# Carbon Stabilized Iron Nanoparticles for Enviromental Remediation

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#### **Experimental Part**

**S.1 Materials** Iron nitrite (Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O), Alfa Aesar Company, 404.15 g/mol) is used as iron precursor. Sodium chloride (NaCl, Alfa Aesar Company) serves as solid stabilizers to disperse iron nitrate and to prevent the products from agglomeration. Poly (vinyl alcohol) (PVA, MW=88000-96800, degree of polymerization 2000-2200, Alfa Aesar Company) is used as the carbon precursor to reduce iron oxide to metal at mild temperature. Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O7, 99%) and 1, 5 diphenylcarbazide (DPC) are purchased from Alfa Aesar Company. O-Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85 wt%) and acetone (98%) are purchased from Fisher Scientific. All the chemicals are used as-received without any further treatment.

<u>S.2 Fe-C core-shell nanoparticles fabrication</u> The salt solution was prepared by dissolving iron nitrate, sodium chloride and PVA in the corresponding amount of deionized water. The molar ratio of iron nitrate and sodium chloride was controlled at 1:20. The homogeneous solid sample was obtained by drying at 70 °C under magnetic stirring to evaporate deionized water. The nanoparticles were manufactured by annealing the solid solution through two steps. The first step is heating the solid salt at 190 °C in a tube furnace for about 2 hours under air atmosphere. As a result, Fe(NO<sub>3</sub>)<sub>3</sub> was decomposed to form Fe<sub>2</sub>O<sub>3</sub> NPs. In the second step, PVA was carbonized to form carbon-based magnetic composites. Fe<sub>2</sub>O<sub>3</sub> was reduced to Fe NPs at 750 °C in nitrogen atmosphere by carbon decomposed from PVA; meanwhile, the extra carbon served as a shell to protect iron nanoparticles from oxidation. The product was collected and washed with deionized water several times to remove NaCl. And then the product was treated with hydrogen chloride with a pH value of 1.0 to remove the uncoated Fe NPs and to introduce the carboxyl groups to the nanoparticle surface. Finally, the sample was dried in vacuum oven at 40 °C for 24 hours. The schematic representation of experiment is shown in Chart S1. In order to demonstrate that

sodium chloride serves as the spacer to prevent the nanoparticles from agglomeration, the above experiment without sodium chloride was repeated.



Chart S1. Schematic representation of carbon stabilized Fe nanoparticle formation.

**Removal of Cr(VI) from model polluted water** Prepared  $K_2Cr_2O_7$  stock solution with a concentration of 400 µg/L is investigated for environmental remediation applications. Fe-C core-shell NPs were added in 30 ml  $K_2Cr_2O_7$  aqueous solution. The interaction between Cr(VI) and NPs was maintained for 2 hours on a rotating shaker (Fisher Scientific, Centrific 228). The sample solution for UV-vis test is prepared as follows. Clear supernatant after centrifugation (3.25 ml) was added to a clean test tube, followed by adding 10 mol/L H<sub>3</sub>PO<sub>4</sub> in acetone (0.25 ml) and 10 mg/ml DPC in DI water (0.5 ml) by vortex mixing (Scientific Industries, Vortex-GENIE). The solution was then incubated at room temperature for 30 min for color reaction (2). The methodology for the determination of Cr(VI) using 1.5-diphenycarbohydrazide method is well documented.<sup>1.2</sup> DPC gives a sensitive and specific color reaction with Cr(VI) in mineral acid solution.<sup>3</sup> The pink colored chromophore is a chelate of Cr(III) and DPC. The latter is produced and simultaneously combines with chromium when 1.5-diphenycarbohydrazide is oxidized by Cr(VI).<sup>3</sup> The reaction is:

$$Cr_2O_7^{2-} + 2H_4L + 10H^+ \longrightarrow [Cr(III)(HL)_2] + Cr^{3+} + H_2L + 7H_2O$$
 (1)

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where H<sub>4</sub>L is diphenylcarbazide:



The blank reference solution was prepared by adding 3.25 ml DI water, 0.25 ml of 10 mol/L  $H_3PO_4$  in aceton and 0.5 ml of 10 mg/ml DPC in DI water into a clean test tube by vortex mixing. Finally, the concentration of the residue Cr(VI) in the treated solution was read from the standard concentration-absorbance curve determined spectrophotometrically with DPC at 540 nm using UV-vis spectrophotometer.<sup>2</sup> The removal percentage of Cr(VI) was calculated as follows:

Removal of 
$$Cr(VI)\% = (C_0 - C_r)/C_0 \times 100\%$$
 (3)

where C<sub>0</sub> and C<sub>r</sub> are the initial and remaining concentration of Cr (VI) in solution, respectively.

### **S.3 Characterization**

**S.3.1** Transmission electron microscopy (TEM, JEOL 2010F, accelerating voltage of 200 kV) was used to characterize the morphology (size and shape) of the as-produced Fe/C nanoparticles. The samples were prepared by dropping aqueous nanoparticle suspension onto a holey carbon coated copper grid and drying naturally in air.

**S.3.2** The elementary analysis was carried out by X-rays (EDAX) Genesis energy dispersive system attached to scanning electron microscopy (Hitachi S-3400 SEM).

