

Supporting Information

Different Crystallographic Ni(OH)₂ as the Highly Efficient Fenton-like Catalysts for Sulfate Radical Activation

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Experimental Section

Chemicals and Reagents. Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\geq 98.0\%$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98.0\%$), urea ($\text{CH}_4\text{N}_2\text{O}$, $\geq 99.5\%$), trisodium citrate (TSC, $\geq 98.0\%$), ethylene glycol (EG, $\geq 99.0\%$), hydrochloric acid (HCl), sodium persulfate (PDS, $\text{Na}_2\text{S}_2\text{O}_8$, $\geq 99.0\%$), sodium hydroxide (NaOH, $\geq 96.0\%$), sulfuric acid (H_2SO_4 , $\geq 98.0\%$), phenol ($\text{C}_6\text{H}_6\text{O}$, ≥ 99 wt %), bisphenol A (BPA, $\text{C}_{15}\text{H}_{16}\text{O}_2$ ≥ 99.5 wt %), 2, 4, 6-trichlorophenol (2,4,6-TCP, $\text{C}_6\text{H}_3\text{Cl}_3\text{O}$, ≥ 99.0 wt %) 5, 5-dimethyl-1-pyrroline N-oxide (DMPO). All the aqueous solutions were prepared by using distilled and deionized water.

Preparation of mixture of α @ β -Ni(OH)₂. The α @ β -Ni(OH)₂ were prepared by hydrothermal synthesis. 70ml 0.2 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 5.6 ml 0.5 M urea solution and 2 ml 0.01 M TSC were mixed and stirred for 30 min under ambient conditions. Then, the mixture transferred to a Teflon lined stainless steel autoclave of 150 ml capacity and by hydrothermal treatment at 150 °C for 24 h. After centrifugation to remove the free solution, the obtained product by washed 3 times with water and ethanol and dried at vacuum drying oven.

Synthesis of α -Ni(OH)₂ nanosheets. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.544 g) and urea (0.452 g) were dissolved in 30 ml DI water and was stirred for 60 min. The mixture was then put into a Teflon lined stainless steel autoclave of 100 ml capacity and by hydrothermal treatment at 120 °C for 4 h. After centrifugation to remove the free solution, the obtained product by washed 3 times with water and ethanol and dried at vacuum drying oven.

Preparation of stacked hexagonal β -Ni(OH)₂. 0.4 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 40 ml 5 M NaOH solution and stirred for 30 min. After centrifugation, the mixture was put into a Teflon-lined autoclave of 45 ml capacity the autoclave and by hydrothermal treatment at 180 °C for 12 h. After hydrothermal treatment, a green suspension was obtained. After centrifugation to remove the free solution, the obtained product by washed 3 times with water and ethanol and dried at vacuum drying oven.

Synthesis of amorphous Ni(OH)₂. 0.5 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was dropped into NaOH solution with pH 12.5 and stirred for 24 h. After centrifugation, the precipitate was washed with water and ethanol for 3 times and dried at vacuum drying oven. In addition, in order to remove water in the catalysts, the product was dried at 150°C for 4 h to further grinded into powder.

Materials Characterization. The crystal structure of the synthesized samples was examined by X-ray powder diffraction (XRD), which was carried out on a Rigaku D/max 2500 powder diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphological features of the as-synthesized catalysts were visualized by transmission electron microscopy (TEM) (model JEM-F200). The high-resolution transmission electron microscopy (HRTEM) observation and selected area electron diffraction (SAED) were carried out with an acceleration voltage of 200 kV. The catalysts were also characterized by X-ray photoelectron spectroscopy (XPS), which was performed on a PerkinElmer PHI 5000C, Fourier transform infrared spectrometer (FTIR, Nicolet 6700), and Raman scattering spectra (SENTERRA R200). The leaching of nickel from catalysts was quantified by coupled plasma atomic emission spectrometry (ICP-AES, iCAP6300, Thermo). Electron paramagnetic resonance (EPR) spectra (Bruker, Emxplus) were performed to record the reactive radicals in activating H₂O₂, which are captured via 5,5-dimethylpyrroline-oxide (DMPO). N₂ sorption scanning curves were measured using a Nova-2200 e.

