measurements, large scale synthesis was carried out according to the literature(*16*). First, 12 mg of 4-NP was dissolved in 4 mL of H_2O under magnetic stirring in the tube, followed by addition of a 1 mL 5 mg/mL catalysts. Then, 24.0 mg of $NaBH_4$ was dissolved in 1 mL of H_2O and the solution was immediately added into the tube. After stirring for about 10 min, the color of the mixture became colorless. The complete reduction was confirmed by UV−vis absorption spectroscopic measurement, in which the peak of 4-NP at about 400 nm disappeared. Afterward, the mixture was extracted with ethyl acetate three times and the products in the organic phase were collected and dried over anhydrous sodium sulfate ($NaSO_4$). Finally, the reduction products were obtained after evaporating the solvent under reduced pressure.

Experiment results

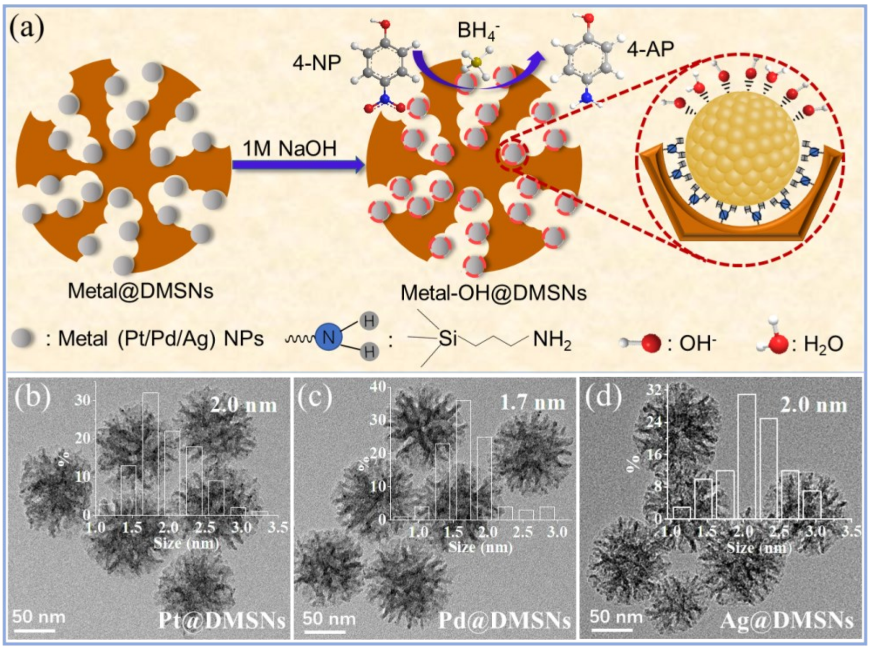

Figure S1. (a) Schematic illustration of the synthesis procedure of Pt, Pd and Ag NPs supported DMSNs catalysts. TEM image of Pt@DMSNs (b), Pd@DMSNs (c) and Ag@DMSNs (d). The inset is the particle size distribution. The average diameter for Pt, Pd and Ag NPs is about 2.0, 1.7 and 4.1 nm, respectively.

Table S1. The metal contents (wt%) of different samples determined by ICP-OES analysis.

Sample	theoretical value (wt%)	actual value (wt%)
Pt@DMSNs	2.0	1.4
Pd@DMSNs	2.0	1.4
Ag@DMSNs	2.0	1.3

