

Electronic Supplementary Information

One-step solid-state synthesis of carbon nanotubes with surface functionality and their application in water treatment

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Supporting Information: Experimental details.

All chemicals were analytical grade and used as received without further purification.

Synthesis of CoAl-sal LDH precursor. The CoAl-sal LDH precursor was prepared by a simple coprecipitation method. In a typical procedure, a mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with Co/Al ratio of 2.0 was dissolved in 50 mL of deionized water to form a clear solution ($[\text{Co}^{2+}] + [\text{Al}^{3+}] = 1.2 \text{ M}$). The salt solution was added dropwise to 0.08 mol of sodium salicylate dissolved in 100 mL of deionized water. The pH was maintained at 7 by the simultaneous addition of 2 M NaOH solution. A three-fold excess of sodium salicylate above the necessary stoichiometric amount required for charge neutrality was used in the reaction mixture to reduce the probability of incorporating competing nitrate and carbonate anions into the product LDH. The resulting suspension was transferred into a Teflon-lined autoclave, crystallized at 100 °C for 24 h, filtered, and the solid product washed with deionized water. The resulting pink suspension was directly dried in an oven at 50 °C for 12 h to afford the solid CoAl-sal LDH product.

Synthesis of CNTs. A sample of the CoAl-sal LDH precursor (1.3 g) was placed in a ceramic boat which was placed in a furnace and purged with N_2 gas for 2 min. Under continuous flow (60 mL/min) of N_2 gas, the furnace temperature was raised at a ramping rate of 5 °C/min and then kept at 600 °C for 2 h. After slow cooling down naturally to room temperature, a fluffy CNTs powder (58 mg) together with a dense $\text{Co}/\text{Al}_2\text{O}_3$ powder (525 mg) was obtained.

Characterization. The CoAl-sal LDH precursor and pyrolysis products were characterized by X-ray diffraction (XRD, Shimadzu XRD-6000 diffractometer with $\text{Cu K}_{\alpha 1}$ radiation, $\lambda = 0.1541 \text{ nm}$, 40 kV, 30 mA), Fourier transform IR (FTIR, Bruker Vector-22), thermogravimetry-differential thermogravimetry (TG-DTG, Perkin-Elmer Diamond TG apparatus), X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM scanning X-ray microprobe 100 mm beam size, using an Al K_{α} X-ray source operated at 2 kV and 20 mA.), scanning electron microscopy (SEM, Hitachi S-4700), and transmission electron microscopy (TEM, Hitachi H-800).

Removal of Congo red and Evans Blue dyes. The as-synthesized CNTs (30 mg) was added to 50 mL of a solution of Congo red ($C_{32}H_{22}N_6O_6S_2Na_2$, Amresco Inc.) with a concentration of 100 mg/L under vigorous stirring at pH 4. UV-vis absorption spectra were recorded at given time intervals to monitor the concentration of dye in the solution. The pH values of the solutions were adjusted using HNO_3 or NaOH. To estimate the maximum adsorption capacity for Congo red, the initial concentrations of Congo red were varied in the range 100–1000 mg/L, and the dosage of CNTs was kept at 0.6 g/L. For the adsorption of Evans Blue ($C_{34}H_{24}N_6O_{14}S_4 Na_4$), 100 mL of an aqueous solution (100 mg/L) without adjusted pH was mixed with 40 mg of CNTs and stirred for 4 h at room temperature (20 °C). UV-vis adsorption spectra (UV-2501PC) were recorded at different intervals to monitor the process.

Removal of Pb(II) and Cd(II). Solutions containing Pb(II) and Cd(II) with a concentration of 50 mg/L were prepared using $Pb(NO_3)_2 \cdot 6H_2O$ and $Cd(NO_3)_2 \cdot 6H_2O$, respectively. To obtain the adsorption isotherms, 40 mg of CNTs was added to 100 mL of the above solutions under vigorous stirring at room temperature and inductively coupled plasma emission spectroscopy (ICP-ES) was used to measure the concentration of metal ions at given time intervals to monitor the process.

Supporting Information: Figures.