Catalytic Activity Test. The performance of the catalysts for degrading phenol was tested by the Fenton-like process. Typically, 1.0 g L⁻¹ of prepared α @ β -Ni(OH)₂, α -Ni(OH)₂, β -Ni(OH)₂ and amorphous Ni(OH)₂ catalysts and 40 mL of 50 mg/L aqueous phenol solution were added to the 100 mL reactor, respectively. Then, different dosages of aqueous PDS solution were added and the pH was adjusted and maintained to a specific value by adding 0.01 mol/L H₂SO₄ or 0.01 mol/L NaOH solution. 1 mL of solution was immediately withdrawn and at once filtered through a 0.45 μ m PTFE syringe filter in order to trap the catalyst power. The high-performance liquid chromatography (HPLC, SPD-16, Shimadzu Co.) was used to determine the concentrations of phenol pollutants. Fenton-like Process for degradation of BPA and TCP as phenol removal process and the concentrations of organic pollutants were also measured by HPLC. Gas samples were collected from the top of the flask using a 500 μ L syringe at different time intervals and then injected into a gas chromatography (GC7900) to detect CO₂ for calculating the mineralization efficiency of phenol. Then the flask was placed in front of a 100W white LED lamp (CEL-LED100) with a 420 nm cut filter. Before the lamp was switched on, it took 10 min for H₂O₂ diffusion. According to the stoichiometric consumption of [H₂O₂] calculated based on (Eq. 1),



the mineralization efficiency was calculated by the following (Eq. 2):

$$\text{Mineralization efficiency} = \frac{[CO_2]}{6 \times [\textit{phenol}]} \times 100\% \quad (2)$$

Mineralization Capability Test. Mineralization rate was measured using a total organic carbon analyzer (TOC, multi-3100, Analytik Jena). Total organic carbon (TOC) removal (mineralization) efficiency was evaluated using the following relationship (Eq. 3):

$$\text{Mineralization Efficiency} = \frac{TOC}{TOC_0} \times 100\% \quad (3)$$

TOC —the TOC value of the contaminant concentrates after degradation,

TOC₀ —the TOC value of the contaminant concentrates after degradation,

Electrochemical Characterization Measurement. The electrocatalytic study was carried out with a conventional three-electrode system: a glassy carbon electrode (GCE) as working electrode, a Pt wire as the counter electrode, and saturated calomel electrode (SCE) (6 M KCl) as the reference electrode. The GCE was cleaned prior to each run by polishing with 0.3 mm and 0.05 mm alumina slurry and then rinsing with ultrapure water. A cyclic voltammetry (CV) was scanned in the range between -0.1 and +0.5 V with the scan rate of 10 mV s⁻¹. Electrochemical impedance spectra (EIS) were performed on the Zennium electrochemical workstation (Zahner) with three electrode system, where a Pt foil and Ag/AgCl electrode were used as the counter and reference electrodes, respectively.

The preparation method of the working electrodes is as follows. 5 mg of catalyst powder was dispersed in 1 mL of 3:1 v/v water/isopropyl alcohol mixed solvent with 45 μL of Nafion solution (5 wt %, Sigma-Aldrich). The mixture was then ultrasonicated for about 0.5 h to generate a homogeneous ink. Next, 8 μL of the dispersion was transferred onto the GCE. Finally, the as-prepared catalyst film was dried at room temperature. For comparison, a bare glassy carbon electrode that had been polished and cleaned was also dried for electrochemical measurement.

