

Electronic Supplementary material (ESI) for Nanoscale
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Electronic Supplementary Information (ESI)

Synthesis of Nanostructured Materials by Using Metal-Cyanide Coordination Polymers and Their Lithium Storage Properties

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Experimental section

Synthesis of LiCoO₂ nanocrystals In a typical procedure, 0.08 mmol K₃[Co(CN)₆]₂ and 0.6 g SDBS were dissolved in 20 mL deionized water under vigorous stirring to form a clear solution. Meanwhile, 0.15 mmol Co(CH₃COO)₂·4H₂O was added into 20 mL pure water to prepare another clear solution. Then, the Co(CH₃COO)₂·4H₂O solution was added into the above solution drop by drop slowly using a syringe. After that, the reaction was aged at room temperature for 24 h. At the end of the reaction, the resulting pink precipitation was collected by centrifugation and washed several times with distilled water and finally dried in a vacuum oven at 30 °C. To obtain LiCoO₂ nanoparticles, the as-synthesized Prussian blue analogue product was ground with a stoichiometric amount of LiOH·H₂O and calcined at 750 °C for 3 hours with a temperate ramp of 2 °C min⁻¹ in air. For comparison, the bulk LiCoO₂ powders were also synthesized *via* a conventional sol-gel process. Typically, LiCH₃COO·2H₂O,

$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and citric acid with a molar ratio of 1.05:1:2 were dissolved in 50 mL of distilled water. The solution was dried at 70 °C and sintered at 400 °C for 2 h and 750 °C for 8 h in air atmosphere.

Synthesis of $\text{Fe}_2\text{O}_3@ \text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanocubes The Prussian blue nanoparticles used as starting materials were firstly prepared by a method reported by Yamauchi's group¹ with some modification. In brief, polyvinylpyrrolidone (PVP, K30, 3.0 g) and $\text{K}_3\text{Fe}(\text{CN})_6$ (0.132 g) were added to a HCl solution (0.1 M, 40 mL) and magnetically stirred for half an hour. After thorough mixing, the vial was then placed into an electric oven and heated at 80 °C for 20 h. The resultant blue precipitates were separated by centrifugation, washed with deionized water several times, and finally dried at room temperature for 12 h. For the synthesis of FeFe@CoNi hybrid Prussian blue analogues nanocomposites, the procedure was similar to that of the preparation of $\text{Co}_3[\text{Co}(\text{CN})_6]_2$. The as-made FeFe core nanoparticles (11.5 mg), 0.6 mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.9 mmol sodium citrate were dissolved in 20 mL water to form a clear solution. Meanwhile, 0.4 mmol $\text{K}_3[\text{Co}(\text{CN})_6]_2$ was added into 20 mL deionized water to prepare another clear solution. After that, the two solutions were mixed together and aged at room temperature over night. Then, the precipitation was filtered, washed thoroughly using pure water and dried at room temperature. The porous $\text{Fe}_2\text{O}_3@ \text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanocubes were obtained by thermal decomposition of the as-synthesized product in a tube furnace at 400 °C for 1 h with a heating rate of 5 °C min^{-1} .

Characterization

The crystal structures of the as-prepared powders were characterized by powder X-ray diffraction using Cu K α radiation. The morphologies of the samples were investigated by field-emission scanning electron microscopy (FESEM, LEO 1430VP, Germany) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010). FTIR spectrum of the sample was recorded on a Nicolet 750 Fourier transform infrared spectrometer using the KBr method. Thermogravimetric analysis was carried out under air flow from room temperature to 700 °C at a heating rate of 10 °C min^{-1} . N_2 adsorption-desorption isotherms at 77 K were determined by using a Micromeritics

ASAP 2020 instrument.

Electrochemical Measurements

The electrochemical tests were performed with CR2016 coin-type cells. The working electrodes were prepared by mixing active material, conductive carbon black and poly(vinylidene fluoride) (PVDF) at a weight ratio of 80:10:10 in *N*-methyl-2-pyrrolidone (NMP). The slurry was pasted onto aluminum foil, and then dried under vacuum at 120°C for 12 h. Test cells were assembled in an argon-filled glovebox using lithium foil as the counter electrode and a polypropylene membrane (Celgard 2400) as the separator. The electrolyte was a solution of 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 vol%). The galvanostatic charge-discharge tests were carried out on a LAND-CT2001A battery testing system (Wuhan Jinnuo Electronics, Ltd.) at different current rates with cut-off voltages of 3.0-4.3 V at room temperature. Cyclic voltammetry was performed on an electrochemical workstation (CHI 660C) in the potential range 3.12-4.30 V at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectra were obtained by using a CHI 660C electrochemical workstation with amplitude of 5 mV in the frequency range 100 kHz to 0.01 Hz.