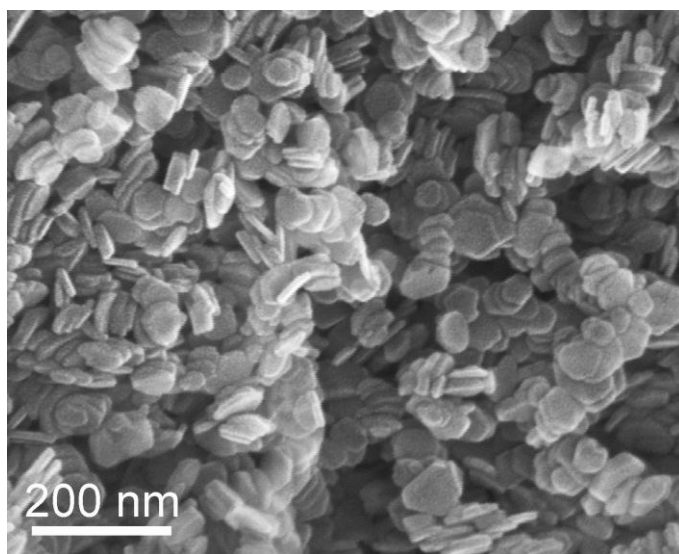


Figure S1. SEM image of the CoAl-Sal LDH precursor.

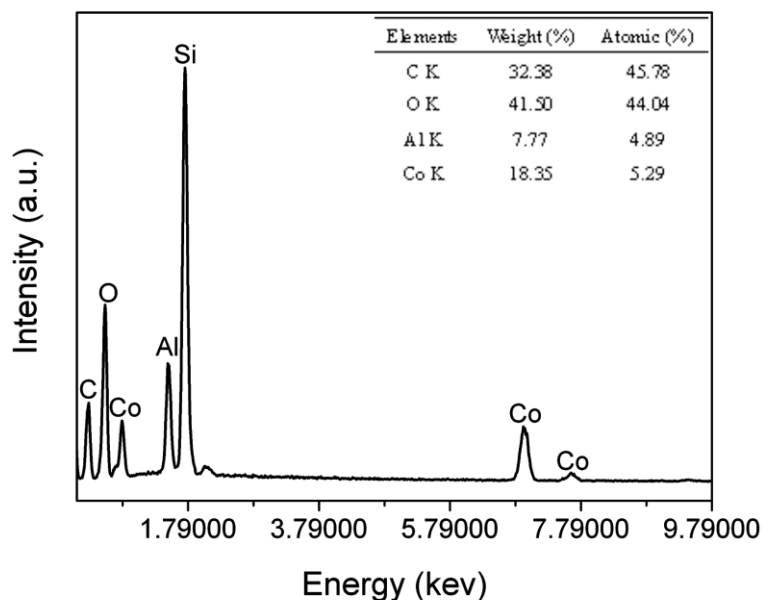


Figure S2. EDX spectrum of the CoAl-Sal LDH precursor.

Figure S2 shows the EDX spectrum of the CoAl-Sal LDH precursor. The presence of Co, O, C, Al and no detectable content for N, confirm the absence of any co-intercalation of NO_3^- from the $\text{Co}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ reactants. The results are consistent with the chemical composition $\text{Co}_{0.63}\text{Al}_{0.54}(\text{OH})_2(\text{HOC}_6\text{H}_4\text{COO})_{0.87} \cdot 1.33\text{H}_2\text{O}$.

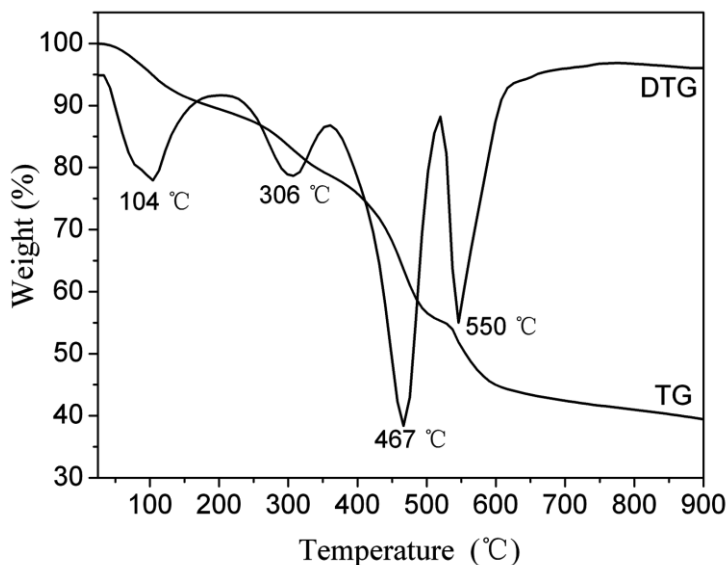


Figure S3. TG–DTG curves of the CoAl-Sal LDH precursor in flowing N₂ with a heating rate of 5 °C/min.

