[Electronic Supplementary Information]

Guiding by in-situ hot stage in TEM to synthesize magnetic metal nanoparticles from a MOF

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Section 1. Materials and characterization

Materials characterization. ^{1}H-NMR spectrum was measured with Bruker Avance DPX400 NMR. The X-ray diffraction patterns were recorded on a SHIMADZU LabX XRD-6000 diffractometer with Cu-Ka radiation (λ = 1.5418 Å) in the 2θ range of 4-80° with a step size of 0.02° and a time of 4 second per step. Nitrogen adsorption-desorption measurements were measured with a Micro Meritics TriStar Ⅱ 3020 surface area and pore size analyzer at 77 K. The morphology of the sample were inspected on a scanning electron microscope of JEOS JSM-6510. Transmission electron microscope (TEM) and high resolution TEM (HRTEM) images were obtained using JEM-2100 TEM system with a field emission gun operating at 200 kV. An in-situ hot stage holder and heater control from Gatan SmartSet Model 901 was used in this study. Raman spectra were measured on an inVia microscopic confocal laser Raman spectrometer. The catalytic reduction of 4-NP was obtained on a UV-2450 UV/vis spectrophotometer.

Chemicals. 3,4,9,10-Perylene tetracarboxylic dianhydride (PTCDA, purity) was purchased from Sigma-Aldrich Chemical Co. $Ni(NO_3)_2 \cdot 6H_2O$ (AR) was purchased from Tianjin Fuchen Chemical Reagents Factory. 4-nitrophenol and $NaBH_4$ were of analytical grade and were purchased from Aladin Industrial Corporation. Dimethylformamide (DMF) and ethanol were purchased from Xilong Chemical Co., Ltd.

Synthesis of 3,4,9,10-Perylene tetracarboxylic acid (PTCA). 3,4,9,10-Perylene tetracarboxylic dianhydride (0.39 g, PTCDA) was dissolved in a aqueous solution of 5% KOH under stirring at 60–70℃. After hydrolyzing for 1h, 1 M HCl was added dropwise utill a precipitate formed and pH was about 2. Then the precipitate was filtered and dried at room temperature to yield 0.35 g of red powder.

Synthesis of Ni-MOF. $Ni(NO_3)_2 \cdot 6H_2O$ (0.116 g, 0.4 mmol) was dissolved in a mixture solvent (1.4 ml of dimethylformamide, 1.4 ml of ethanol, 1.4 ml of water). Then PTCA (0.021 g, 0.05 mmol) was added into the above solvent under sonicating. The resulting mixture was heated in a Teflon autoclave at 100 ℃ for 5 days. When the temperature was cooled down to ambient, the orange red powders were acquired and washed with DMF and distilled water several times and dried at room temperature. The as-prepared powders were called as Ni-MOF.

Synthesis of Ni-NPC. In a typical synthesis, the precursor Ni-MOF were paved in a ceramic boat and placed into a furnace. The powder were carbonized under a nitrogen flow and heated to different temperature with a heating rate of 5 ℃·min^{-1}. After the pre-set temperature was reached, the powders were annealed for 3 h, denoted as Ni-NPC-X (X is consider as pre-set temperature).

Catalytic tests on reduction of 4-NP. Two milligrams of Ni-NPC-600 were homogeneously dispersed in 2.05 mL of deionized water by ultrasonication, followed by the addition of 0.3 mL of 4-nitrophenol solution (1 mM), and the mixture was stirred for 10 min at room temperature. Then, 0.65 mL of $NaBH_4$ aqueous solution (0.2 M) was added to the mixture, which was stirred until the deep yellow solution became colorless. During the reaction, a small portion of the mixture was taken at regular intervals and analyzed by UV-Vis spectroscopy. For recycling, 10 eq catalysts were added to mixture solution (10 eq deionized water, 10 eq 4-nitrophenol, 10 eq $NaBH_4$) under stirring, after the reaction completed, the catalysts were separated from the mixture using a magnet and a portion of solution were taken for UV/Vis measurements. Then, the catalysts were rinsed with water several times and re-dispersed into a mixture of new reactants to proceed the next cycle.

