Supporting information

Experimental section

Reagents and materials: All chemical reagents were purchased from commercial suppliers and used as received without further purification. Copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99%) was purchased from Shanghai Titan Scientific Co., Ltd. Ni foam and Selenium powder (Se, 99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Commercial NF was purchased from Suzhou Cheng Er Nuo Technology Co., Ltd. 4-nitrophenol (4-NP) and 4-aminophenol (4-AP) were obtained from Shanghai Macklin Biochemical Co., Ltd. Sodium borohydride ($NaBH_4$, 98%) was purchased from Aladdin Industrial Cooperation. Deionized (DI) water was homemade in the lab.

Physical characterizations:

XRD data were acquired by Brukef D8 instrument with Cu-Kα radiation. SEM measurements were carried out on a Hitachi S-4800 Scanning Electron microscope. TEM images were collected on a JEOL JEM 2100F electron microscopy. XPS spectra were recorded on a Kratos AXIS Ultra ^{DLD} X-ray photoelectron spectrometer. ^{1}H NMR spectra were acquired on a Bruker Avance NEO 600 MHz. Electron paramagnetic resonance (EPR) spectra were acquired on a Bruker EMXplus-6/1 spectrometer at room temperature.

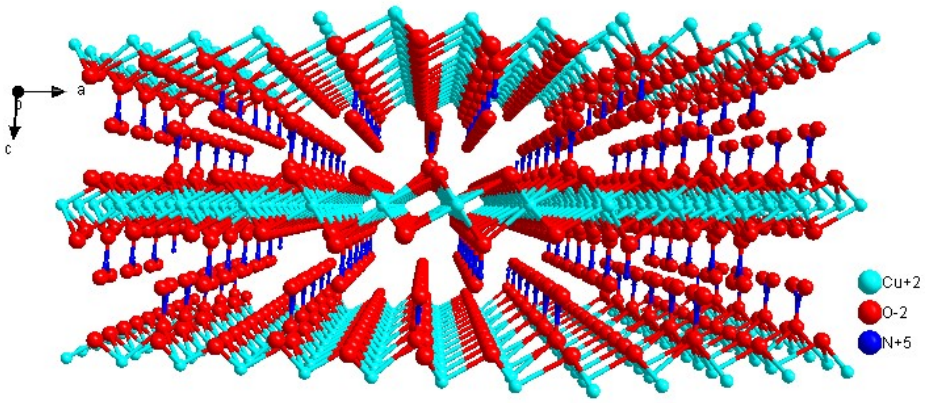

Fig. S1 2D structure diagram of $Cu_2(OH)_3(NO_3)$

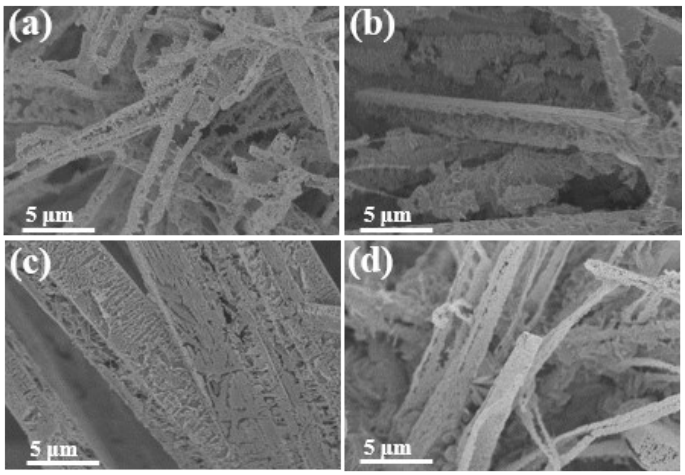

Fig. S2 SEM of (a) N,Se-CuO(0.3-350-1), (b) N,Se-CuO(0.2-350-1), (c) N,Se-CuO(0.1-350-1) and (d) N,Se-CuO(0 -350-1).