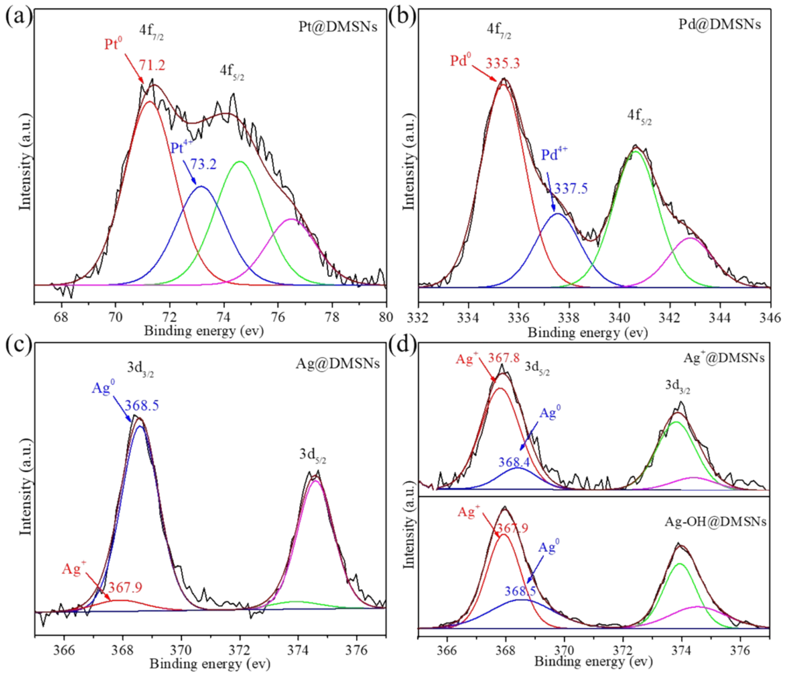

Figure S2. XPS spectra of Pt (a), Pd (b) and Ag (c) NPs supported DMSNs catalysts. XPS spectra of Ag^+@DMSNs catalyst without the last step of metal reduction and Ag-OH@DMSNs with OH^- pre-adsorbed (d).

Table S2. Surface compositions of catalysts determined by XPS.

Sample	Pt component (%)		Pt position (eV)	
	Pt^0	Pt^{4+}	Pt^0	Pt^{4+}
Pt@DMSNs	65.2	34.8	71.2	73.2
	Pd component (%)		Pd position (eV)	
	Pd^0	Pd^{4+}	Pd^0	Pd^{4+}
Pd@DMSNs	73.3	26.7	335.4	337.5
	Ag component (%)		Ag position (eV)	
	Ag^0	Ag^+	Ag^0	Ag^+
Ag@DMSNs	92.6	7.4	368.5	367.9
Ag^+@DMSNs	17.2	82.8	368.4	367.8
Ag-OH@DMSNs	36.3	63.7	368.5	367.9

Table S3. Comparison of recent reports on Ag-based catalysts catalyzed reduction of 4-NP by $NaBH_4$.

Catalyst	Catalyst used (mg)	K^a (10^{-3} s^{-1})	K/M^b (s^{-1} g^{-1})	Ref.
Ag–Fe_2O_3	2.00	4.90	2.45	(*63*)
Fe_3O_4@SiO_2–Ag	1.00	7.67	7.67	(*64*)
Ag@hm-SiO_2	2.00	18.00	9.00	(*65*)
AgNPs/PD/PANFP	0.14	2.28	16.31	(*66*)
SiO_2@Ag-2	0.50	9.32	18.64	(*67*)
$Ag_{2.4\%}$Ni@SBA-16C	0.40	37.90	94.80	(*68*)
Pt@Ag NPs	0.05	5.92	118.40	(*69*)
2.0%Ag-OH^-@DMSNs	0.15	21.17	141.13	(*19*)
Ag-OMS-C	0.20	30.00	150.00	(*70*)
Ag@LTA	0.15	22.67	151.13	this work

[a] The reaction rate constant.

[b] The reaction rate constant per total weight of used catalyst.

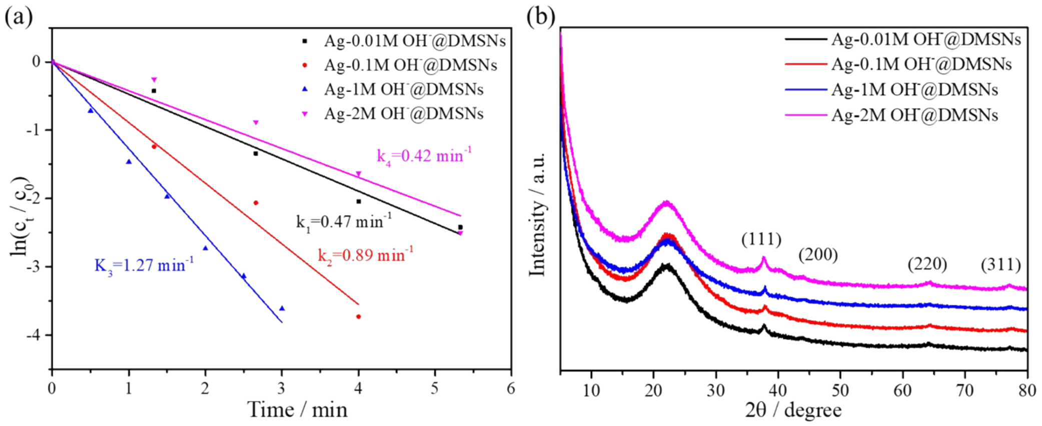

Figure S3. Plot of $\ln(C_t/C_0)$ against the reaction time of the reduction of 4-NP (a) and XRD patterns (b) of different content of OH^- was introduced into Ag@DMSNs.

