

Electronic Supplementary Information (ESI)

Sacrificial template synthesis of $(\text{Co}_x\text{Ni}_{1-x})_{0.85}\text{Se}$ nanostructures with different morphologies for reduction of 4-nitrophenol

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Experimental section

Synthesis of Co–Ni–precursors structures

In our synthesis process, all chemical reagents were of analytical grade and were used without further purification. Firstly, the Co–Ni–precursors with different shapes were prepared using a facile solvo-/hydrothermal method (Scheme 1, Step I). Typical process for preparation of Ni–Co–precursor with sheet-like morphology as summarized following: 0.238 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.238 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 0.2 g urea were dissolved in 40 mL mixed solvent (20 mL H_2O and 20 mL ethylene glycol), then the solution was transferred into a Teflon lined stainless steel autoclave with a capacity of 50 mL, and was kept at 140 °C for 10 h. Similar to synthesise of Co–Ni–precursors with sheet-like morphology, when only the mixed solvent was replaced by H_2O or methanol, the Co–Ni–precursors with flower-like or urchin-like morphology were obtained. Finally, the precipitates of Co–Ni–precursors were washed with deionized water and ethanol for five times each, and then dried at 70 °C for 10 h.

Synthesis of $(\text{Co}_x\text{Ni}_{1-x})_{0.85}\text{Se}$ NSs with different morphologies

As shown in Scheme 1 (Step II), the $(\text{Co}_x\text{Ni}_{1-x})_{0.85}\text{Se}$ nanostructures (NSs) with different morphologies were prepared. Typically, the $(\text{Co}_x\text{Ni}_{1-x})_{0.85}\text{Se}$ NSs were synthesized as follows: 0.08 g of the Co–Ni–precursors structures with sheet-like, flower-like or urchin-like shapes were dispersed in 38 mL H_2O under ultrasonic for 30 min (KQ-50B supersonic cleaner, Kun Shan Ultrasonic Instruments Co., Ltd, China; ultrasonic frequency: 40 kHz; ultrasonic power: 50 W), and then 2 mL of freshly prepared NaHSe solution (1 M) were loaded into a Teflon lined stainless steel autoclave of 50 mL capacity, and was kept at 160 °C for 24 h, and then cooled to room temperature naturally. The sheet-like, flower-like and urchin-like $(\text{Co}_x\text{Ni}_{1-x})_{0.85}\text{Se}$ NSs were washed with deionized water and absolute ethanol for five times each, and dried in a vacuum at 80 °C for 5 h.

Characterization

The X-ray powder diffraction (XRD, Shimadzu XRD-6000, Japan), scanning electron microscopy (SEM, Hitachi S-4800, Japan), energy dispersive X-ray (EDX, INCAx-Sight OXFORD) spectra attached to SEM, and X-ray photoelectron spectra (XPS, Thermo ESCALAB 250XI, US) were applied to characterize the structure, morphology and composition for the final products, respectively. Surface area was determined by Brunauer–Emmet–Teller (BET) method

using ASAP 2020 (USA) from Quanta Chrome at $-196\text{ }^{\circ}\text{C}$.

Catalytic reaction

The catalytic reaction process is similar to our previous reports with modified.[1] Typically, 20 mL 4-nitrophenol (4-NP) aqueous solution ($2.5 \times 10^{-4}\text{ M}$) and 1 mg of $(\text{Co}_x\text{Ni}_{1-x})_{0.85}\text{Se}$ NSs catalysts were mixed together and purged with argon for 10 min to remove the dissolved oxygen, and then the mixture was irradiated by ultrasonic waves for 5 min. Next, 10 mL (0.02 M) of aqueous NaBH_4 solution was added to the reaction mixture and time-dependent absorption spectra were recorded in the UV-vis spectrophotometer (U-4100, Hitachi, Japan) at $\sim 25\text{ }^{\circ}\text{C}$.