Section 2. Figures S1-13
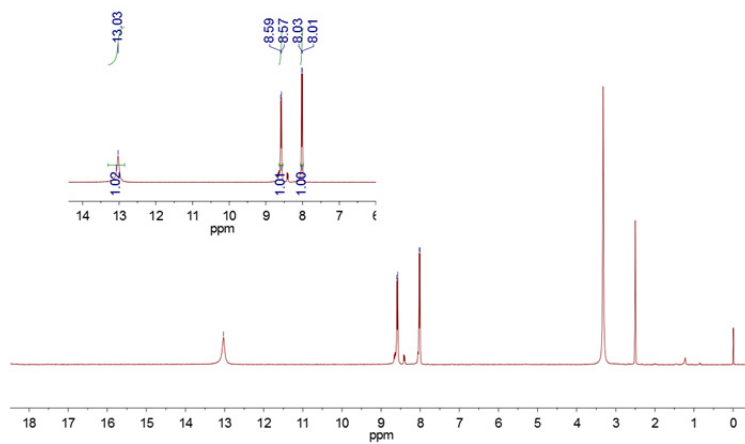
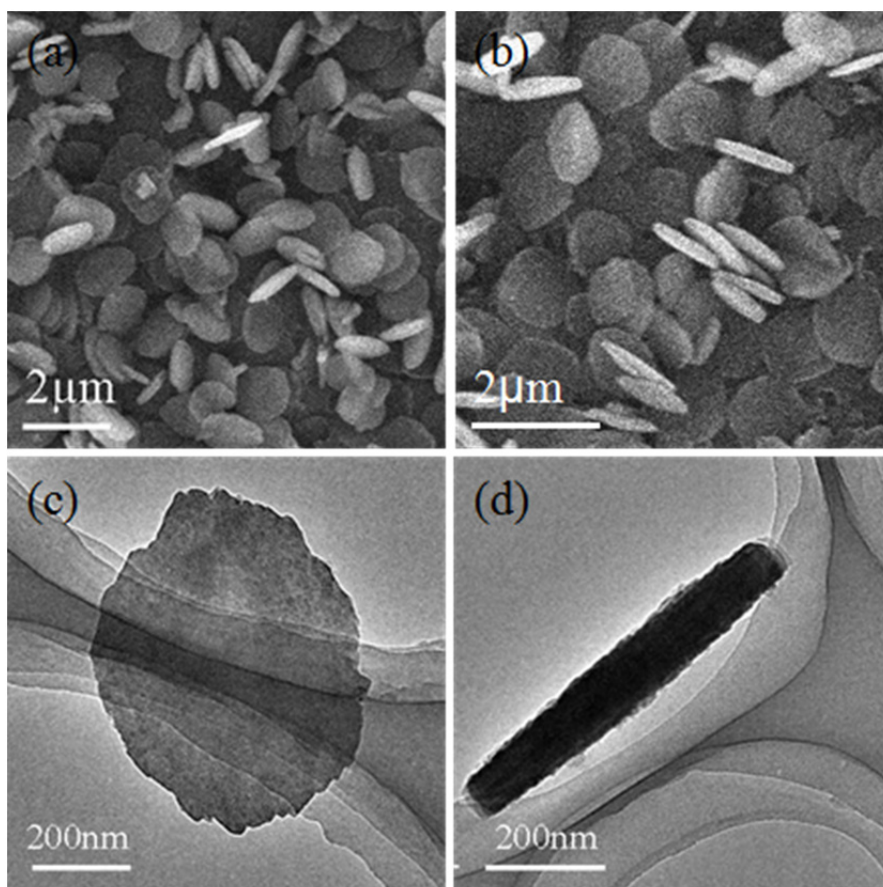Fig. S1 ^{1}H-NMR spectrum of PTCA in D_2O.