Figures

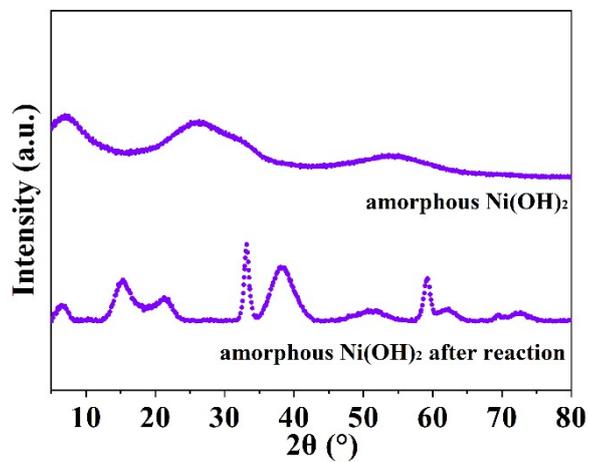


Fig. S1. XRD patterns of fresh and after 4 runs of amorphous- Ni(OH)_2 .

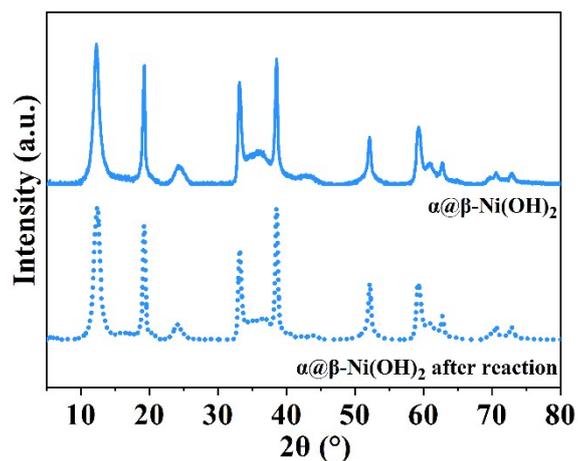


Fig. S2. XRD patterns of fresh and after 4 runs of $\alpha@ \beta$ - Ni(OH)_2 .

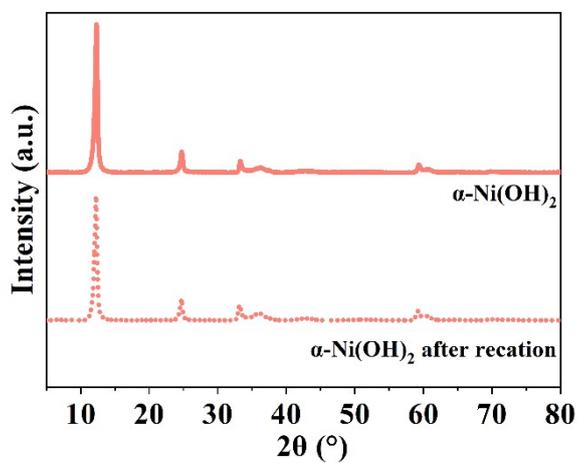


Fig. S3. XRD patterns of fresh and after 4 runs of α - Ni(OH)_2 .

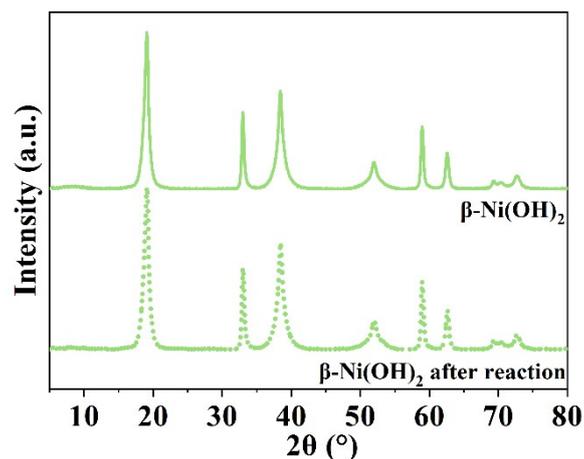


Fig. S4. XRD patterns of fresh and after 4 runs of β -Ni(OH)₂.