Ref. [1] a) K.-L. Wu, X.-W. Wei, X.-M. Zhou, D.-H. Wu, X.-W. Liu, Y. Ye, Q. Wang, *J. Phys. Chem. C*, 2011, **115**, 16268; b) K.-L. Wu, R. Yu, X.-W. Wei, *CrystEngComm*, 2012, **14**, 7626;

Table S1 Contents of Co/Ni/Se molar ratios of the products were determined by EDX analysis.

Samples	Average composition by EDX	Chemical formula
Sheet-like $(\text{Co}_x\text{Ni}_{1-x})_{0.85}\text{Se}$	$\text{Co}_{0.173}\text{Ni}_{0.285}\text{Se}_{0.542}$	$(\text{Co}_{0.376}\text{Ni}_{0.62})_{0.85}\text{Se}$
Flower-like $(\text{Co}_x\text{Ni}_{1-x})_{0.85}\text{Se}$	$\text{Co}_{0.207}\text{Ni}_{0.244}\text{Se}_{0.549}$	$(\text{Co}_{0.444}\text{Ni}_{0.523})_{0.85}\text{Se}$
Urchin-like $(\text{Co}_x\text{Ni}_{1-x})_{0.85}\text{Se}$	$\text{Co}_{0.221}\text{Ni}_{0.233}\text{Se}_{0.546}$	$(\text{Co}_{0.476}\text{Ni}_{0.502})_{0.85}\text{Se}$

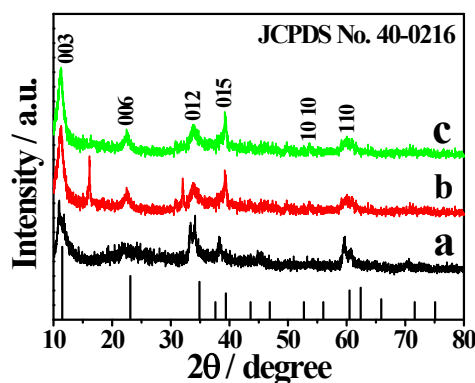


Fig. S1 XRD patterns of Co–Ni–precursors structures with (a) sheet-like, (b) flower-like, and (c) urchin-like morphologies, respectively.

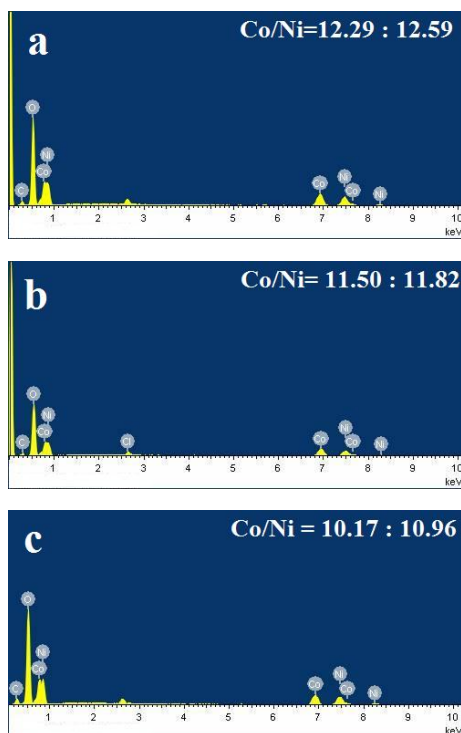


Fig. S2 EDX spectra of Co-Ni-precursors structures with (a) sheet-like, (b) flower-like, and (c) urchin-like morphologies, respectively.