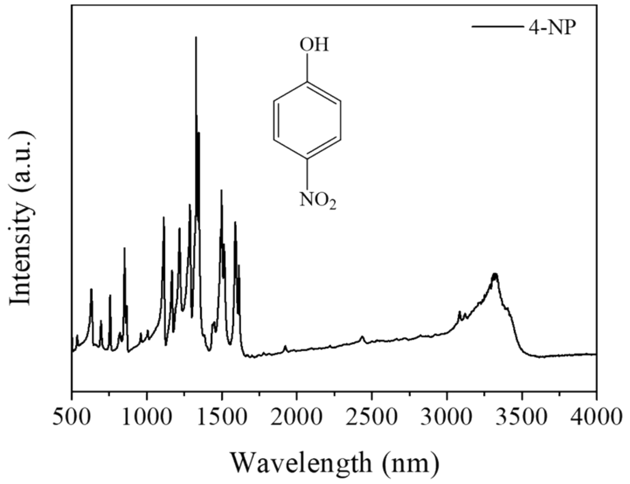

Figure S4. FTIR spectrum of commercial 4-NP.

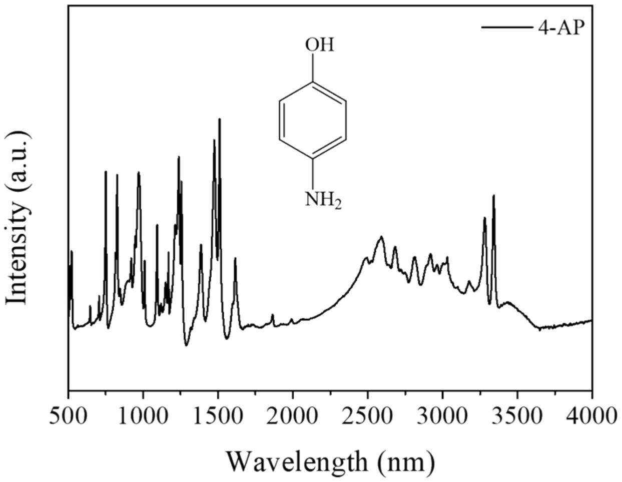

Figure S5. FTIR spectrum of commercial 4-AP.

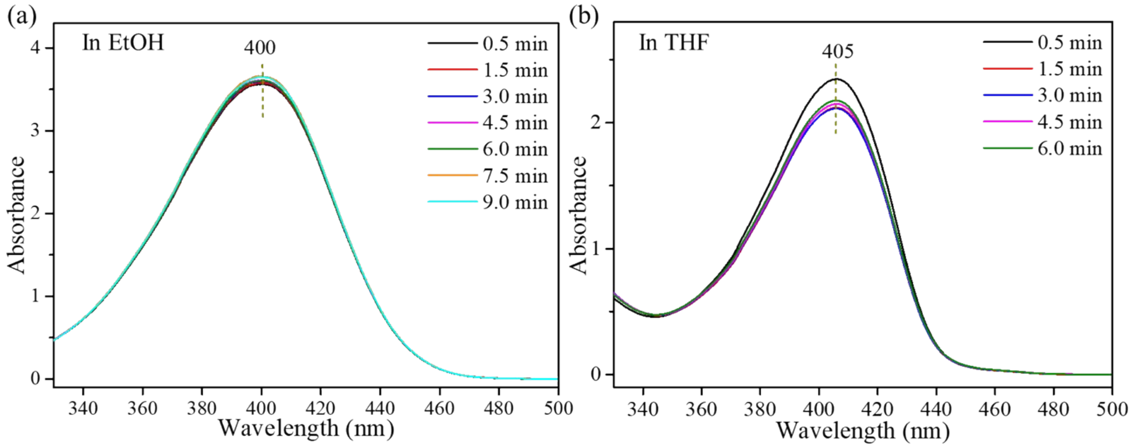

Figure S6. UV-vis absorption spectra of Ag@DMSNs reduction of 4-NP using NaBH4 in ethanol.

