## Supporting Materials for

# Magnetic Polyaniline Nanocomposites Toward Toxic Hexavalent Chromium Removal

Hongbo Gu,<sup>1,2</sup> Sowjanya B. Rapole,<sup>1,3</sup> Jaishri Sharma,<sup>3</sup> Yudong Huang,<sup>2</sup> Dongmei Cao,<sup>4</sup> Henry A. Colorado,<sup>5</sup> Zhiping Luo,<sup>6</sup> Neel Haldolaarachchige,<sup>7</sup> David P. Young,<sup>7</sup> Bryan Walters,<sup>8</sup> Suying Wei<sup>3,\*</sup> and Zhanhu Guo<sup>1\*</sup>

<sup>1</sup>Integrated Composites Lab (ICL), Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX 77710 USA

> <sup>2</sup>School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, Heilongjiang 150001China

<sup>3</sup>Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX 77710 USA

<sup>4</sup>Material Characterization Center, Louisiana State University, Baton Rouge, LA 70803 USA

<sup>5</sup>Materials Science and Engineering, University of California, Los Angeles, CA 90066 USA

<sup>6</sup>Microscopy and Imaging Center, and Materials Science and Engineering Program, Texas A&M University, College Station, TX 77843 USA

<sup>7</sup>Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803 USA

<sup>8</sup>Earth Analytical Sciences, Inc., Beaumont, TX 77705 USA

\*Corresponding author

E-mail: suying.wei@lamar.edu (S.W.) and zhanhu.guo@lamar.edu (Z.G.)

## **Polyaniline background**

As a class of conjugated polymers, PANI consists of alternating reduced and oxidized repeating units and its chemical structure is shown in **Scheme S1**. For the first state, (1-Y) is 0 to give a completely reduced state, 0.5 to give the "half-oxidized" polymer, 1 to give the fully oxidized state,<sup>1</sup> which are termed as "leucoemeraldine" (LEB), "emeraldine" (EB) and "pernigraniline" (PB), respectively.<sup>2</sup>



Pernigraniline

Scheme S1 Different states of Polyaniline.

#### **Cr(VI)** Concentration Determination

The potassium dichromate ( $K_2Cr_2O_7$ ) stock solution was prepared by dissolving potassium dichromate (1.1315 g) into deionized water (100.0 mL) to give a concentration of 4.0 g L<sup>-1</sup>. The Cr(VI) standard solution was prepared by diluting 25.0, 50.0, 75.0, 100.0, 125.0, 175.0, 225.0, 250.0 and 300.0 µL potassium dichromate stock solution with 100.0 mL deionized water. DPC solution was prepared by dissolving 50.0 mg DPC in 10.0 mL acetone (prepared freshly for each use). Phosphoric acid (4.5 M) was prepared by diluting 30.0 mL concentrated phosphoric acid (85 % w/w) to 100.0 mL with deionized water.

The final concentration of Cr(VI) was determined by the colorimetric method, which is based on the specific reaction of DPC with Cr(VI) in a mineral acid solution.<sup>3</sup> The final pink color comes from a chelate of Cr(III) and DPC, which is formed when DPC is oxidized by Cr(VI) and measured colorimetrically at 540 nm by ultraviolet-visible spectroscopy (UVvis). The chelation between Cr(VI) and DPC can be described as Equation (S1):

$$Cr_2O_7^{2-} + 3H_4L + 6H^+ = [Cr^{III}(HL)_2]^+ + Cr^{3+} + H_2L + 7H_2O$$
 (S1)

where H<sub>4</sub>L is DPC and its structure is shown below:

$$0 = C < NH - NH - C_6H_5 NH - NH - C_6H_5$$

and H<sub>2</sub>L is diphenylcarbazone and its structure is shown below:

$$0 = C <_{N = N - C_6H_5}^{N = N - C_6H_5}$$

The fitting function of the standard curve obtained from this method is  $A=9.7232\times10^{-4}C$  (*C* is the Cr(VI) concentration, *A* is the absorbance obtained from UV-vis test, which is similar to our previous work<sup>4</sup> and is used to calculate the Cr(VI) concentration in the solution. The

blank in the experiments means that the initial Cr(VI) concentration is 0.0 g L<sup>-1</sup>.



**Figure S1** UV-vis absoprion of 4.0 mg L<sup>-1</sup> different pH Cr(VI) solutions (20.0 mL) with 10.0 mg PNCs after 5 min treatment period at room temperature.







**Figure S3** UV-vis absoprion of 10.0 mg PNCs for 20.0 mL Cr(VI) neutral solutions with different initial Cr(VI) concentrations after 5 min treatment period at room temperature.



**Figure S4** UV-vis absoprion of different PNC doses for 20.0 mL Cr(VI) neutral solution with an initial Cr(VI) concentration of 9.0 mg  $L^{-1}$  after 5 min treatment period at room temperature.



Figure S5 FT-IR spectra of (a) the synthesized and treated PNCs with Cr (VI) solution with a pH value of (b) 1.0, (c) 2.0, (d) 5.0, (e) 9.0 and (f) 11.0, respectively.