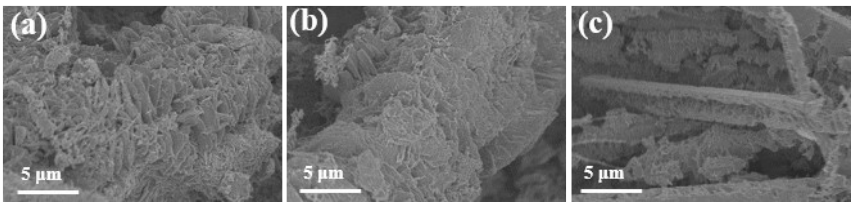

Fig. S3 SEM of (a) N,Se-CuO(0.2-250-1), (b) N,Se-CuO(0.2-300-1) and (c) N,Se-CuO(0.2-350-1).

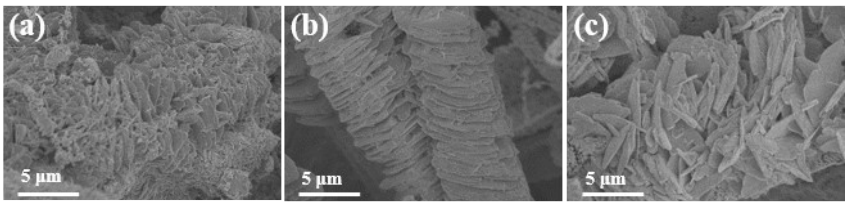

Fig. S4 SEM of (a) N,Se-CuO(0.2-250-1), (b) N,Se-CuO(0.2-250-2) and (c) N,Se-CuO(0.2-250-3).

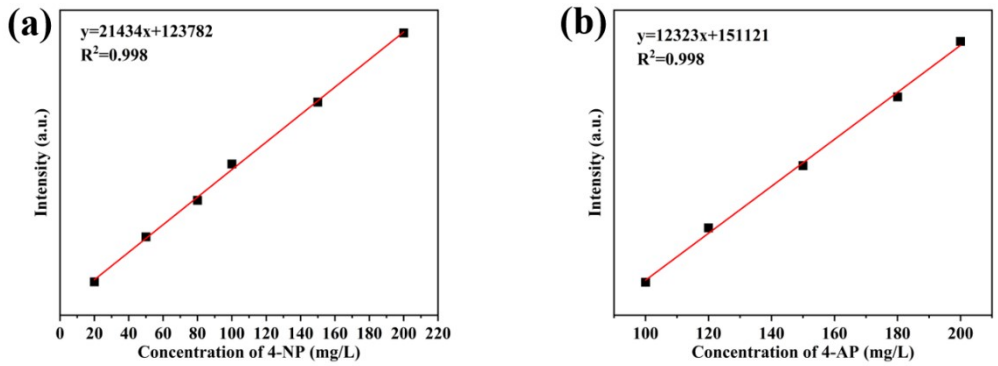

Fig. S5 The fitted standard curves of (a) 4-NP and (b) 4-AP.

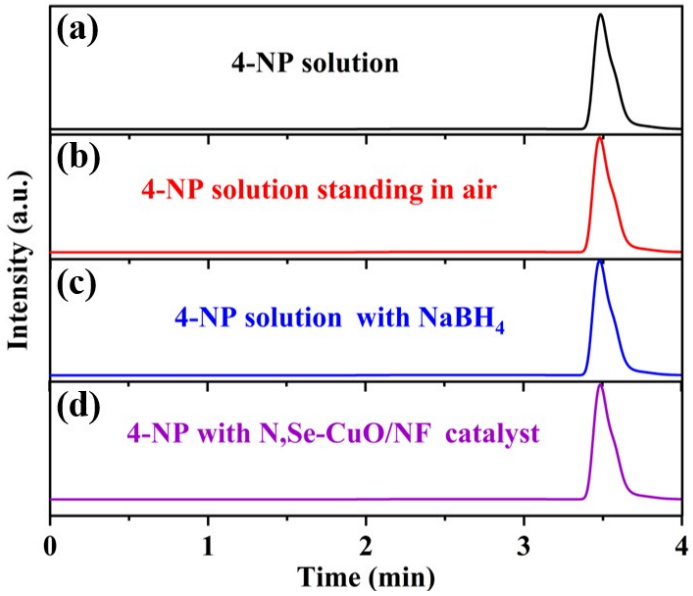

Fig. S6 (a) Liquid chromatogram of 4-NP solution. (b) Liquid chromatogram of 4-NP solution after standing in air for 100 minutes. (c) Liquid chromatogram of 4-NP solution after adding $NaBH_4$ for 100 minutes. (d) Liquid chromatogram of 4-NP solution after the adding N,Se-CuO/NF catalyst for 100 minutes.