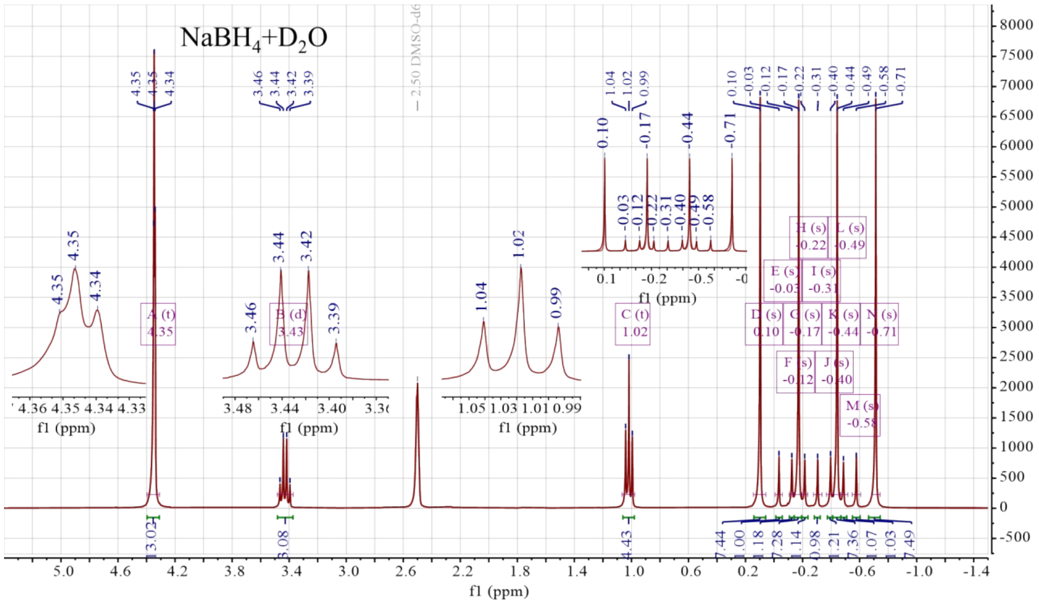

Figure S7. ^{1}H NMR spectrum of $NaBH_4$ and D_2O.

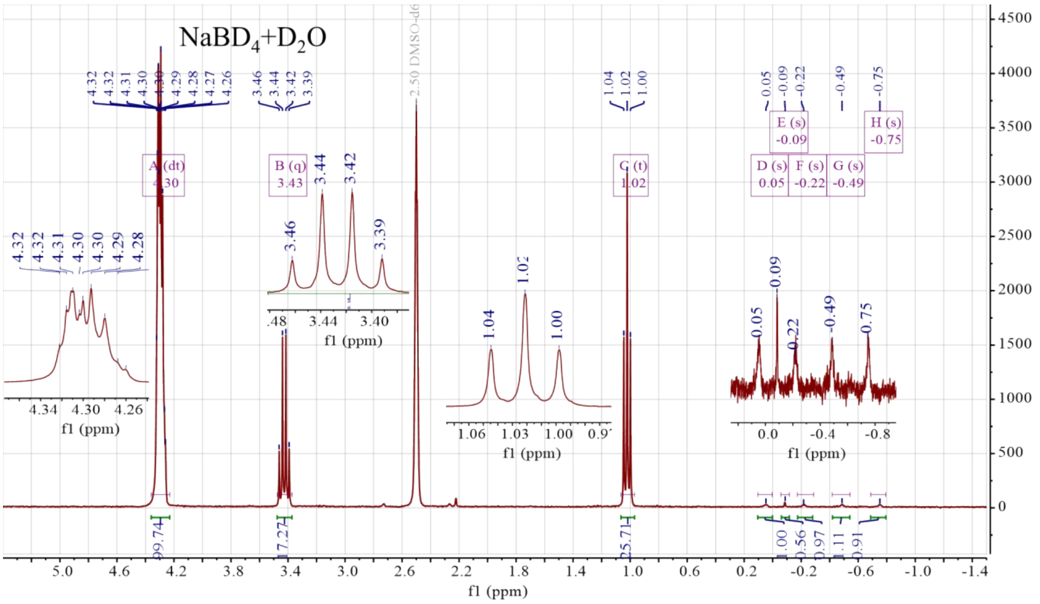

Figure S8. ^{1}H NMR spectrum of $NaBD_4$ and D_2O.