Figure S3 shows the thermal behavior of the CoAl-Sal LDH precursor in the temperature range 30–900 °C. Four weight loss stages are observed in the TG–DTG curves of CoAl-sal LDH. The first weight loss of about 11% in the temperature range from room temperature to approximately 200 °C can be assigned to removal of water physisorbed on the external surface and interlayer structural water. The second and third weight loss of approximately 34% occurs in the temperature range 200–520 °C and results from dehydroxylation of the brucite-like layers as well as decomposition of the salicylate anions. The last weight loss about 12% with a peak at 550 °C in the DTG curve is attributed to the formation of metallic cobalt through reduction of Al-doped CoO by the intermediate decomposition products of the salicylate anions.

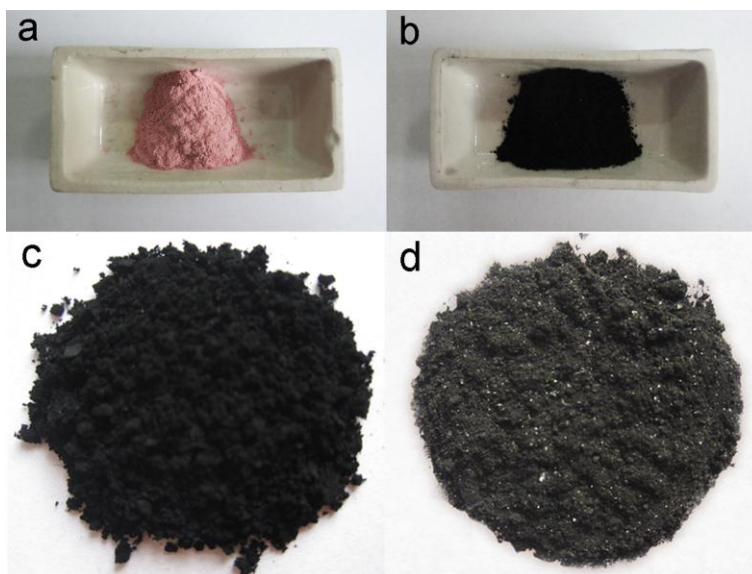


Figure S4. Photographs of (a) the CoAl-Sal LDH precursor (b) the as-synthesized products of solid-state pyrolysis of the CoAl-Sal LDH precursor (c) CNTs and (d) Co/Al₂O₃ nanocomposites.

Figure S4 shows the photographs of the CoAl-Sal LDH precursor and the as-synthesized CNTs and Co/Al₂O₃ nanocomposites. Upon pyrolyzed at 600 °C for 2 h, the initial pink solid (1.3 g) LDH precursors became black and expanded slightly in volume. Closer examination showed that the product consisted of a fluffy black powder on the surface of a dense grey powder, and these two components could be easily separated by hand giving 58 mg (CNTs) and 525 mg (Co/Al₂O₃ nanocomposites), respectively, of materials.

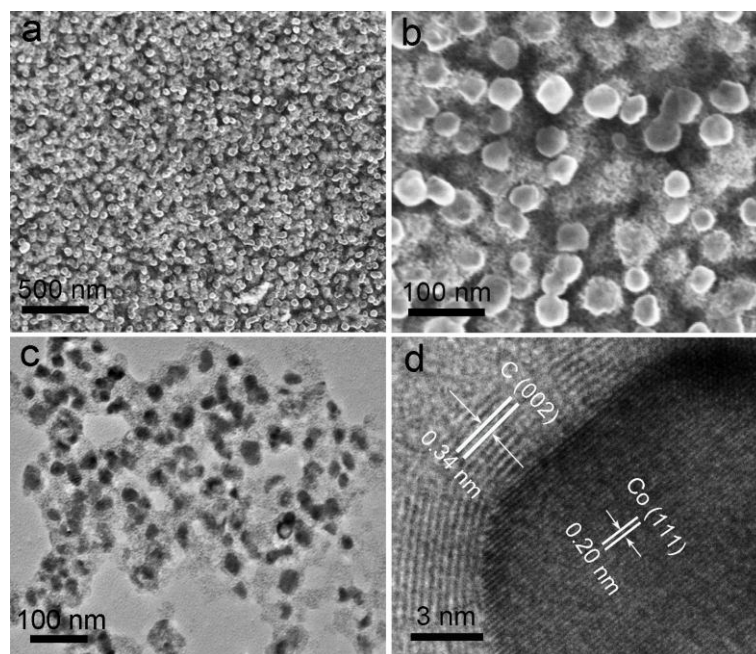


Figure S5. (a, b) SEM images and (c, d) TEM images of the Co/Al₂O₃ nanocomposites obtained by one-step pyrolysis of the CoAl-Sal LDH precursor.