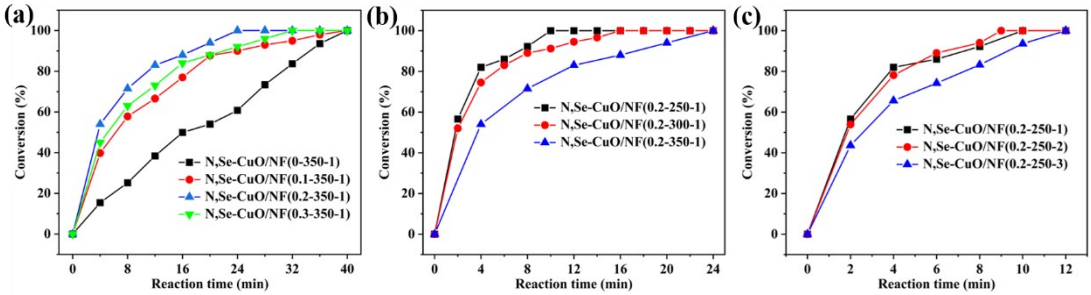

Fig. S7 Catalytic conversion efficiency of the N,Se-CuO/NF catalysts synthesized at different (a) qualities of selenium powder, (b) temperatures and (c) calcination time.

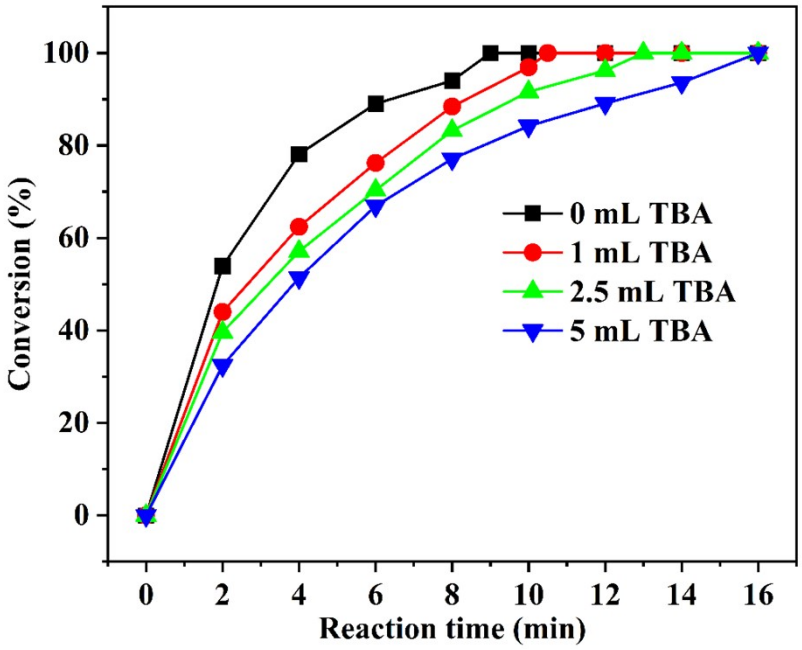

Fig. S8 Effect of TBA on catalytic reduction efficiency of N,Se-CuO/NF(0.2-250-2).