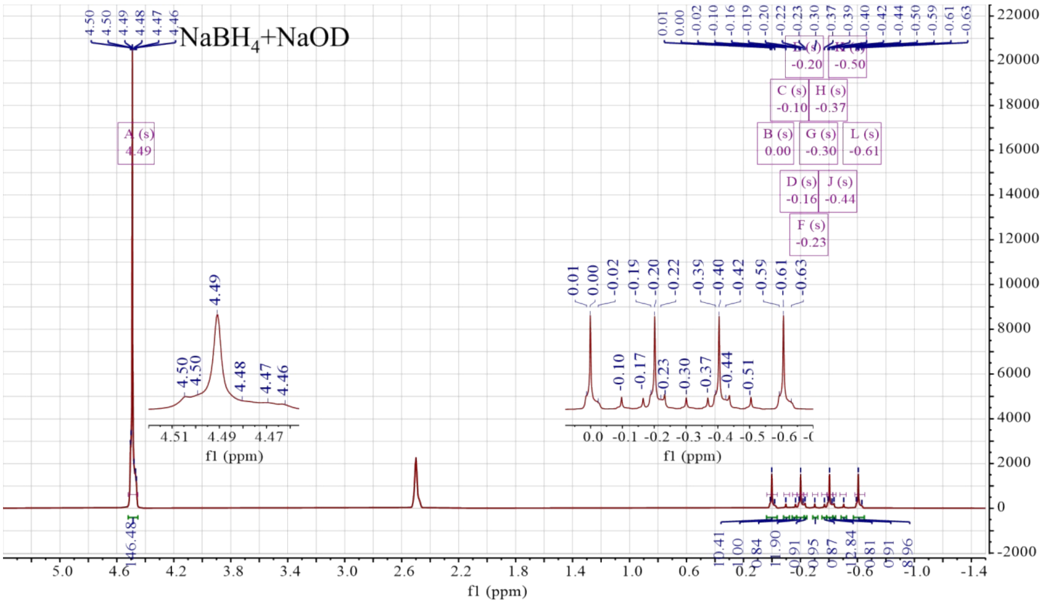

Figure S9. ^{1}H NMR spectrum of $NaBH_4$ and NaOD.

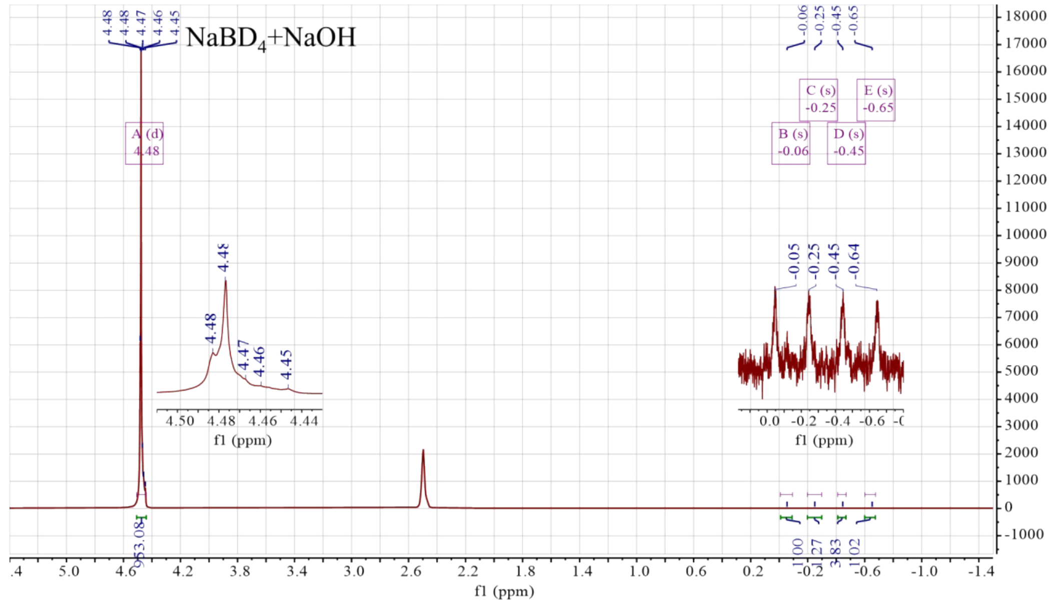

Figure S10. ^{1}H NMR spectrum of NaBD$_4$ and NaOH.