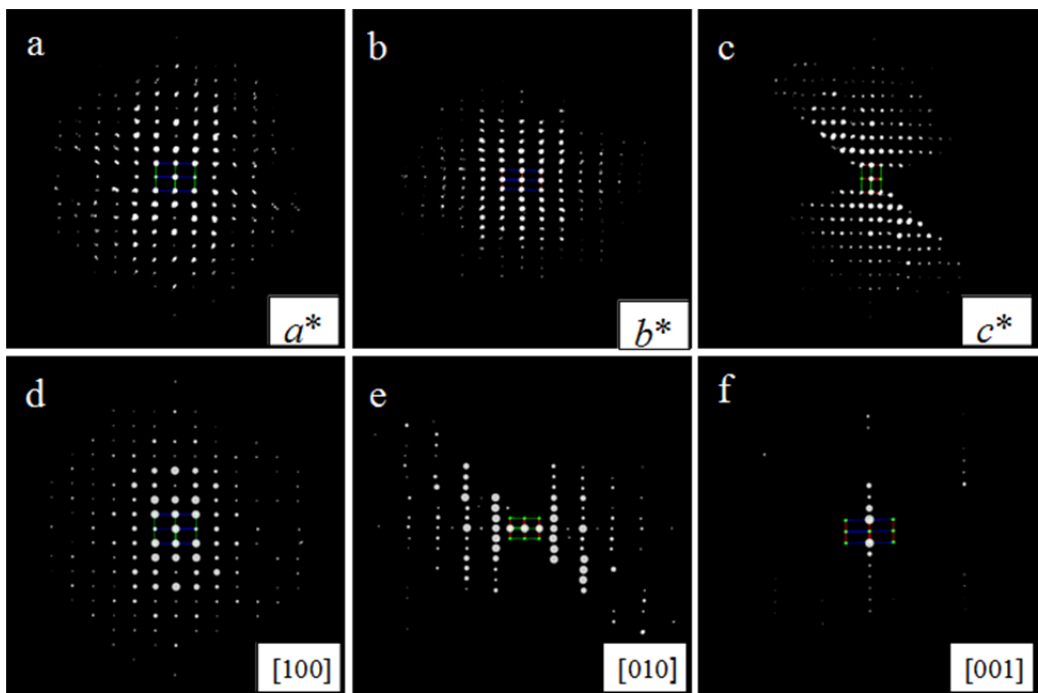Fig. S2 SEM (a and b) and TEM images (c and d) of Ni-MOF.

Fig. S3 (a-c) Projections of 3D reconstructed reciprocal space and (d-f) intersections of reconstructed reciprocal space of Ni-MOF in [100], [010] and [001] axes, respectively.
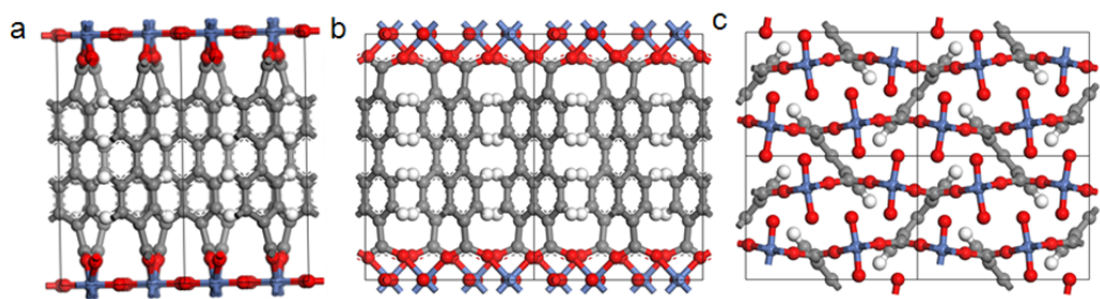

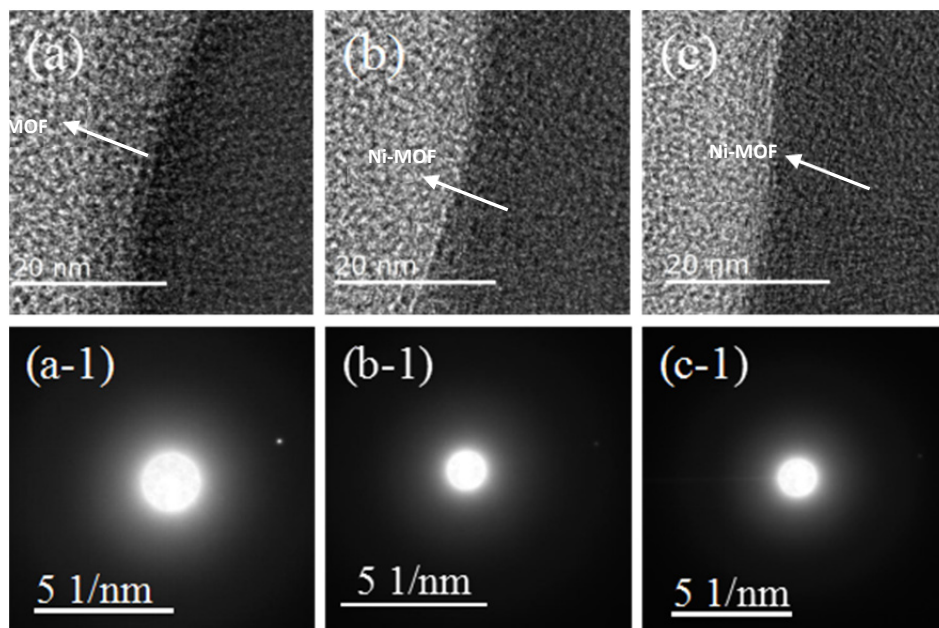Fig. S4 The section from the orientation of *a*, *b* and *c* in the lattice of Ni-MOF.