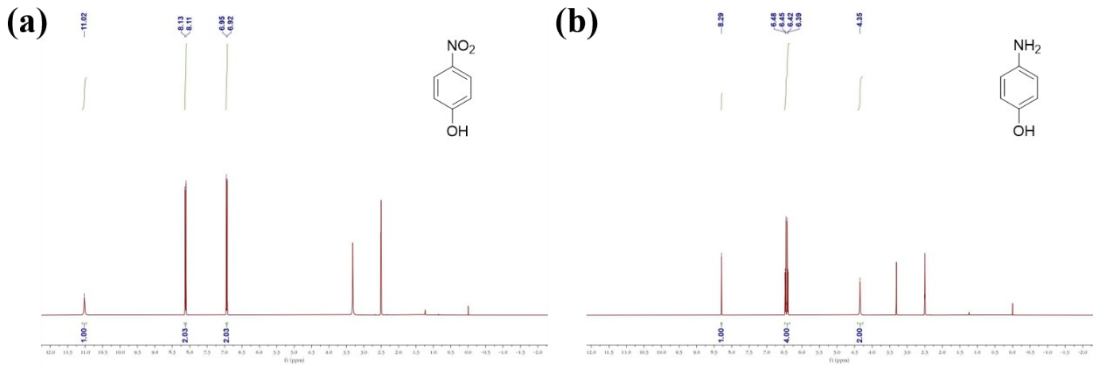

Fig. S9 (a) ^{1}H NMR spectrum of 4-nitrophenol, ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.02 (s, 1H), 8.12 (d, J = 9.2 Hz, 2H), 6.94 (d, J = 9.2 Hz, 2H). (b) ^{1}H NMR spectrum of product, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (s, 1H), 6.49 – 6.35 (m, 4H), 4.35 (s, 2H).

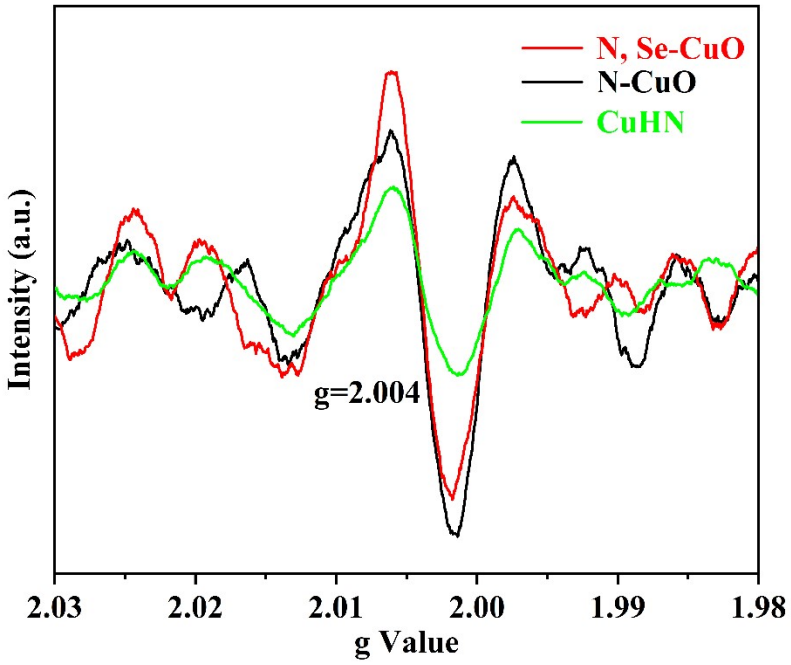

Fig. S10 EPR spectrum of CuHN, N-CuO and N,Se-CuO.