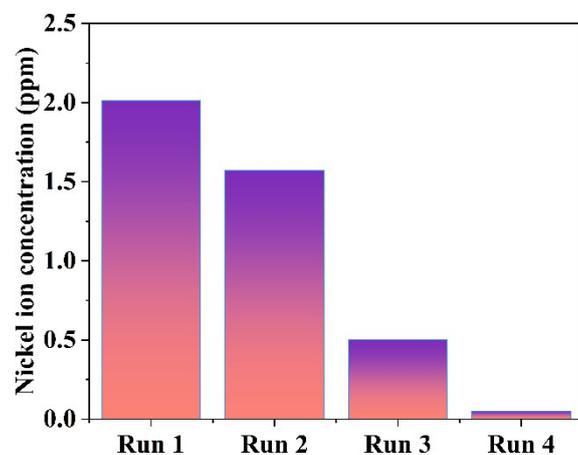


Fig. S5. The Nickel ion concentration in the solution during the cycle experiment.

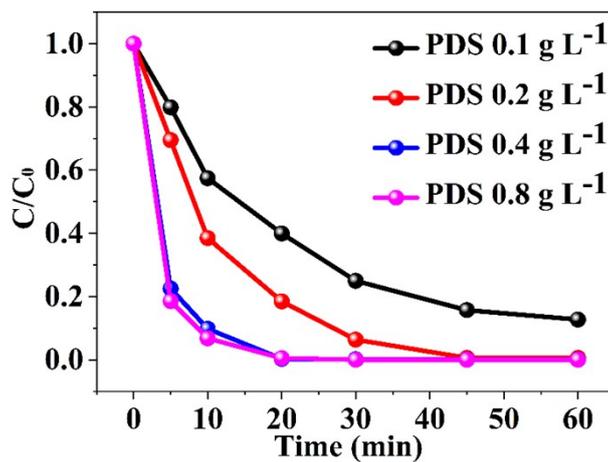


Fig. S6. The degradation of phenol at different dosage of PDS in α @ β -Ni(OH)₂ system.

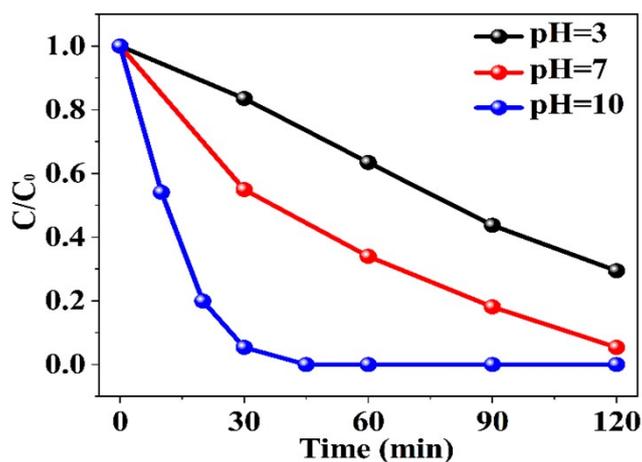


Fig. S7. The degradation of phenol at different pH in $\alpha@ \beta$ -Ni(OH)₂ system.