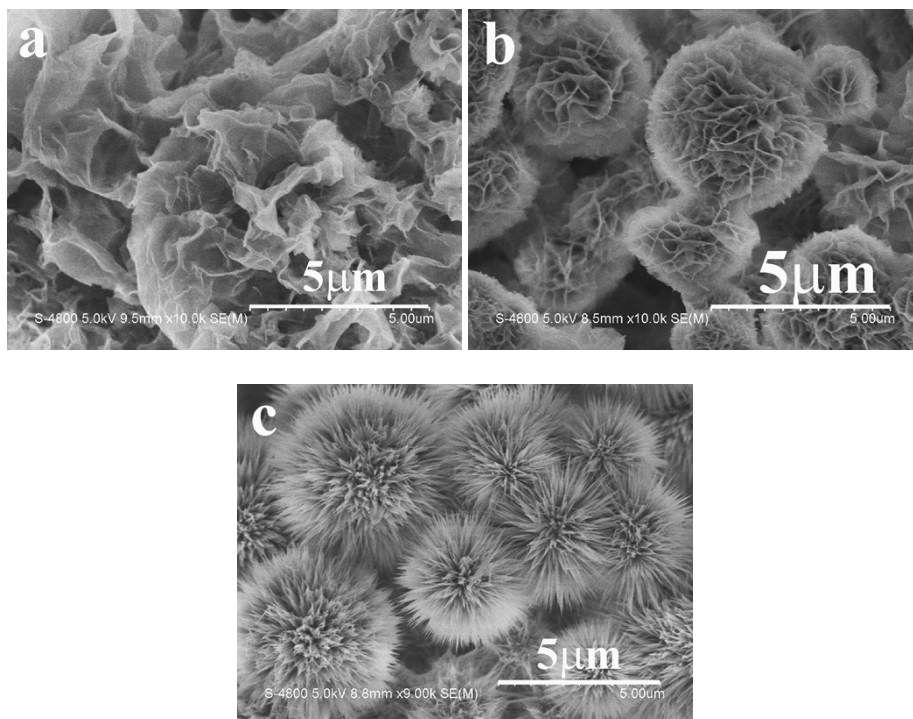


Fig. S3 SEM images of Co-Ni-precursors structures with (a) sheet-like, (b) flower-like, and (c) urchin-like morphologies, respectively.