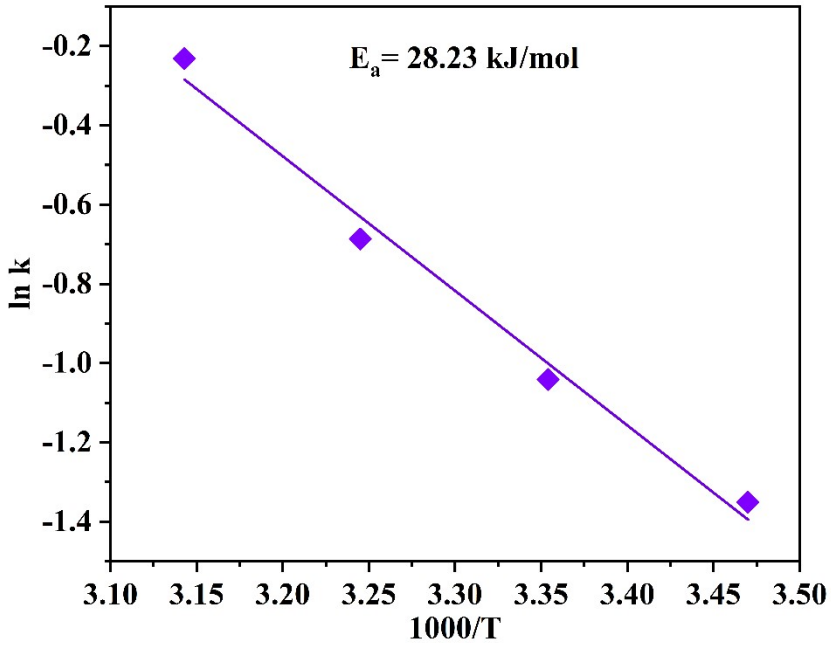

Fig. S11 The linear fitting curve of ln(*k*) vs. 1000/T.

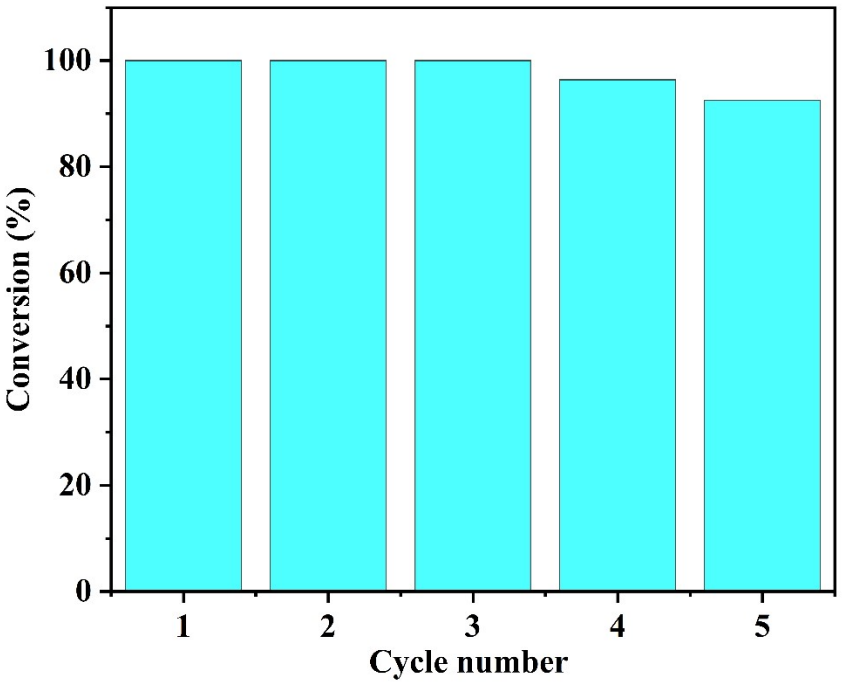

Fig. S12 Recycle testing of N,Se-CuO/NF(0.2-250-2) catalyst.

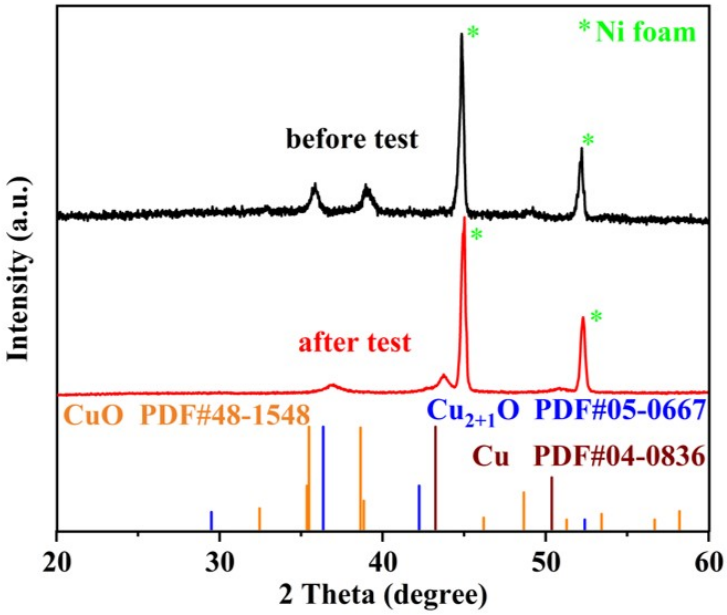

Fig. S13 XRD patterns of N,Se-CuO/NF(0.2-250-2) before and after five-cycle test.