Fig. S5 HRTEM images (a) 1 h, (b) 2 h, (c) 3 h and the corresponding Selected Area Electron Diffraction (SAED) patterns (a-1)-(c-1) of Ni-MOF irradiating under electron.
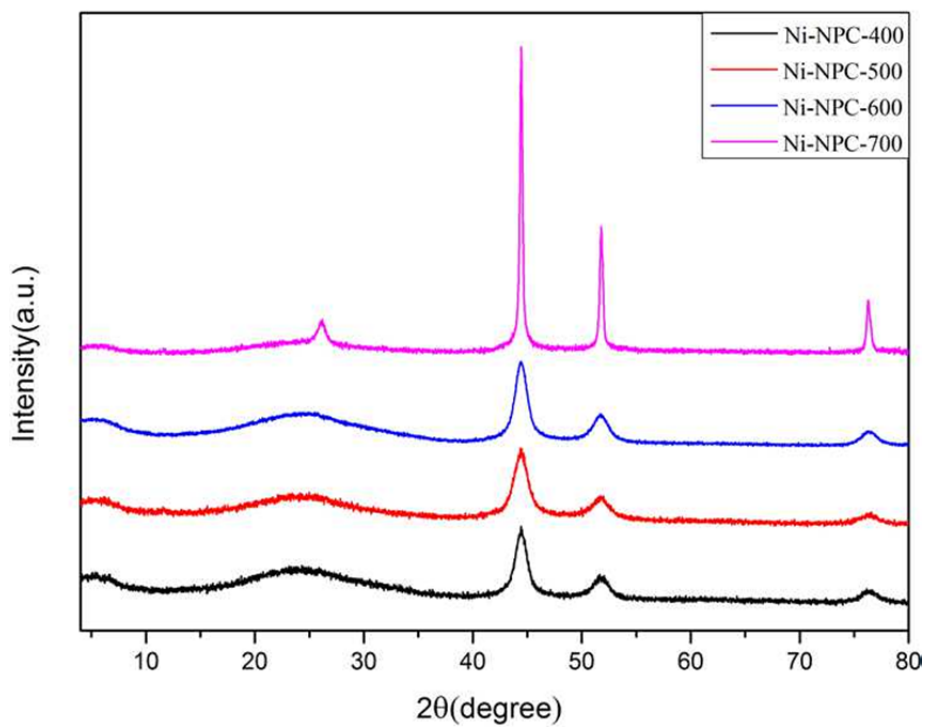