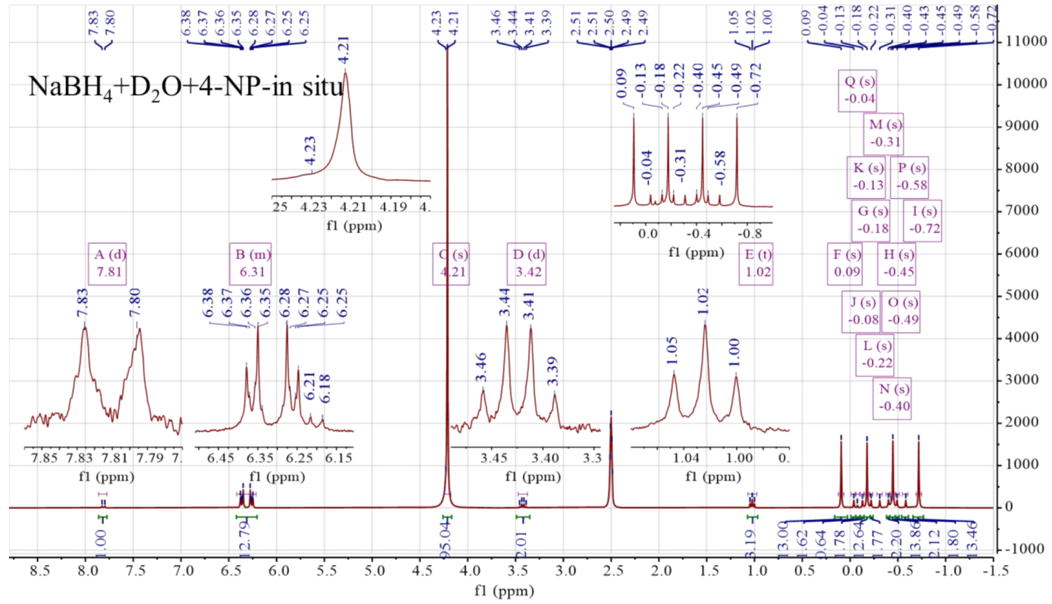

Figure S11. ^{1}H NMR spectrum of the reduction product using NaBH$_4$ and D$_2$O in the middle of the reaction.