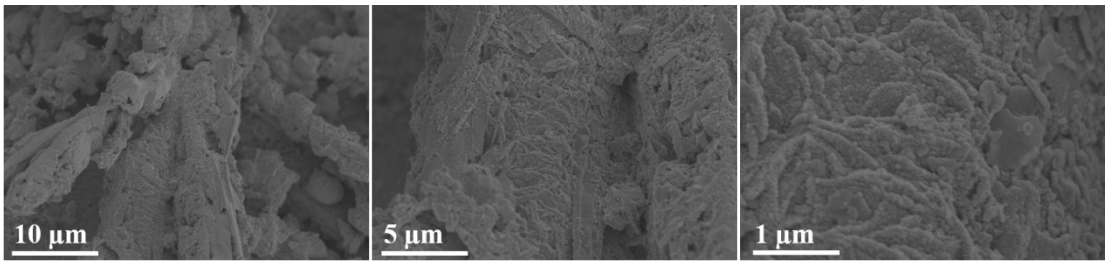

Fig. S14 SEM patterns of N,Se-CuO/NF(0.2-250-2) after five-cycle test.

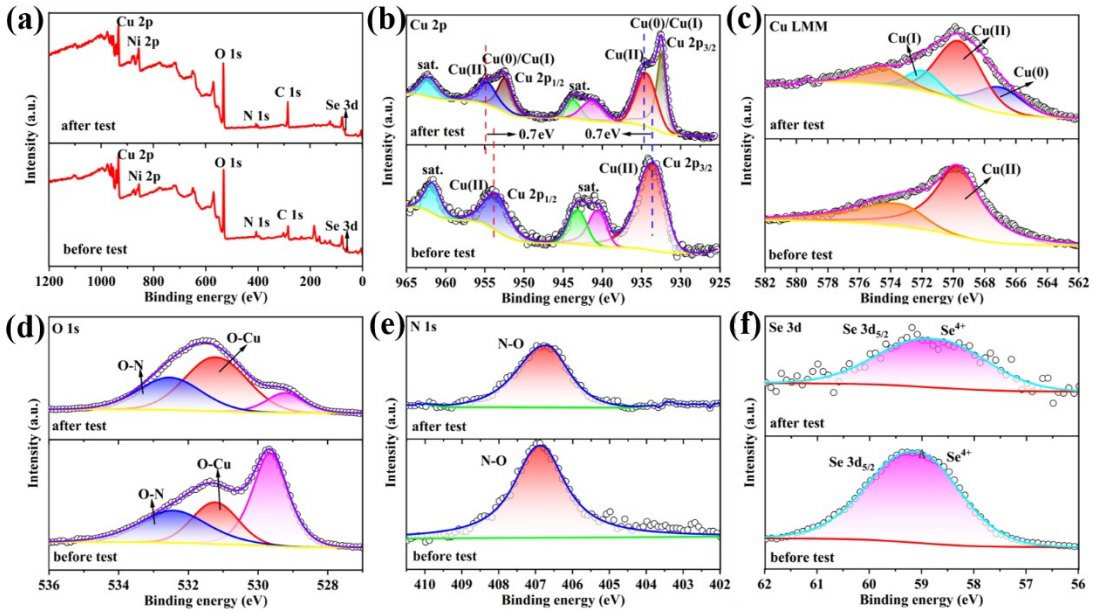

Fig. S15 XPS patterns of N,Se-CuO/NF(0.2-250-2) before and after five-cycle test.

