Electronic Supplementary Material for Chemical Communications

Controllable Synthesis of Graphitic Carbon nanostructures from Ion-Exchange Resin-Iron Complex via Solid-State Pyrolysis Process

Lei Wang, Chungui Tian, Baoli Wang, Ruihong Wang, Wei Zhou and Honggang Fu*

Laboratory of Physical Chemistry, School of Chemistry and Materials Science,

Heilongjiang University,150080 Harbin P. R. China.

Tel. +86-451-86608458; Fax：+86-451-86673647;

E-mail address: fuhg@vip.sina.com

Supporting Information

Experimental:

1. The basic structure of the ion-exchange resins used in the synthesis

The basic structure of commercial polyacrylic weak-base anion-exchange resin (PAWBA) is shown in Fig. S1(a). PAWBA network exists of poly-methyl acrylate chain segments that react with polyethylene polyamine followed by chlorination to get this weak-base anion-exchange resin. The Cl^- ions in this polymer can be exchanged by other anions.

The basic structure of commercial polystyrenic strong-base anion-exchange (PSSBA) is given in Fig. S1(b). PSSBA network exists of polystyrene chain segments that are covalently cross-linked with divinylbenzene. The functional quaternary amidocyanogen groups $-N(CH_3)_3Cl$ are attached to the styrene repeat units. The Cl^- ions in this polymer can be exchanged by other anions.

The basic structure of commercial polyacrylic weak-acid cation-exchange (PAWAC) is displayed in Fig. S1(c). PAWBA framework

is composed with polyarcrylic. The Na^+ connects with carboxyl can be exchanged by other cations.

2. Synthesis of carbon nanocapsules

In a typical synthesis, 10 g PAWBA were mixed with 100 mL of 0.1 mol L^{-1} $K_3[Fe(CN)_6]$ aqueous solution to obtain the corresponding resin derivatives, namely PAWBA-$[Fe(CN)_6]^{3-}$. The carbon nanocapsules were obtained by the following process. First, the PAWBA-$[Fe(CN)_6]^{3-}$ composites were placed in a ceramic boat with the inside diameter of 2.5 cm and length of 5 cm. Then, the quartz boats were placed at the middle of a ceramic tube with the inside diameter of 3 cm and length of 120 cm. N_2 was flowed from one end of the tube. And the exhaust gas that came from the reaction process was poured out from the other end of the tube. Then the tube was heated to different temperature with the heating ratio of 10 ℃·min^{-1} in a horizontal tube furnace over the different course of time. After slow cooling to room temperature, black products appeared in the quartz-boat was obtained.

3. Synthesis of carbon nanoplates and nanosheets

10 g PSSBA and 10 g PAWAC were mixed with 100 mL of 0.1 mol L^{-1} $K_3[Fe(CN)_6]$ and 100 mL of 0.1 mol L^{-1} $FeCl_2$ aqueous solution to get the corresponding derivatives denoted as PSSBA-$[Fe(CN)_6]^{3-}$ and PSSBA-Fe^{2+}, respectively. The carbon nanoplates and nanosheets were obtained by heating treatment of PSSBA-$[Fe(CN)_6]^{3-}$ and PAWAC-Fe^{2+}, respectively. The procedure for synthesizing these carbon nanostructures was same with that for preparation of carbon nanocapsules.

Moreover, the data of carbon material balance are shown in Table S3.

4. Adsorption and Desorption Tests

30 mg of the carbon nanocapsules and 20 mL of Rhodamine B (RhB)

aqueous solution (10 mg L^{-1}) were mixed followed by stirring at room temperature for 15 min. After that, the solid with adsorbed RhB were separated by a magnet (see Fig. S6). The desorption experiment was performed by immersion of the solid into 20 mL ethanol at room temperature under stirring for 20 min. The RhB concentration was determined spectrophotometrically using a model UV-5220 UV-VIS spectrophotometer in matched quartz cells. The amount of RhB in water and ethanol were estimated by a standard spectrophotometric methods at k = 553 and 555 nm, respectively. After two cycles, the products almost keep the same adsorption level (see Table S1). This result indicates that the products have good stability for application as adsorbents.

5. The tests about amount of Fe in the resins and products

After the specific amount of ion-exchange resin was exchanged in the corresponding salt aqueous solution for 24 h, the solution was analyzed by atomic absorption spectrometer (AAS) to measure the amount of exchanged cations (or anions). After carbonization, weight method was used to measure the amount of iron that in the products. The results are listed in the Table S2.