**S.3.3** Fourier transform infrared spectroscopy (FT-IR, a Bruker Inc. Tensor 27 FT-IR spectrometer with hyperion 1000 ATR microscopy accessory) was used to characterize the surface functionality of the nanoparticles.

**S.3.4** The average surface area of Fe@C NPs was analyzed by the BET analysis, which is turn on a Micromeritics TriStar adsorption analyzer (GAA). The instrument and analyses are run by TriStar 3000 version 6.04 software. The experiment amounts to a measurement of how much adsorptive is required by the sample to reach a target pressure, or a series of target pressures. The measurement(s) are processed by the BET method ("model") to calculate specific surface area. An acquisition sequence: Pumpdown rate (programmed) from atmosphere to < 30 mmHg is 1 mmHg/sec, the second slowest setting available on the instrument. From <30 to <1 mmHg the rate is 50 mmHg/sec. Unrestricted evacuation begins when pressure goes below 1.0 mmHg. Getting this far usually takes 30-40 min. Then, after a vacuum stability test is passed, it is a programmed 30 min outgass period before the system does a leak test, during which the sample/system must pass to proceed. (If it's not passed the tube gets another 30 min pumping before the test runs again.) Free space is measured, every time, with helium. When completed, the He is removed with an identical pumpdown and 30 min outgass period before gas adsorption measurements begin. Getting this far usually takes a bit over two hours. The result is the sample has been outgassed once, flushed with helium, and outgassed again. Equilibration time is 10 sec. Equilibrium is defined as a change in pressure less than 0.01%. Early in the sequence, this can take several hundred seconds depending on the sample. Late in the sequence, it's often achieved before the 100 sec is up--but it still goes the full 100. Absolute pressure tolerance is 5.0 mmHg and relative pressure tolerance is 5.0%. The adsorptive is nitrogen. The constant-temperature bath is liquid nitrogen. The instrument is capable of experiments regarding porosity but it's a very much longer acquisition. Measurements are made clear up to 0.99 P/Po. It is actually been done up and back to collect a full adsorption/desorption isotherm. Sometimes they take longer than 24 hours. The most commonly used model is the BJH but a few others exist. Our nano-particles are "non-porous" by these methods. Porosity cannot be calculated from BET measurements.

**S.3.4**. Magnetic properties of the nanoparticles were investigated in a 9-T physical properties measurement system (PPMS) by Quantum Design at room temperature.

**S.3.5**. Cary 50 bio ultra-violet-visible (UV-vis) spectrophotometer was used for the determination of the aqueous Cr(VI) concentration.

**S.4. Sodium chloride serves as the spacer to prevent NPs from agglomeration** Fig. S1 (a-b) shows the products after the solution evaporation with and without NaCl, respectively. When NaCl is used as spacer, the dried solid mixture shows yellow, the original color of iron nitrate, Fig. S1(a). However, without sodium chloride, PVA has a strong interaction with iron nitrate, iron nitrate become dark brown, Fig.S1 (b) indicating the partial decomposition of iron nitrate to form iron oxide. Fe@C NPs (Figure 1 in main text) are formed with a fine powder, Fig S1(c), which is due to the fact that NaCl serves as a solid spacer to prevent the NPs from agglomeration. Without NaCl, the products still show strong magnetization, however, the NPs are agglomerated and present in the bulk form (Fig. S1(d).



**Fig.S1** (a) PVA + Fe(NO<sub>3</sub>)<sub>3</sub> +NaCl solid solution after evaporation, (b) PVA + Fe(NO<sub>3</sub>)<sub>3</sub> solution after evaporation, (c) products using NaCl as spacer (Fe@C NPs), (d) products without NaCl as spacer.

![](_page_7_Figure_0.jpeg)

Fig.S2 FT-IR spectra of Fe-C NPs after post-treated with (a) only deionized water, and (b) deionized water followed by HCl (pH=1).

**S.5 Surface functionality of the nanoparticles** The FT-IR spectrophotometer is used to identify the functional groups present on the surface of Fe/C NPs. Fig.S2 shows the spectra of the NPs with different treatment methods. No characteristic peaks are observed in Fig. S1(a) when the as produced nanoparticles are washed with deionized water. However, broad peaks at 3388 cm<sup>-1</sup> and 1631 cm<sup>-1</sup> are observed after the as-produced nanoparticles washed with hydrogen chloride acid. The broad peak at 3388 cm<sup>-1</sup> is attributed to the stretching vibration of hydroxyl groups (-OH) group as a result of the presence of hydrogen bonding in solid phases. The carbonyl groups (C=O) of metal carbonyl compounds absorb at 1631 cm<sup>-1</sup> are due to the CO stretching vitration. These two peaks are arising from the nanoparticle surface functionlization after acid treatment. This can explain the phenomena of well re-dispersion in deionized water in Fig.2(a). The main reactive groups can be used for subsequent chemical surface engineering.<sup>4</sup> The strong acid treated carbon shells<sup>5,6</sup> with carboxyl functional groups (-COOH) have great potential to

facilitate the delivery of biomolecules or catalytic species for future application such as biomolecular separation, targeted drug delivery and catalysis.<sup>7,8</sup> The peak at 2360 cm<sup>-1</sup> corresponds to carbon dioxide adsorbed from the atmosphere.

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