Fig. S6 PXRD patterns of (a) Ni-NPC-400, (b) Ni-NPC-500, (C) Ni-NPC-600, and (d) Ni-NPC-700.
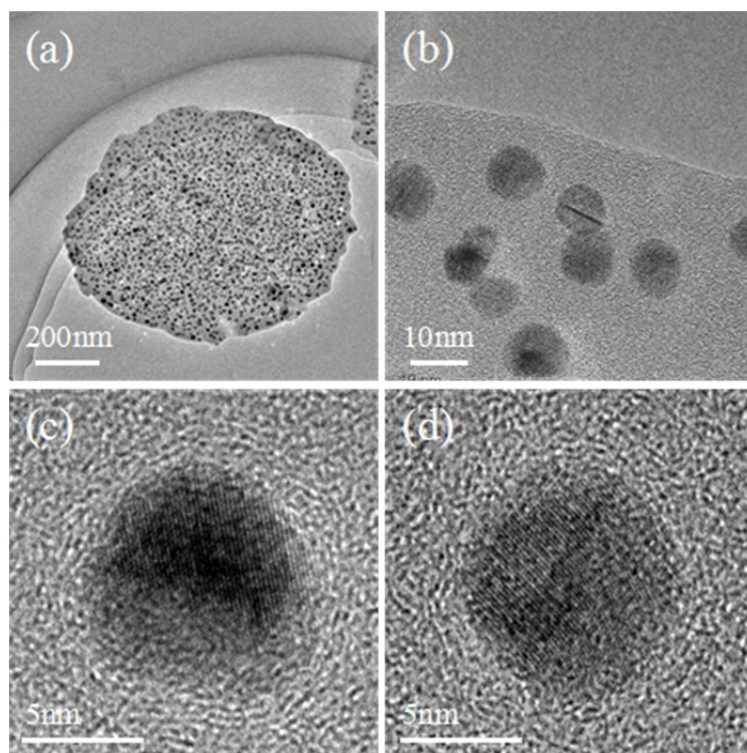
Fig. S7 (a) Low-magnification TEM; (b) high-magnification TEM; and (c-d) enlarged high-magnification of Ni-NPC-400.
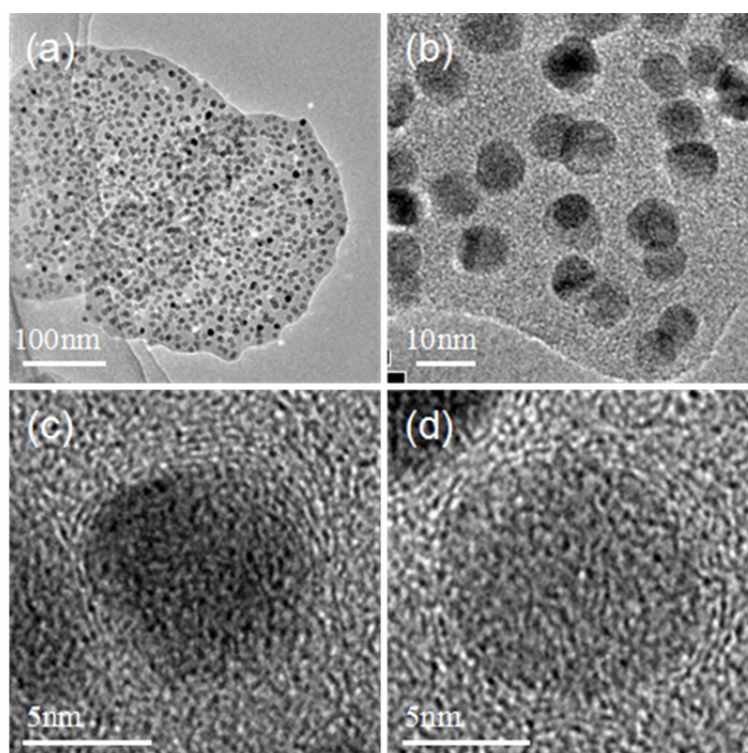