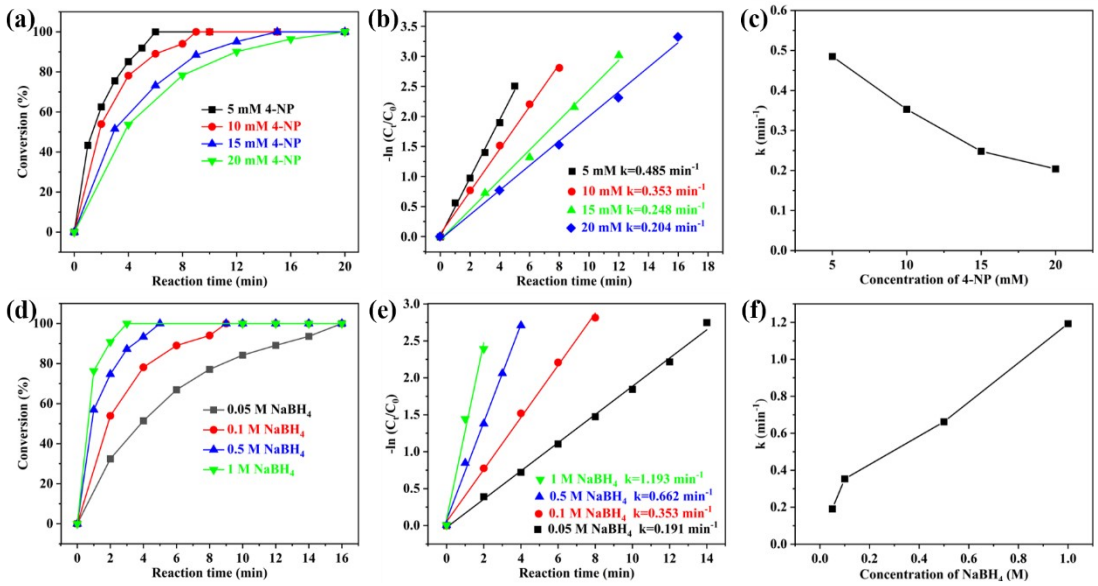

Fig. S16 The effect of concentration of 4-NP on (a) 4-NP reduction efficiency and (b) plots of ln (C_t/C_0) vs. the reaction time over N,Se-CuO/NF(0.2-250-2). The effect of concentration of $NaBH_4$ on (d) 4-NP reduction efficiency and (e) plots of ln (C_t/C_0) vs. the reaction time over N,Se-CuO/NF(0.2-250-2). The relationship of k with the concentration of (c) 4-NP and (f) $NaBH_4$.

Table S1 Element content of N,Se-CuO/NF(0.2-250-2).

Element	Atomic Fraction (%)	Mass Fraction (%)
N	2.54	0.87
O	45.32	17.79
Cu	52.00	81.07
Se	0.14	0.27

Table S2 Comparison of catalytic performance of N, Se-CuO/NF (0.2-250-2) and other typical catalysts for 4-NP reduction.

Catalyst	n($NaBH_4$): n(4-NP)	k (min^{-1})	TOF (mmol/(mg·min))	E_a (kJ/mol)	Ref.
Hollow Porous Cu NPs	400:1	\	7.69×10^{-4}	\	1
Cu/CuO/PET	1000:1	0.29	\	39.9	2
Cu NCs	70000:17	\	\	22.44	3
APBAs/CF-200	2000:3	2.057	5×10^{-5}	19.2	4
Pd NSs	140:1	0.14	9.31×10^{-2}	\	5
Cu microspheroids	102:1	0.239	1.36×10^{-5}	\	6
CDs/CuO/mHA	60:1	0.254	8.33×10^{-6}	\	7
Co@NC–MF	100:1	0.139	1.44×10^{-4}	31.7	8
Fe_3O_4-Cu NCs	40:1	\	0.1	\	9
Cu_2O/h-BN	70:1	\	5.99×10^{-5}	\	10
CuO@C	45:2	0.0151	1.17×10^{-4}	31	11
GO-DAP-Ag NPs	1000:1	\	1.67×10^{-5}	\	12
Ru/PC	781:1	1.29	3.55×10^{-4}	39.11	13
Ag/MR	50:1	\	2.08×10^{-2}	31.17	14
Cu/Cu_xO@CN	400:1	\	3.12×10^{-2}	55.6	15
N, Se-CuO/NF	10:1	0.353	0.247	28.23	This work

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