Characterization:

Transmission electron microscopy (TEM) measurements were carried out on a JEOL-3010 transmission electron microscopy at an operating voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were displayed in a Rigaku D/max-IIIB diffractometer (operating at 40 kV and 20 mA,) with a scanning rate of 4° min^{-1} using Cu K_α radiation (λ = 1.5406 Å). Raman spectra were performed on a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. The atomic absorption was measured on Thermo Elemental SOLAAR.

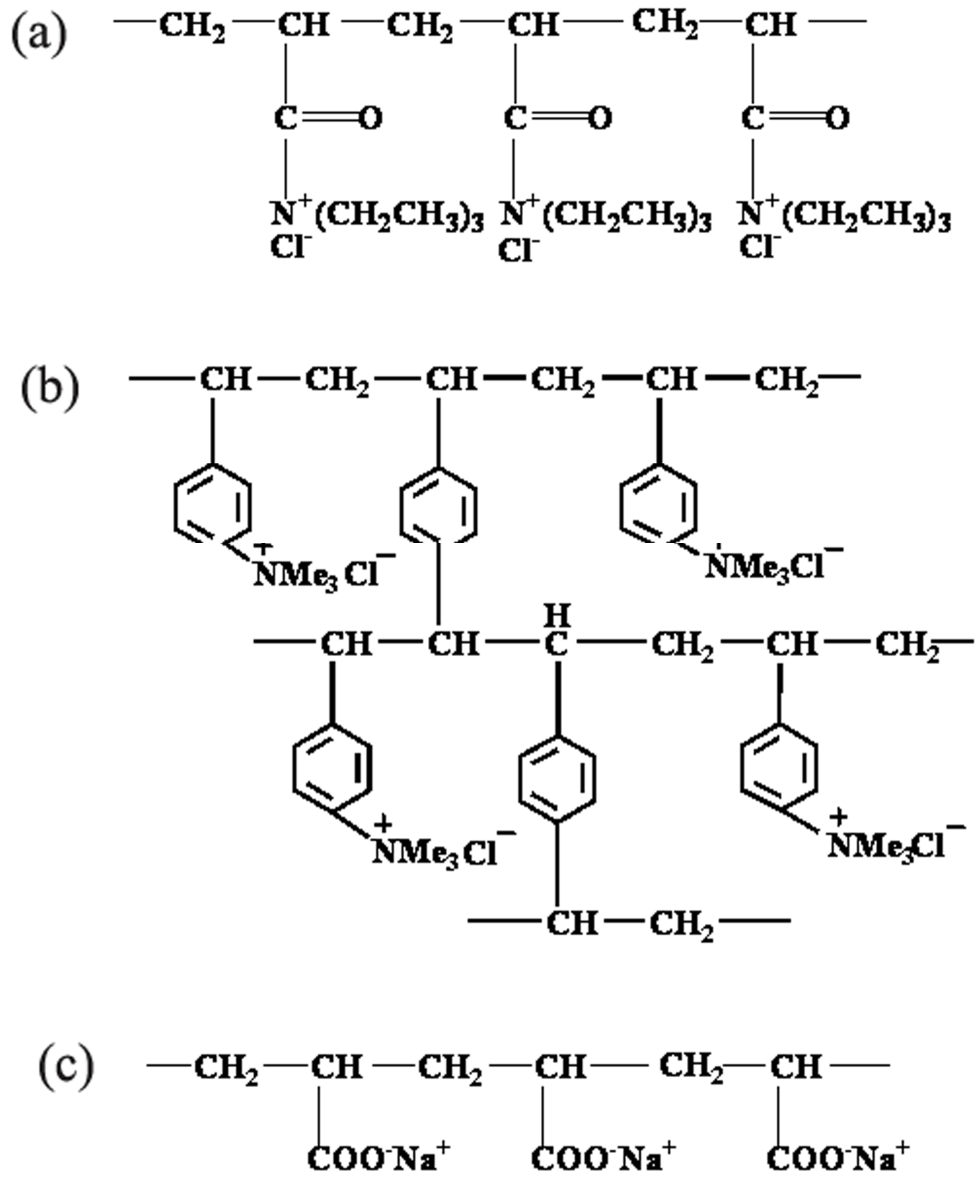

Fig. S1 The structures of ion-exchange resins PAWBA (a), PSSBA (b), PAWAC (c).