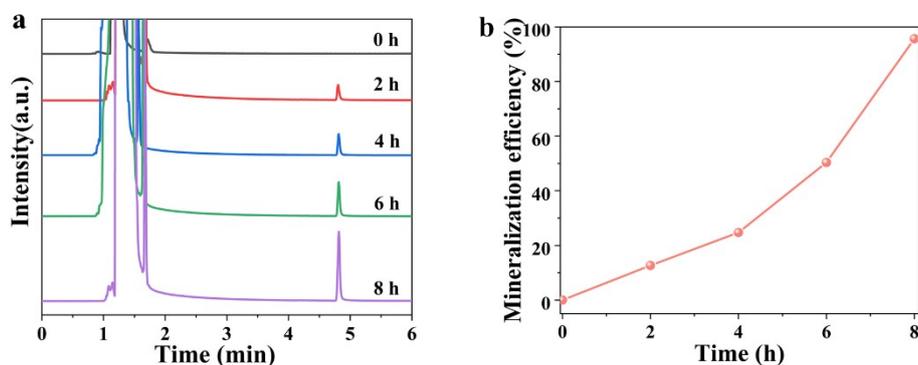


Fig. S8. (a) GC-MS graphs of phenol degradation and mineralization efficiency by $\alpha@ \beta$ -Ni(OH)₂ via PDS activation

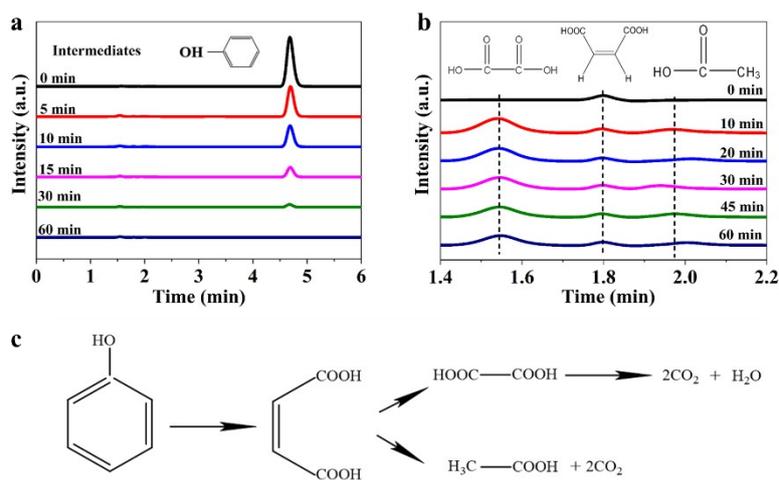


Fig. S9. (a) The removal and dichlorination efficiency of phenol in $\alpha@ \beta$ -Ni(OH)₂/PDS system. (b)The generation of intermediate product of butanedioic acid, acetic acid, and formic acid and proposed degradation pathway of phenol with $\alpha@ \beta$ -Ni(OH)₂/PDS system (c).

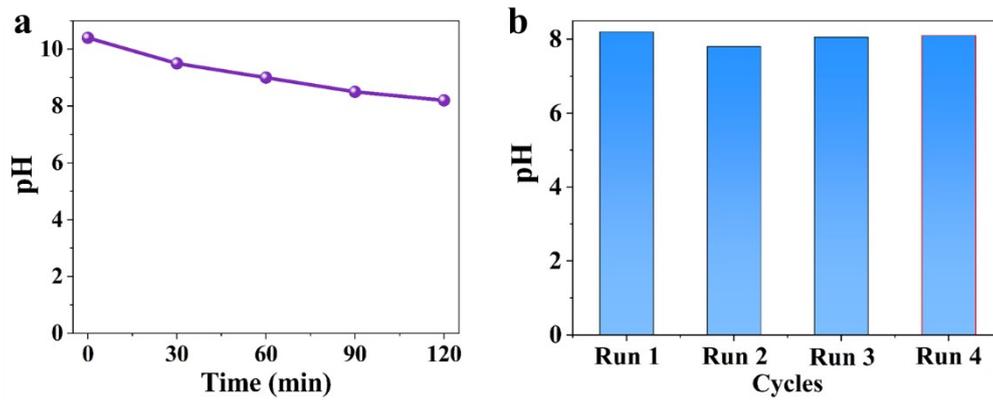


Fig. S10. (a) Changes of pH during the degradation of phenol and the cycle experiment (b) in $\alpha@ \beta$ -Ni(OH)₂ system.