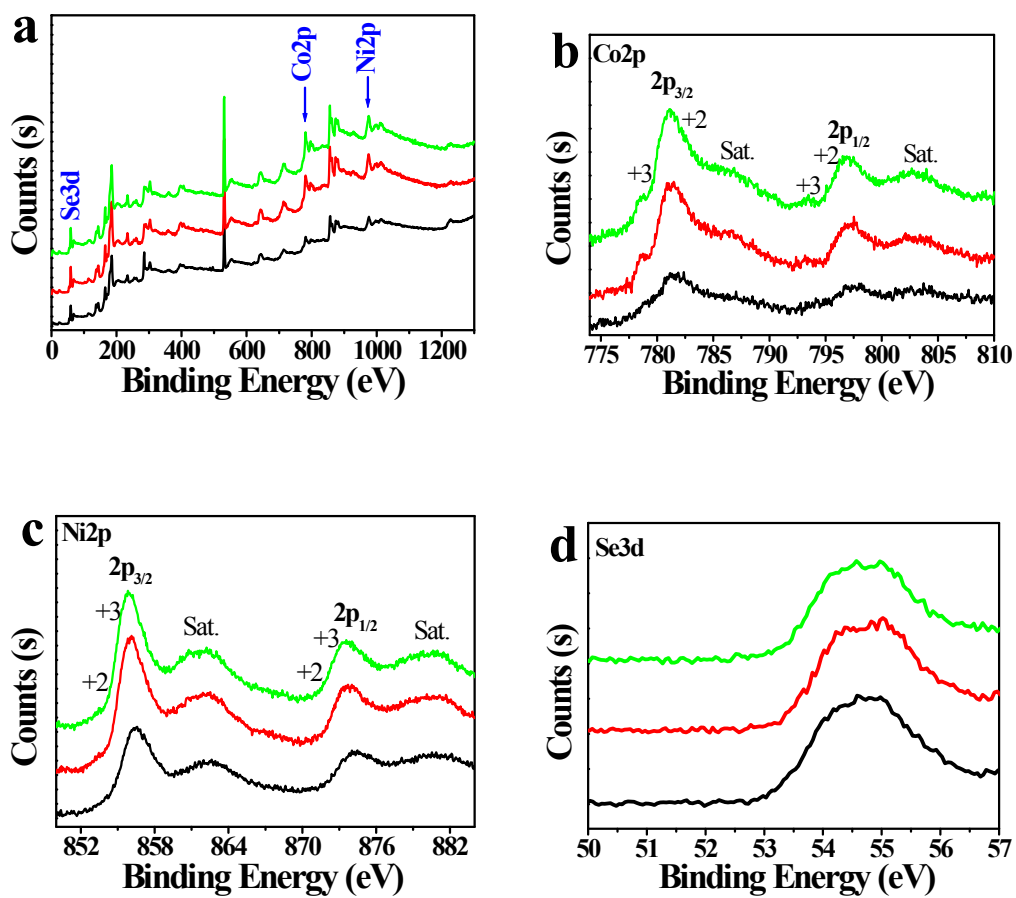


Fig. S4 XPS spectra of (a) survey, (b) Co 2p, (c) Ni 2p, and (d) Se 3d for the $(\text{Co}_x\text{Ni}_{1-x})_{0.85}\text{Se}$ NSs with sheet-like (black line), flower-like (red line), and urchin-like (green line) morphologies, respectively.

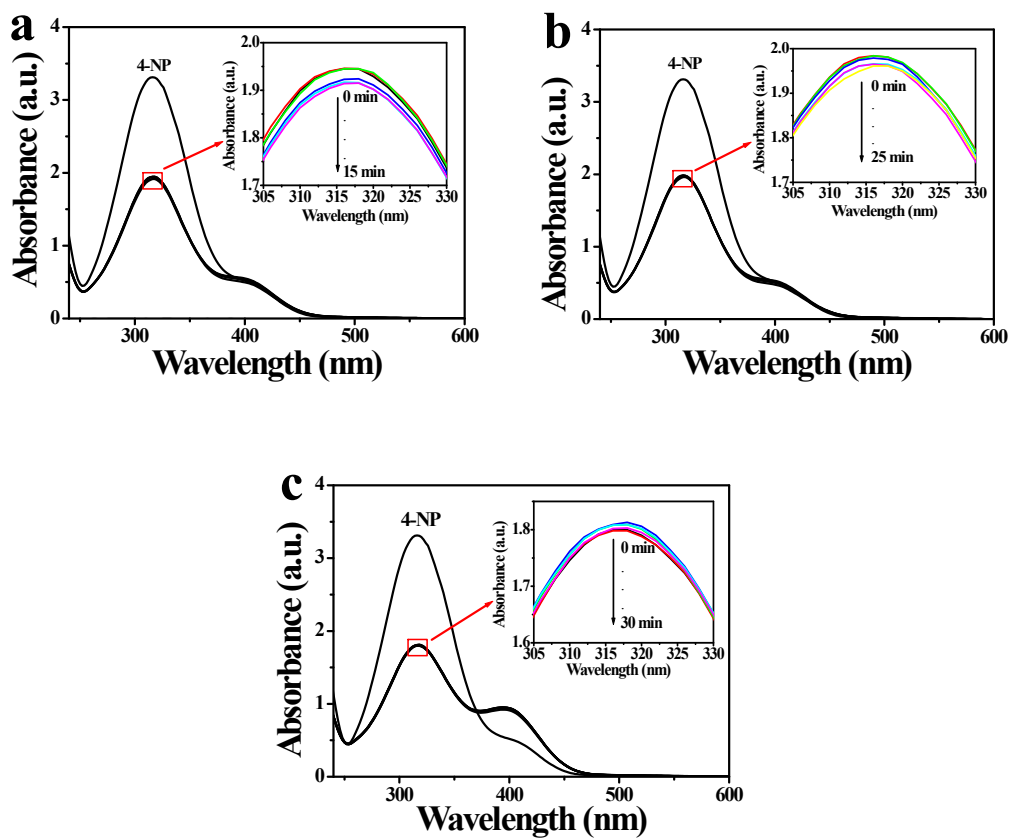


Fig. S5 Time-dependent UV-vis absorption spectra (inset are the magnifying spectra from 305 to 330 nm) change for mixing of 2 mL 4-NP and 1 mg (a) sheet-like, (b) flower-like, and (c) urchin-like $(\text{Co}_x\text{Ni}_{1-x})_{0.85}\text{Se}$ NSs as catalysts in absence of 1 mL NaBH_4 , respectively.