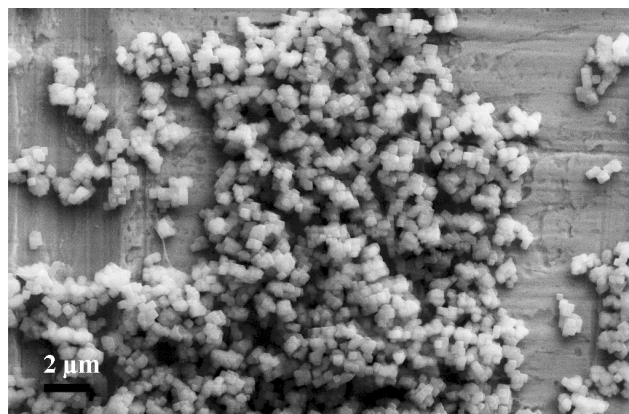


Fig. S1 Low-magnified SEM image of Prussian blue analogue $\text{Co}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$.

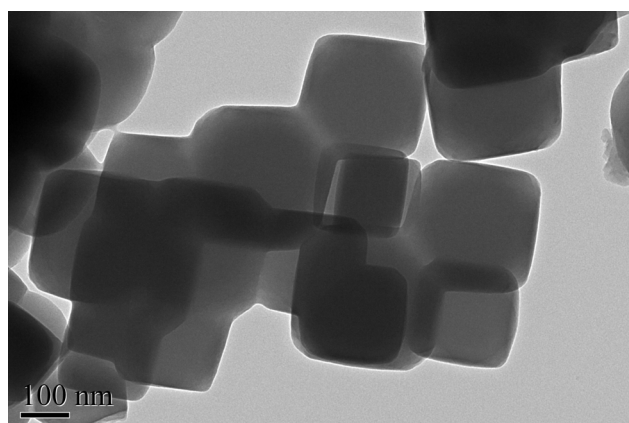


Fig. S2 TEM image of the as-prepared $\text{Co}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$.

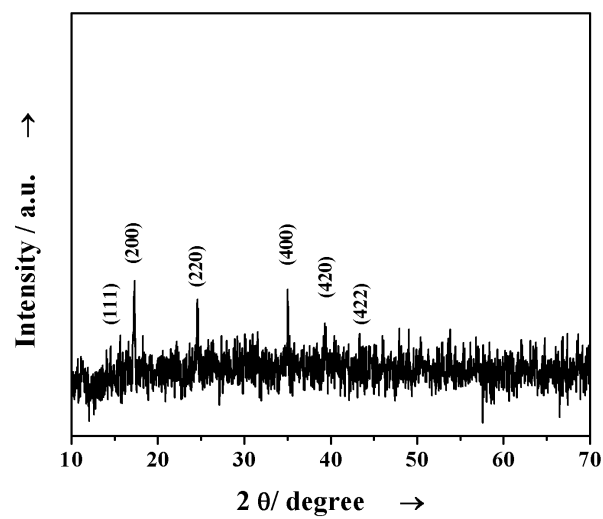


Fig. S3 XRD pattern of $\text{Co}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$.

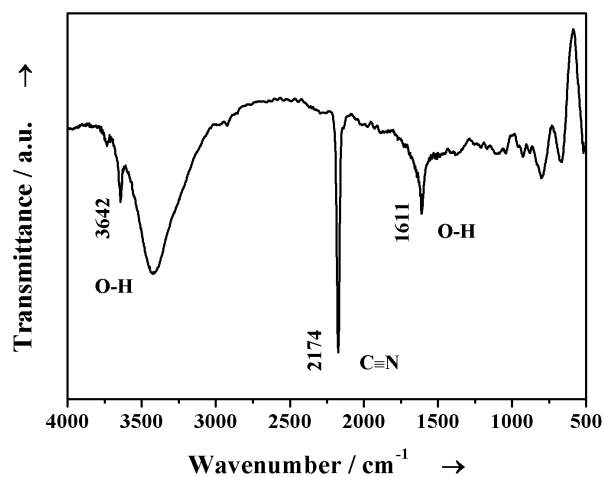


Fig. S4 FTIR spectrum of the as-prepared $\text{Co}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$.

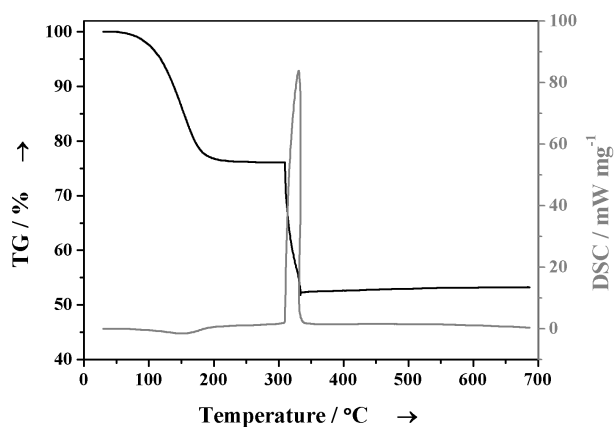


Fig. S5 TG curve of $\text{Co}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ nanoparticles.