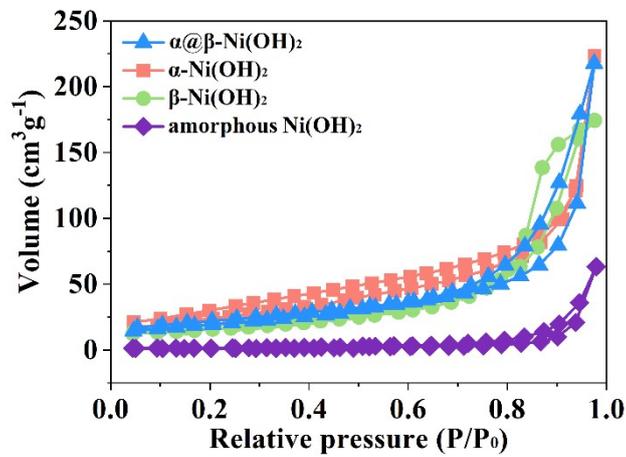


Fig. S11. Nitrogen adsorption-desorption isotherms of various Ni-compounds materials.

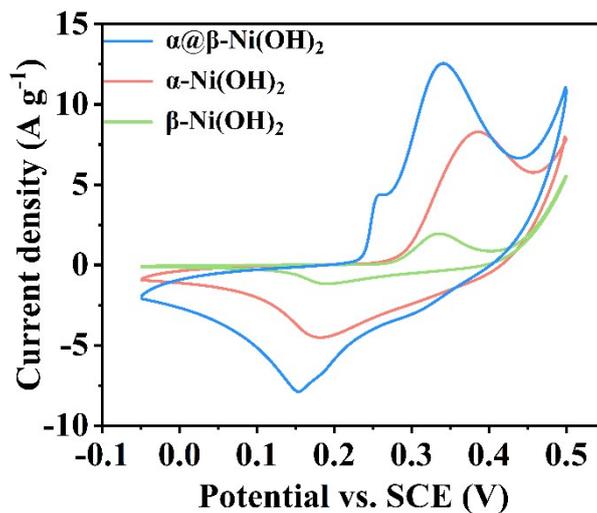


Fig. S12. The cyclic voltammograms of $\alpha@ \beta$ -Ni(OH)₂, α -Ni(OH)₂ and β -Ni(OH)₂ at 10 mV s⁻¹ scan rates.

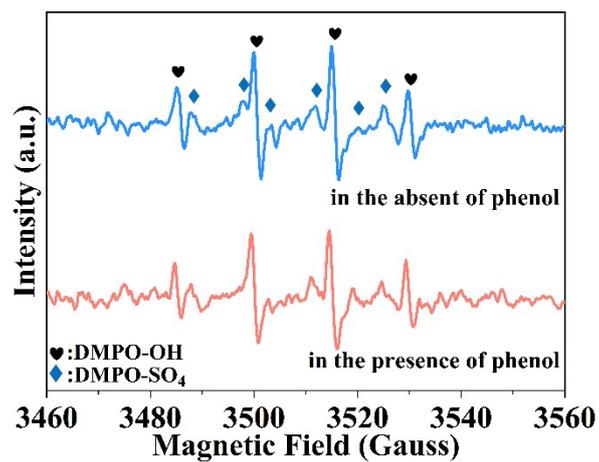


Fig. S13. EPR spectra of $\alpha@ \beta$ -Ni(OH)₂/PDS system in the presence and absence of phenol.

Table

Table S1. The BET surface area of the $\alpha@ \beta$ -Ni(OH)₂, α -Ni(OH)₂, β -Ni(OH)₂, and amorphous Ni(OH)₂.

Catalyst	$\alpha@ \beta$ -Ni(OH) ₂	α -Ni(OH) ₂	β -Ni(OH) ₂	amorphous Ni(OH) ₂
BET (m ² g ⁻¹)	78.44	37.97	64.09	9.81