

## Supporting information

# Novel Synthesis of an Fe<sup>3+</sup>/Fe<sup>2+</sup> Layered Double Hydroxide ('Green Rust') via Controlled Electron Transfer with a Conducting Polymer

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## Materials and instruments

Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O, polypyrrole (PPy, doped, 5 wt% dispersion in H<sub>2</sub>O, cat no. 482552), and poly(sodium 4-styrenesulfonate) (average Mw ~70,000, powder, cat no. 25704-18-1) were purchased from Sigma-Aldrich. FeSO<sub>4</sub>·7H<sub>2</sub>O was obtained from Daejung Chemical. NaOH beads were purchased from Samchun Chemical. All reagents were used without further purification

Powder X-ray diffraction patterns (PXRD) were collected using a Bruker AXS D2 Phaser diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with Ni-filtered Cu-K $\alpha$  radiation ( $\lambda$  = 1.5406 Å), a 1 mm air-scattering slit and a 0.1 mm equatorial slit. The measurement angle range was from 5° to 70° with time step increments of 0.02° and 0.5 s per step. Scanning electron microscopy (SEM) images were obtained using a Quanta 250 FEG microscope (FEI Company, Hillsboro, OR, USA). In addition, the sample surfaces were coated with Pt/Pd plasma for 60 s, and the sample images was obtained using a 30 kV electron beam.

## Synthetic procedures

1. Synthesis of green rust (GR-SO4) through alkaline titration.

GR-SO4 was synthesized by the coprecipitation of divalent and trivalent Fe ions in decarbonated water with a specific the ratio of the ferrous, ferric and hydroxide ions ( $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 3$ ,  $[\text{OH}^-]/([\text{Fe}^{2+}]+[\text{Fe}^{3+}]) = 3/2$ ), as reported previously<sup>S1</sup>. Since  $\text{Fe}^{2+}$  ions can be easily oxidized, the reaction was performed under anoxic conditions under the flow of inert gas during the reaction. The decarbonated water was prepared by boiling and cooling deionized water under the flow of inert gas. With the specific ratio of all ions, the detailed procedure was as follows. First, 4.17 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (0.015 mol) and 1.41 g of  $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  (0.0025 mol) were dissolved in 50 ml of decarbonated water, and 50 ml of 0.3 M NaOH was slowly added. After complete addition, the pH was maintained at approximately 6.9, and the resulting green slurry was stirred at room temperature for 24 h. Finally, green powder was obtained by filtration under an inert atmosphere and lyophilization.

## 2. Synthesis of GR-SO4 in the presence of polystyrene sulfonate (PSS), PPy and a PPy:PSS mixture.

Generally, the procedure for all the samples was identical to the aforementioned procedure, except for the addition of various polymer solutions in decarbonated water. After aqueous  $\text{Fe}^{2+}/\text{Fe}^{3+}$  was titrated with the alkaline solution, 5 ml of an aqueous polymer solution prepared as follows was added to the green suspension, and the resulting suspension was stirred at room temperature for 24 h.

1) *Preparation of the PPy solution:* The PPy solution was titrated with 0.1 M NaOH with  $\text{N}_2$  bubbling until the pH reached approximately 6.9 because the pH of the commercially available PPy solution was acidic.

2) *Preparation of the PSS solutions:* A series of PSS solutions was prepared with  $\text{N}_2$  bubbling by separately dissolving 0.75 g (3 wt%), 1.25 g (5 wt%) and 2.5 g (10 wt%) of PSS in 25 ml of decarbonated water.

3) *Preparation of the PPy:PSS solutions:* A series of PPy:PSS solutions was prepared by adding PSS powder to the titrated PPy solution with  $\text{N}_2$  bubbling as aforementioned. The details are as follows. First, a 0.2 wt% PPy solution was prepared by diluting 1 ml of the commercial PPy solution with 24 ml of decarbonated water. To prepare the 2.2 wt% PPy and 2.8 wt% PSS mixed solution, 11 mg of the commercial PPy solution was diluted with 14 ml of decarbonated water, and 0.7 g of PSS was then added to the diluted PPy solution. For the 7.2 wt% PPy and 2.8 wt% PSS mixed solution, 36 ml of the commercial PPy solution was concentrated to 25 ml by evaporating the water under reduced pressure on a conventional rotary evaporator at 80 °C. Then, 0.7 g of PSS was added to the concentrated PPy solution. For the 0.2 wt% PPy:2.8 wt% PSS solution, a 0.2 wt% PPy solution was prepared as described above, and 0.75 g of PSS was dissolved in the 0.2 wt% PPy solution. To prepare the 0.2 wt% PPy:4.8 wt% PSS and 0.2 wt% PPy:9.8 wt% PSS mixed solutions, 1.2 g of PSS and 2.45 g of PSS were dissolved in a 0.2 wt% PPy solution, respectively. For the 0.66 wt% PPy and 9.24 wt% PSS mixed solution, 3.3 ml of the commercial PPy solution was diluted with 21.7 ml of decarbonated water, and 2.31 g of