Fig. S8 (a) Low-magnification TEM; (b) high-magnification TEM; and (c-d) enlarged high-magnification of Ni-NPC-500.
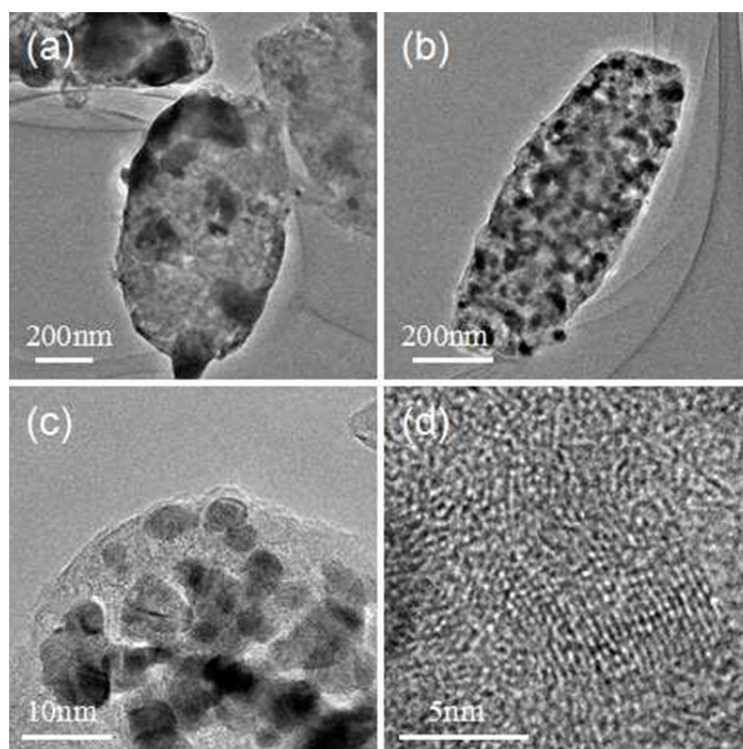
Fig. S9 (a) Low-magnification TEM; (b) high-magnification TEM; and (c-d) enlarged high-magnification of Ni-NPC-700.
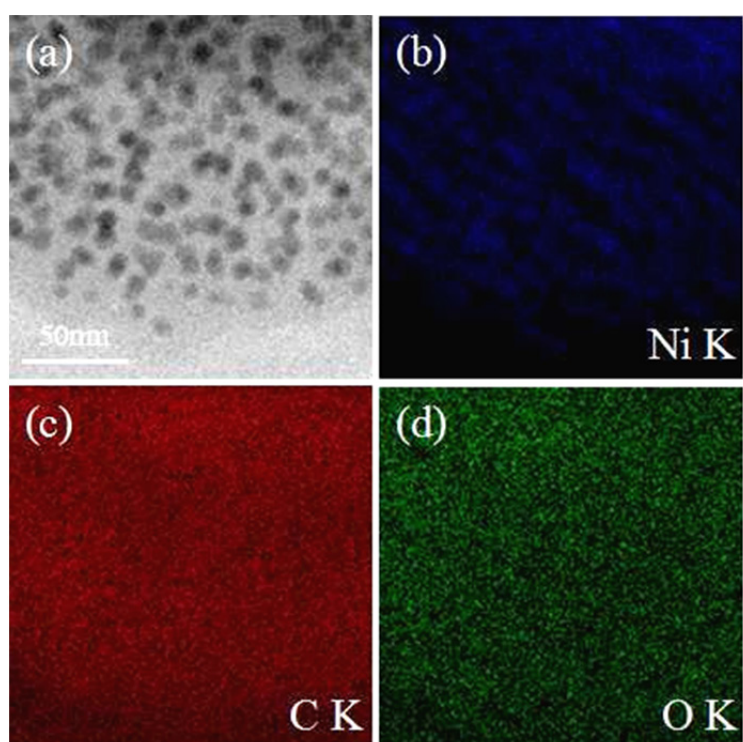