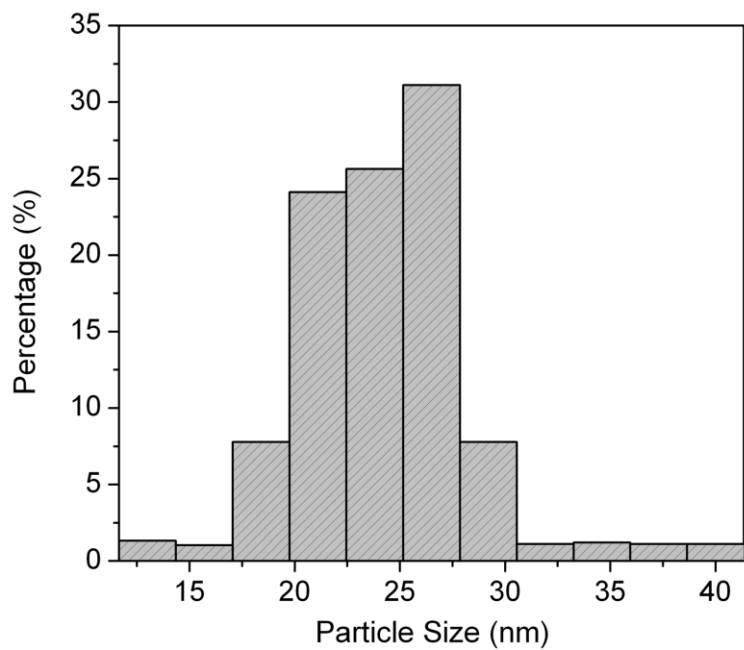


Figure S6. The size histogram of the as-synthesized CNTs.

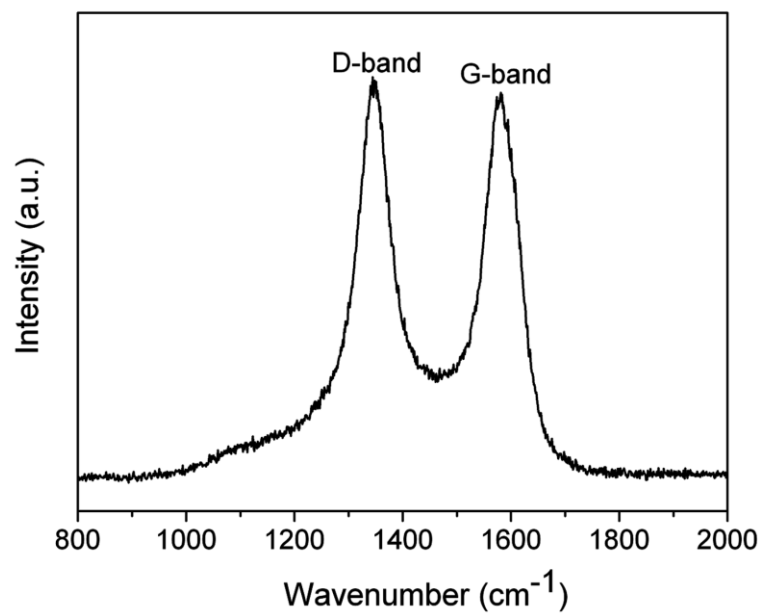


Figure S7. Raman spectrum of the as-synthesized CNTs.

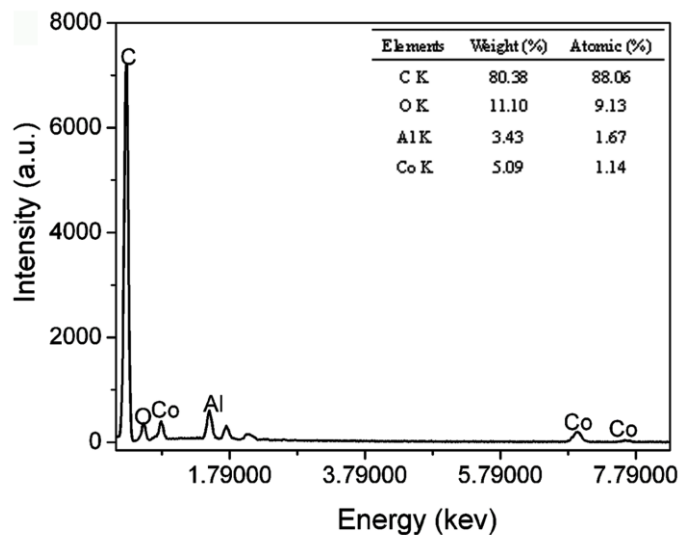


Figure S8. EDX spectrum of as-synthesized CNTs.