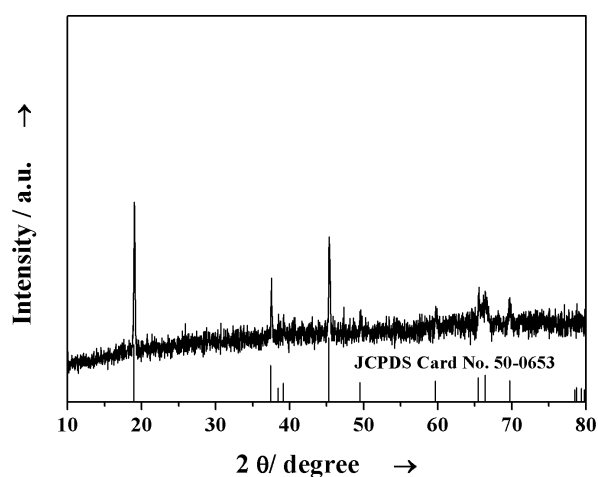


Fig. S6 XRD pattern of the as-prepared LiCoO_2 nanoparticles.

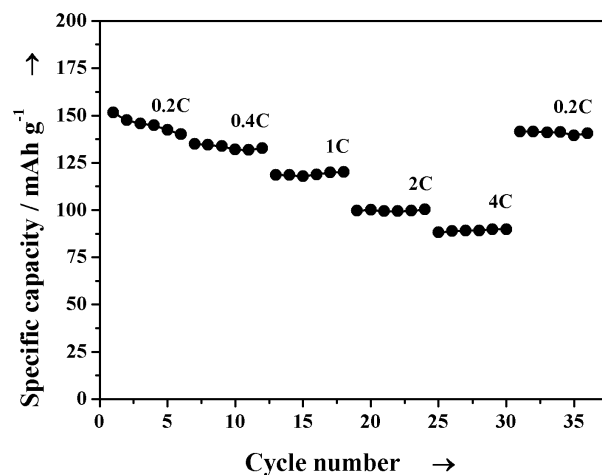


Fig. S7 The rate and cycling performances of LiCoO₂ electrode at different C-rates.

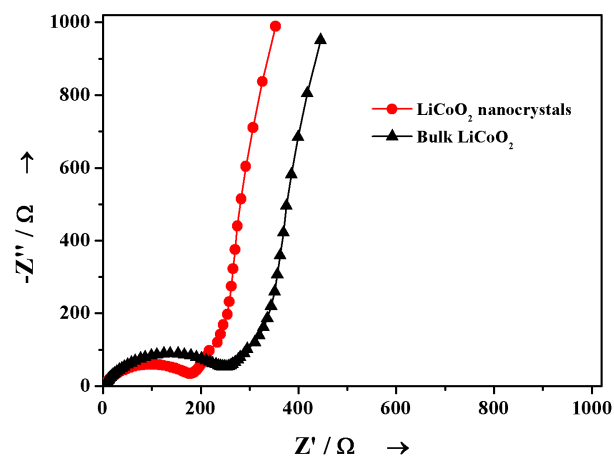


Fig. S8 Electrochemical impedance spectra of LiCoO₂ nanocrystals and bulk LiCoO₂ powders measured at the 5th fully discharged state.