Fig. S10 (a) The image of scanning transmission electron microscope (STEM) and (b-d) elemental mapping data of Ni-NPC-600: (b) nickel, (c) carbon and (d) oxygen.
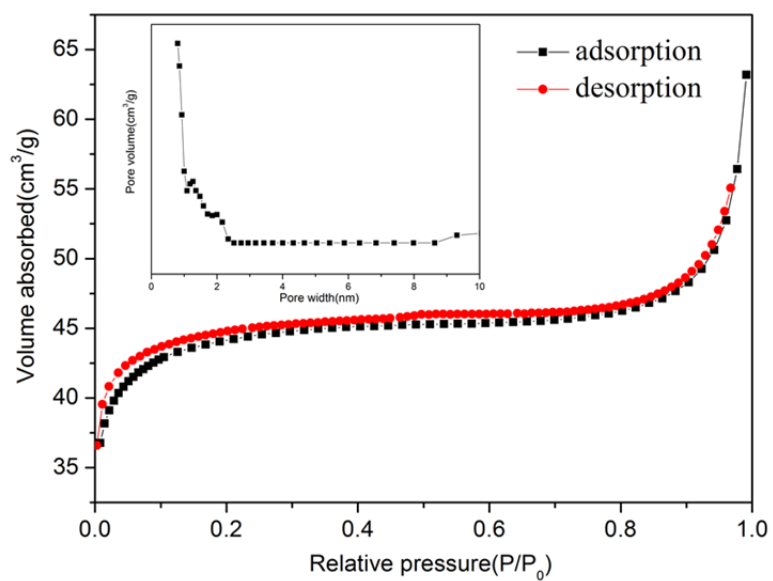
Fig. S11 N$_2$ adsorption/desorption isotherms of Ni-NPC-600. Inset: pore size distribution calculated after fitting NLDFT models to adsorption data.
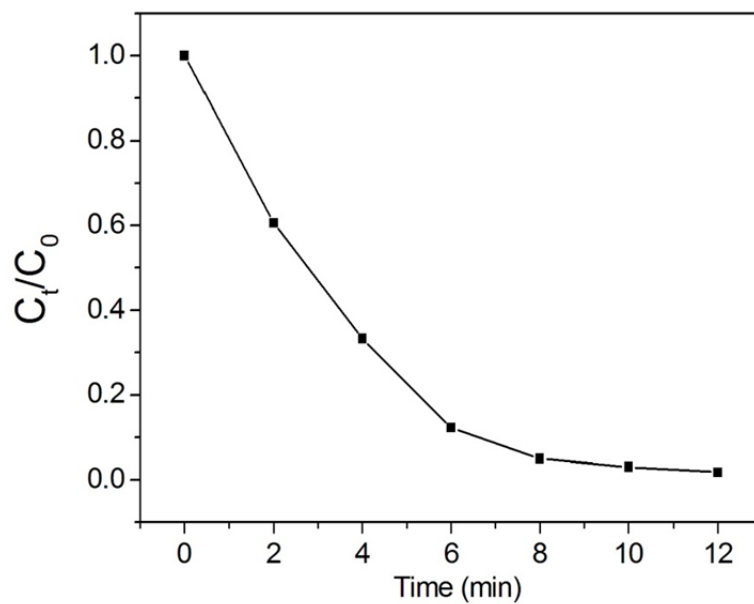

Fig. S12 C$_t$/C$_0$ versus reaction time for the reduction of 4-NP over the Ni-NPC-600.
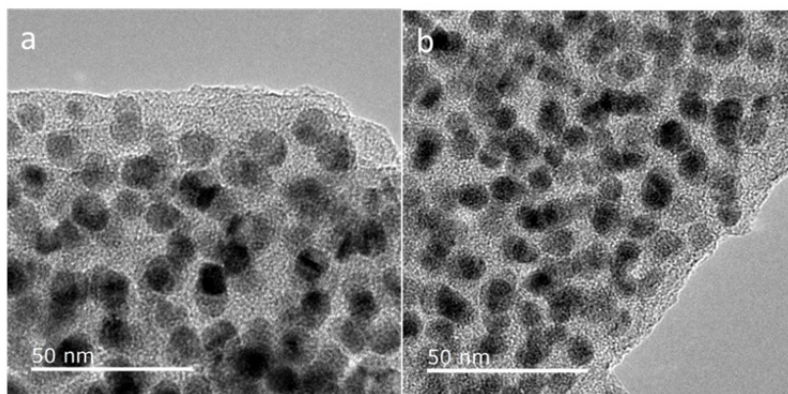
Fig. S13 TEM images of Ni-NPC-600 catalysts after ten cycles (a), and after 15 hours in 4-NP reaction solution (b).

Section 3. Table S1

Table 1. Comparison of the converse of the composite Ni catalysts and noble catalysts for the reduction of 4-NP.

Samples	Type	$K(\times 10^{-3} s^{-1})$	Converse(%)	References
Ni-NPC-600	nanocomposites	5.9	96(10)	this work
Ni/SiO$_2$	magnetic hollow microspheres	1.5	70(8)	19
Ni/SiO2@Au	magnetic hollow microspheres	10	70(8)	19
230nmNi/SiO$_2$	hollow spheres	4.5	80(10)	20
320 nmNi/SiO$_2$	hollow spheres	3.8	80(10)	20
Ni/SNTs(15.2%)	Nanotube	20	80(10)	21
Fe$_3$O$_4$@SiO$_2$-Au@ mSiO$_2$(20nm)	microspheres	5.8	90(8)	17
Pd/Fe$_3$O$_4$	microspheres	5.9	60(7)	18
Ag@Pd/Fe$_3$O$_4$	nanocomposites	33	88(10)	18
Au@C	yolk–shel nanocomposites	6.0	32(10)	22
Au$_{52}$Pd$_{48}$NPs/GNs	nanosheets	6.4	91(4)	23