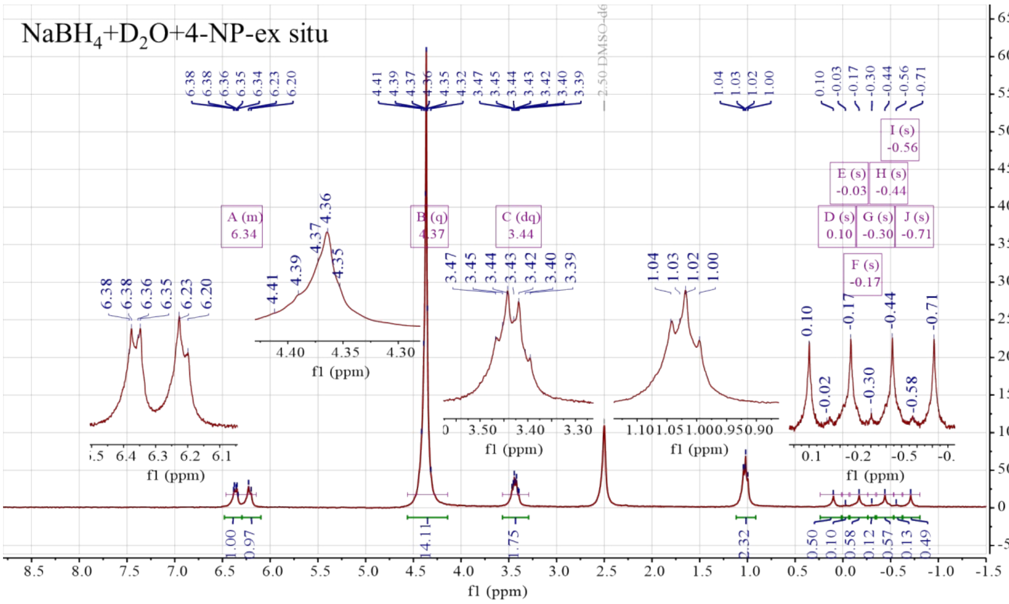

Figure S12. ^{1}H NMR spectrum of the reduction product using NaBH$_4$ and D$_2$O after the reaction.

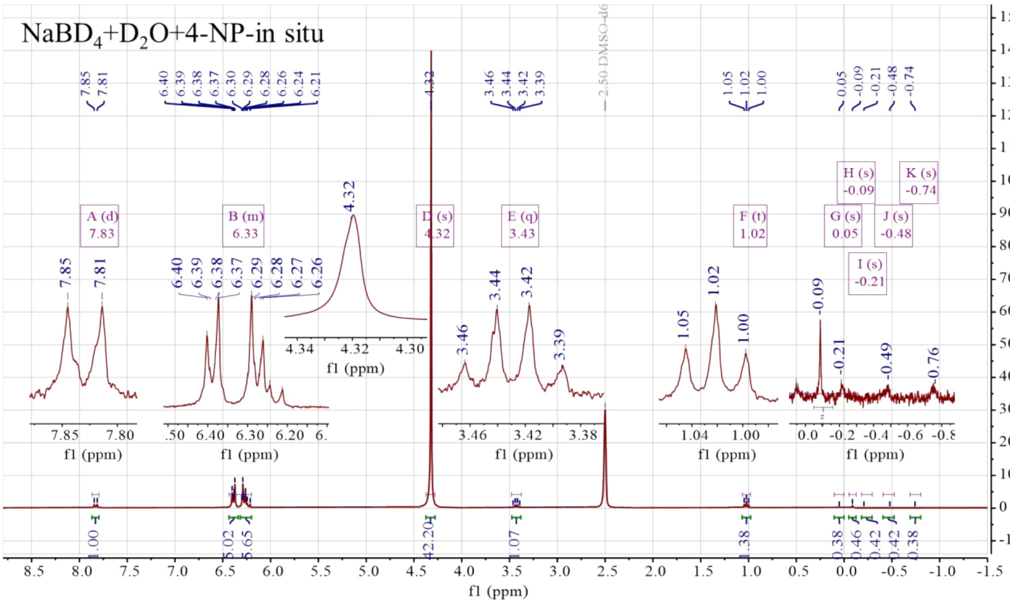

Figure S13. ^{1}H NMR spectrum of the reduction product using NaBD$_4$ and D$_2$O in the middle of the reaction.