#### **Temperature dependent resistivity:**

Figure S6 shows the temperature dependent resistivity of the PNCs before and after treated with Cr(VI) solutions. Generally, the resistivity of the PNCs decreases with increasing temperature, Figure S6A(a), revealing a typical semiconductor behavior in the measured temperature scale.<sup>5</sup> However, the resistivity of the PNCs after treated with Cr(VI) solution increases dramatically and beyond the limit of the equipment when the temperature is lower than 140 K, Figure S6A(b). Even at room temperature, the resistivity of the PNCs has significantly increased from  $6.43 \times 10^2$  to  $1.11 \times 10^4$  ohm.cm after treated with Cr(VI) solution. Typically, the electrical conductivity ( $\sigma$ ) of PANI is highly dependent on its oxidation states.<sup>6,7</sup> For the EB salt form, the  $\sigma$  is about 10<sup>-2</sup> to 10<sup>2</sup> S cm<sup>-1</sup> at room temperature, <sup>8</sup> whereas the fully reduced and fully oxidized forms are insulating.<sup>9</sup> Stejskal *et al.*<sup>10</sup> have reported a non-

conductive protonated pernigraniline (also called PB salt) if stronger oxidizing conditions are employed in the EB form PANI. D'Aprano *et al.*<sup>9</sup> reports on an insulating behavior of the charged "acid-doped" PB salt form of fully oxidized PANI due to a strong localization of the charge carriers. In this study, the PNCs before and after treatment with Cr(VI) are observed to be semi-conductors and the electron transport mechanism is investigated by Mott variable range hopping (also called VRH) approach, representing as Equation (S2):<sup>11,12</sup>

$$\sigma = \sigma_0 \exp[-(\frac{T_0}{T})^{\frac{1}{n+1}}], \quad n=1, 2, 3$$
(S2)

where  $\sigma_0$  represents the conductivity at high temperature limit,  $T_0$  stands for the characteristic Mott temperature, which is the hopping barrier, the energy needed for charge carrier's hopping conduction, and *T* is the Kelvin temperature, the *n* value of 4, 3, and 2 is for three-, two-, and one-dimensional systems, respectively. The observed linear relationship between  $\ln(\sigma)$  and  $T^{1/4}$ , Figure S6B, indicates a quasi 3-d VRH mechanism. The  $T_0$  obtained from the slope of the figure is  $1.97 \times 10^7$  and  $4.10 \times 10^7$  K for the untreated and treated PNC samples, respectively. This indicates a semi-conductive rather than insulating behavior of the PNCs. Generally, the parameter  $T_0$  is inversely proportional to the localization length of the charge carriers,<sup>13</sup> which means the larger  $T_0$  the stronger charge carrier scattering and an increased resistivity. The increased  $T_0$  after treated with Cr(VI) solution means that the  $\sigma$  becomes poorer and there is some EB salt form existed in the treated samples, though the resistivity is increased dramatically after treatment with Cr(VI).



**Figure S6 (A)** Resistivity *vs.* temperature curves; **(B)**  $\ln(\sigma) \sim T^{-1/4}$  curves of **(a)** the synthesized PNCs and **(b)** the PNCs after 5 min treatment with 20.0 mL Cr (VI) solution (pH=1.0; 4.0 mg L<sup>-1</sup>).

### **Kinetics:**

Typically, for a chemical reaction:

$$m \operatorname{A+n} \operatorname{B+p} \operatorname{C} \to \operatorname{D}$$
 (S3)

where A, B and C are the reactants; *m*, *n* and *p* are the corresponding coefficients in the stoichiometric equation; D represents the product. The reaction rate (v) can be obtained from the rate law or rate equation:<sup>14</sup>

$$\upsilon = \frac{\mathrm{d}[D]}{\mathrm{d}t} = -k(T)[A]^m [B]^n [C]^p \tag{S4}$$

where the coefficient k(T) is the rate constant of the reaction and is associated with the temperature (*T*). The units of the rate constant depend on the order of the reaction. The order of the reaction is correlated kinetically to each active component.<sup>15</sup> Usually, the overall reaction order for the Equation (S4) is m+n+p. If the overall order is zero, the reaction is called zero-order reaction, the overall order is one, it's called first-order reaction, *et al.* And if the concentration of one or more kinetically active components is constant (because it's a

catalyst or it's in great excess compared with others.) or nearly constant during the reaction process, then the constant concentration will be included in the rate constant k, so this reaction is called "pseudo-n<sup>th</sup>-order" reaction, and the rate constant is called pseudo rate constant.<sup>15</sup>

### List of Abbreviation

Full name	Abbreviation
Hexavalent chromium	Cr(VI)
Polyaniline	PANI
Polymer nanocomposites	PNCs
Surface initiated polymerization	SIP
Fourier transform infrared spectroscopy	FT-IR
X-ray photoelectron spectroscopy	XPS
Energy-filter Transmission electron microscopy	EFTEM
p-toluene sulfonic acid	PTSA
Hydrochloric acid	HCl
<b>Environmental Protection Agency</b>	EPA
Leucoemeraldine	LEB
Emeraldine	EB
Pernigraniline	PB
Nanoparticle	NP
Saturation magnetization	$M_s$
Ammonium persulfate	APS
Potassium dichromate	$K_2Cr_2O_7$
1,5-diphenylcarbazide	DPC
Phosphoric acid	$H_3PO_4$
Thermo-gravimetric analysis	TGA
Brunauer–Emmett–Teller	BET
Inductively coupled plasma optical emission spectrometry	<b>ICP-OES</b>

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