PSS was then added to the 0.66 wt% PPy solution. Lastly, for the 0.3 wt% PPy and 4.7 wt% PSS mixed solution, 1.5 ml of the commercial PPy solution was diluted with 23.5 ml of decarbonated water, and 1.175 g of PSS was added to the 0.3 wt% PPy solution.

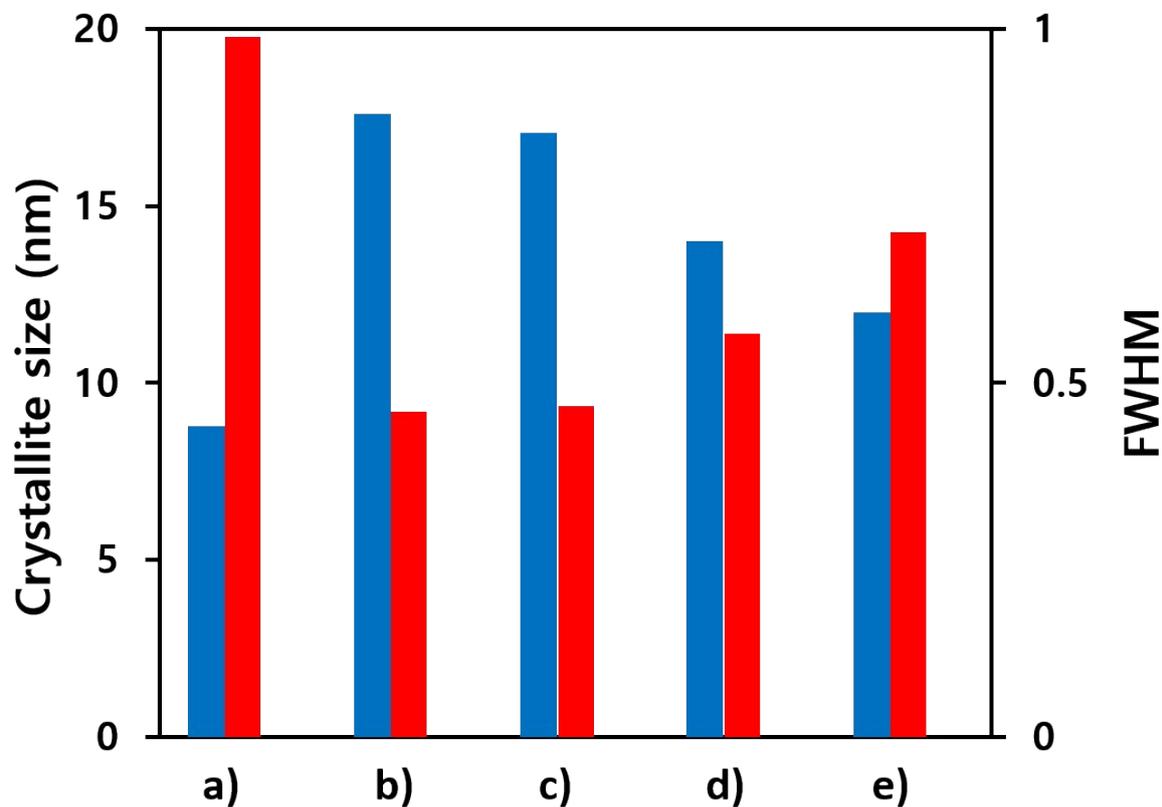


Figure S1. Calculated crystallite size (blue bars) by Scherrer equation and FWHM (red bars) from XRD patterns of (a) GR-SO<sub>4</sub> and hybrids with varying mixing amounts of PPy and PSS: (b) 0.2 wt% PPy and 2.8 wt% PSS, (c) 0.2 wt% PPy and 4.8 wt% PSS, (d) 0.2 wt% PPy and 9.8 wt% PSS, (e) 0.66 wt% PPy and 9.24 wt% PSS, and (f) 0.3 wt%:PPy and 4.7 wt% PSS.

## References

- S1. A. Gehin, C. Ruby, M. Abdelmoula, O. Benali, J. Ghanbaja, P. Refait, J.-M. R. Genin, *Solid State Sci.*, 2002, **4**, 61-66.