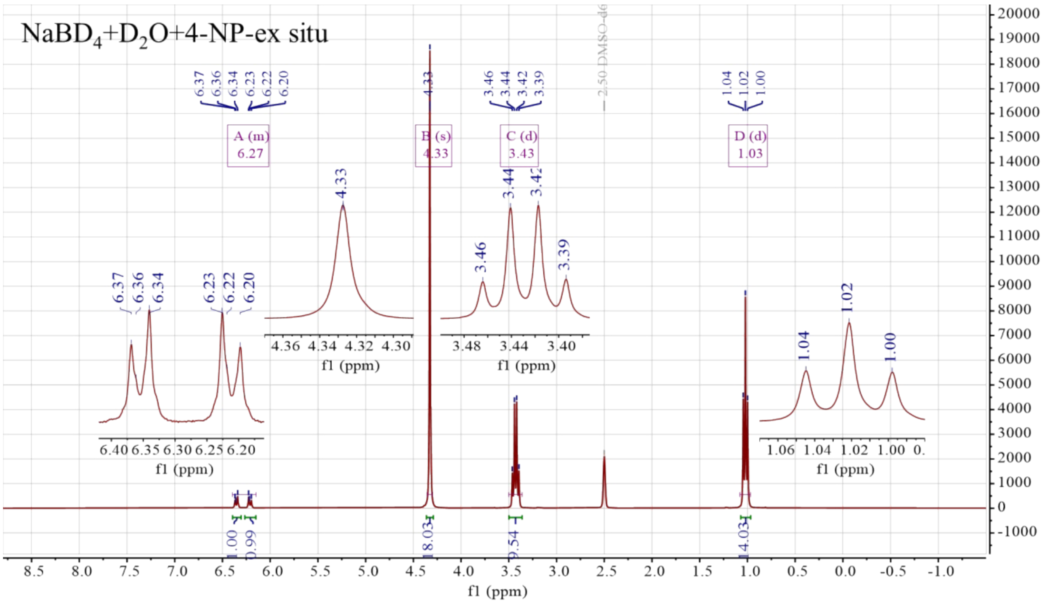

Figure S14. ^{1}H NMR spectrum of the reduction product using $NaBD_4$ and D_2O after the reaction.

Reference

1. K. Zhang *et al.*, Facile large-scale synthesis of monodisperse mesoporous silica nanospheres with tunable pore structure. *J. Am. Chem. Soc.* **135**, 2427-2430 (2013).
2. X.-D. Hu, B.-Q. Shan, R. Tao, T.-Q. Yang, K. Zhang, Interfacial Hydroxyl Promotes the Reduction of 4-Nitrophenol by Ag-based Catalysts Confined in Dendritic Mesoporous Silica Nanospheres. *J. Phys. Chem. C* **125**, 2446-2453 (2021).
3. H. Xiao-Dan, Y. Taiqun, S. Bingqian, P. Bo, Z. Kun, Topological Excitation of Singly Hydrated Hydroxide Complex in Confined Sub-Nanospace for Bright Color Emission and Heterogeneous Catalysis. *ChemRxiv* (2020).
4. Y. Zhao *et al.*, Mechanistic Study of Catalytic Hydride Reduction of −NO2 to −NH2 Using Isotopic Solvent and Reducer: The Real Hydrogen Source. *J. Phys. Chem. C* **123**, 15582-15588 (2019).
5. S. Liu, Y. Chen, L. Dong, Ag–Fe2O3nanocomposites with enhanced catalytic activity for reduction of 4-nitrophenol. *Mater. Res. Express* **3**, 075024 (2016).
6. Y. Chi *et al.*, Synthesis of Fe3O4@SiO2–Ag magnetic nanocomposite based on small-sized and highly dispersed silver nanoparticles for catalytic reduction of 4-nitrophenol. *J. Colloid Interface Sci.* **383**, 96-102 (2012).
7. W. Li *et al.*, Hollow mesoporous SiO2 sphere nanoarchitectures with encapsulated silver nanoparticles for catalytic reduction of 4-nitrophenol. *Inorg. Chem. Front.* **3**, 663-670 (2016).

8. S. Lu *et al.*, Preparation of silver nanoparticles/polydopamine functionalized polyacrylonitrile fiber paper and its catalytic activity for the reduction 4-nitrophenol. *Appl. Surf. Sci.* **411**, 163-169 (2017).
9. L. Tzounis *et al.*, Controlled growth of Ag nanoparticles decorated onto the surface of SiO2 spheres: a nanohybrid system with combined SERS and catalytic properties. *RSC Adv.* **4**, 17846-17855 (2014).
10. C. S. Budi, J. R. Deka, D. Saikia, H.-M. Kao, Y.-C. Yang, Ultrafine bimetallic Ag-doped Ni nanoparticles embedded in cage-type mesoporous silica SBA-16 as superior catalysts for conversion of toxic nitroaromatic compounds. *J. Hazard. Mater.* **384**, 121270 (2020).
11. Z.-S. Lv, X.-Y. Zhu, H.-B. Meng, J.-J. Feng, A.-J. Wang, One-pot synthesis of highly branched Pt@Ag core-shell nanoparticles as a recyclable catalyst with dramatically boosting the catalytic performance for 4-nitrophenol reduction. *J. Colloid Interface Sci.* **538**, 349-356 (2019).
12. H.-T. Fan *et al.*, Ordered mesoporous silica cubic particles decorated with silver nanoparticles: a highly active and recyclable heterogeneous catalyst for the reduction of 4-nitrophenol. *Dalton Trans.* **48**, 2692-2700 (2019).