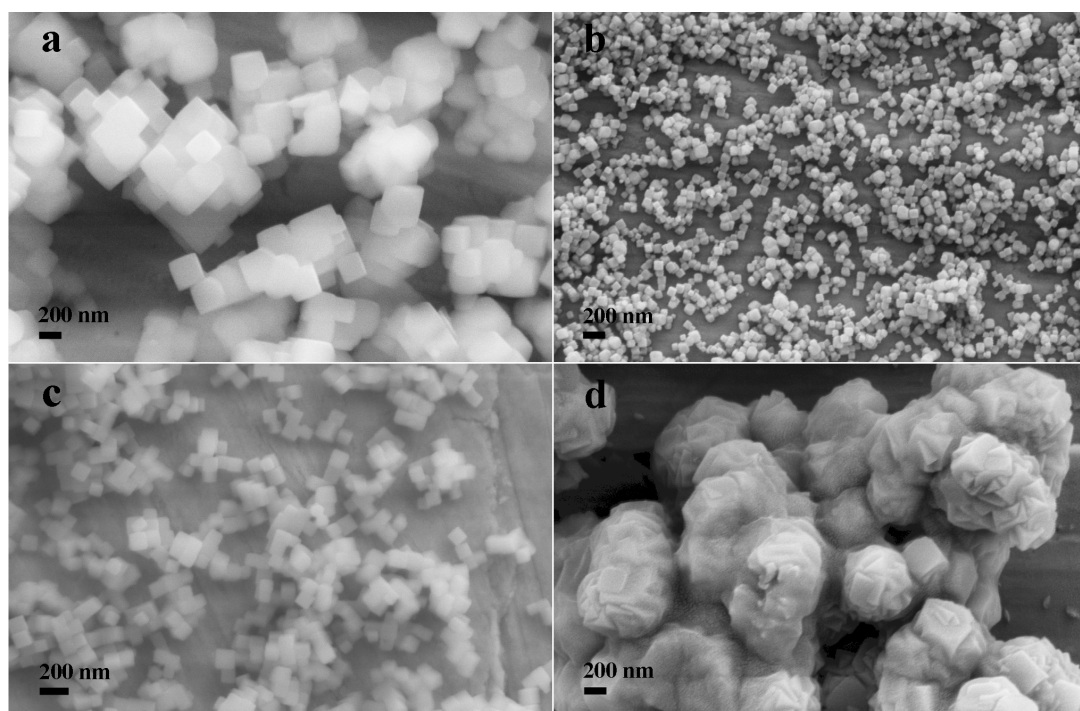


Fig. S9 SEM images of $\text{Co}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ obtained with different surfactants with the other experimental parameters kept constant: (a) SDBS, (b) poly(vinylpyrrolidone), (c) sodium citrate, 30.9 mg and (d) sodium citrate, 19.30 mg.

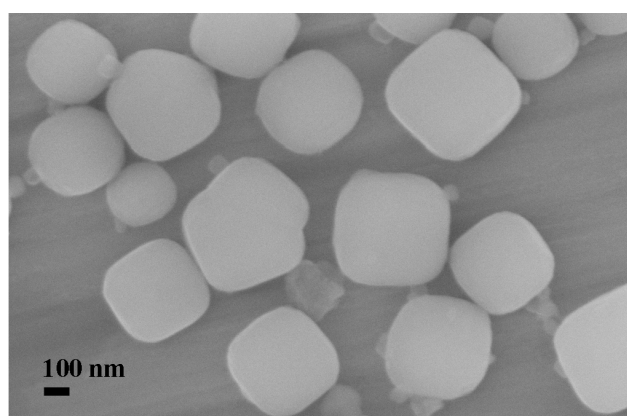


Fig. S10 SEM image of $\text{FeFe}@CoNi$ hybrid Prussian blue analogues nanoparticles synthesized using this method. The Prussian blue nanoparticles used as starting materials were firstly prepared by a method reported by Yamauchi's group.¹

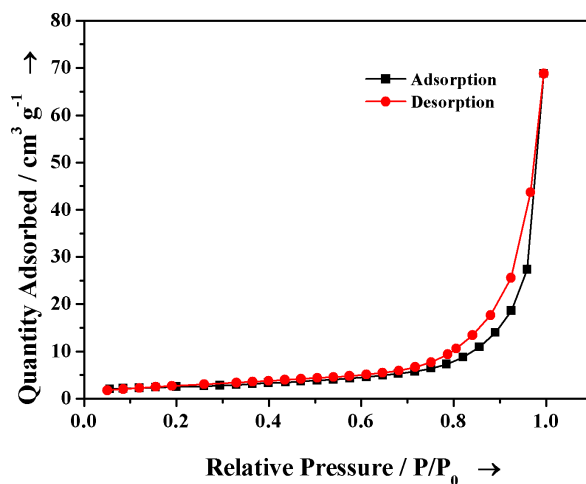


Fig. S11 Nitrogen adsorption/desorption isotherm of the $\text{Fe}_2\text{O}_3@\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanocubes.

The porous features of $\text{Fe}_2\text{O}_3@\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanocubes were further investigated by N_2 adsorption-desorption analysis. As shown in Fig. S11, the synthesized nanocubes exhibited type IV isotherms with a H3 hysteresis loop, indicative of mesoporous characteristics. The specific surface area calculated with the BET model is $8.64 \text{ m}^2 \text{ g}^{-1}$. Together with the SEM observation, one can conclude that the presence of porous structure in $\text{Fe}_2\text{O}_3@\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ should promote rapid diffusion of Li ions.

1. M. Hu, S. Furukawa, R. Ohtani, H. Sukegawa, Y. Nemoto, J. Reboul, S. Kitagawa and Y. Yamauchi, *Angew. Chem. Int. Ed.*, 2012, **51**, 984-988.