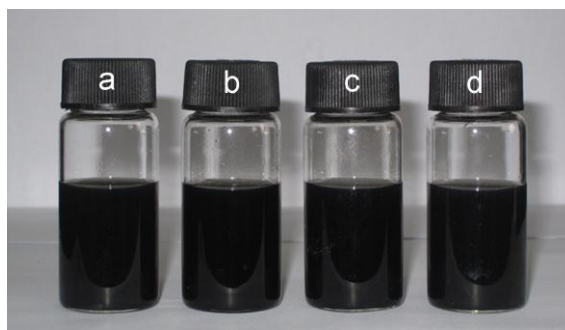


Figure S9. Photographs of dispersions of the as-prepared CNTs in (a) ethanol (b) pyridine (c) THF and (d) acetone. The concentrations of all samples were 0.2 mg/mL.

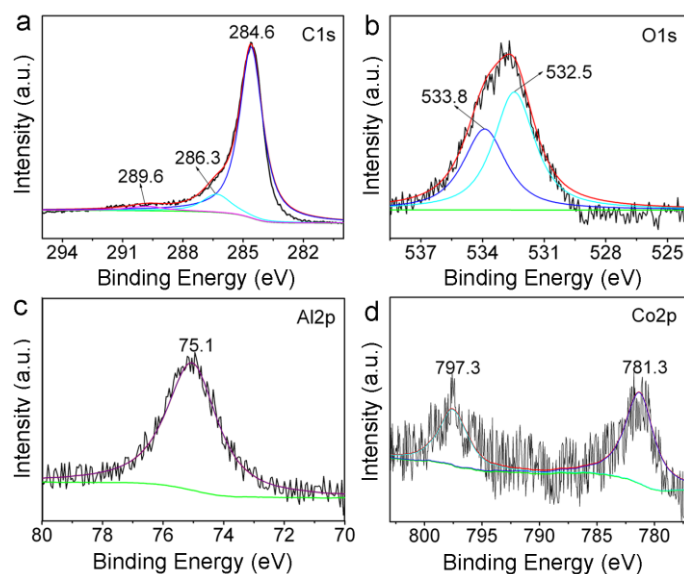


Figure S10. Representative XPS spectra of the CNTs prepared by one-step pyrolysis of the CoAl-Sal LDH precursor. (a) C 1s scan; (b) O 1s scan; (c) Al 2p scan; (d) Co 2p scan.

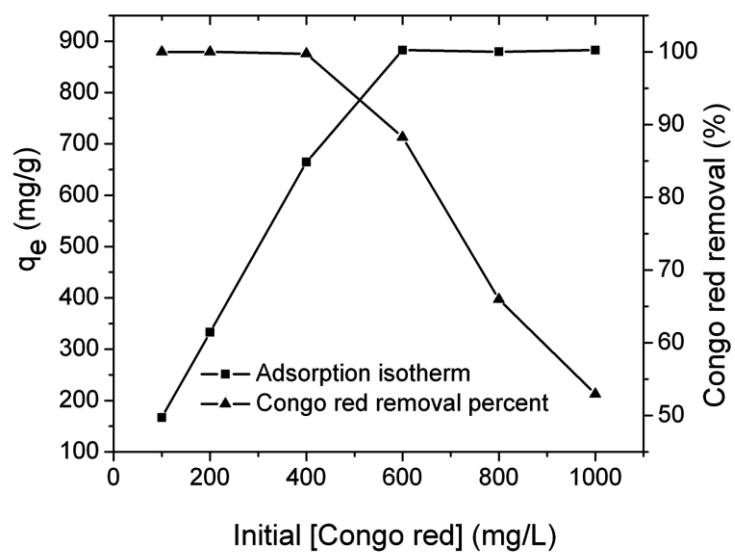


Figure S11. Adsorption isotherm and percentage removal of Congo red as a function of initial concentration.