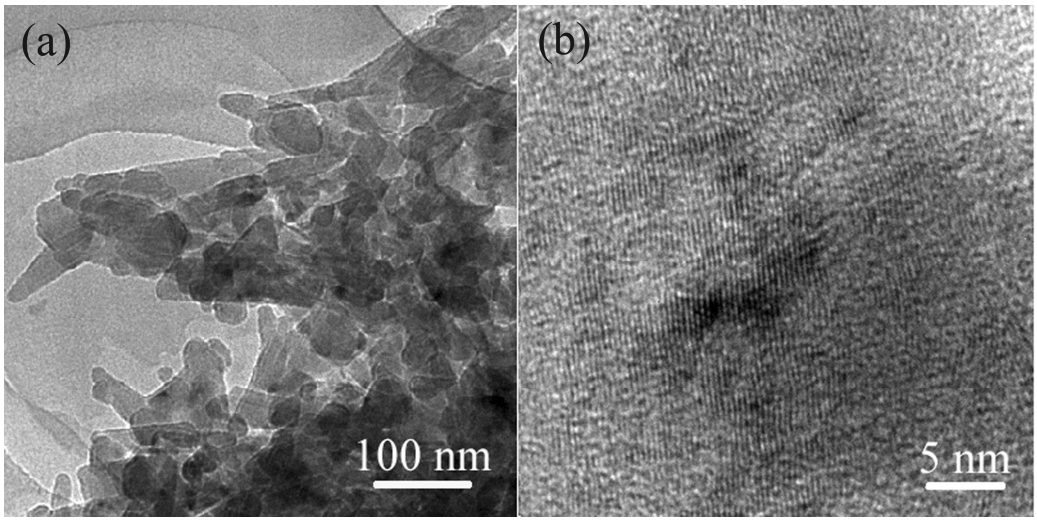

Fig. S2 TEM (a) and HRTEM (b) images of the carbon nanoplates.

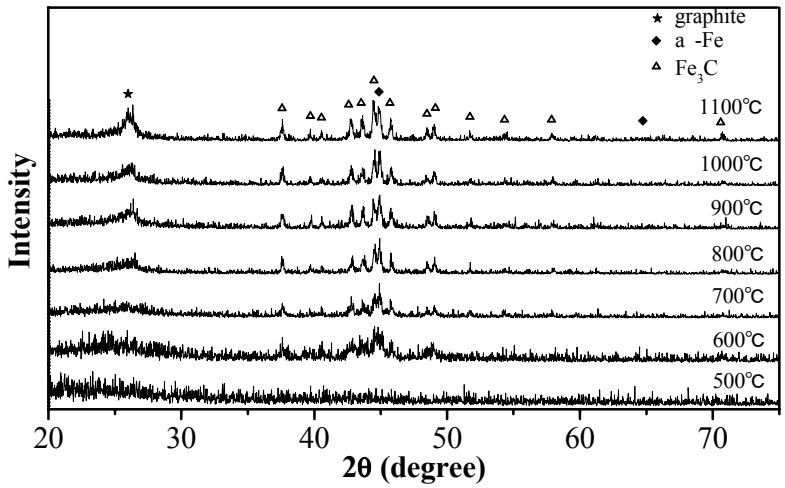

Fig. S3 XRD patterns of the samples derived from PSSBA-$[Fe(CN)_6]^{3-}$ after carbonization at different temperatures.

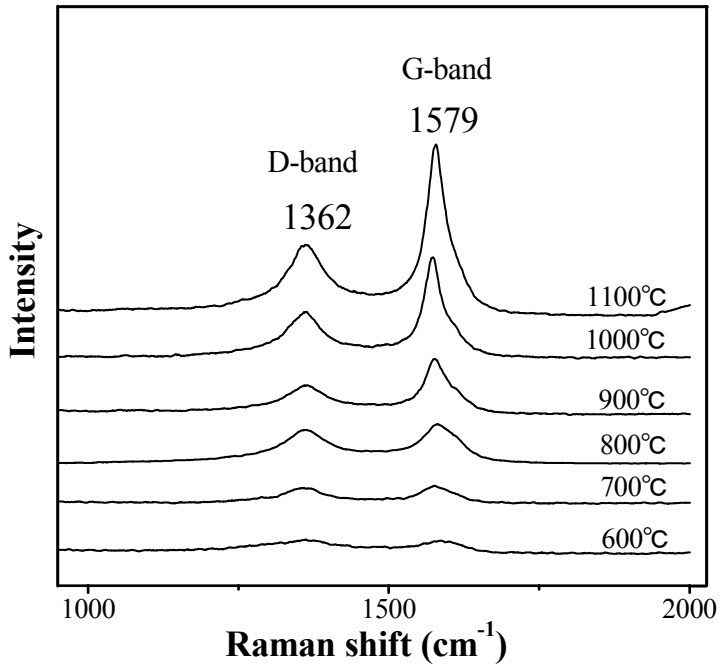

Fig. S4 Raman spectrum of the samples derived from PSSBA-$[Fe(CN)_6]^{3-}$ carbonized at different temperatures.

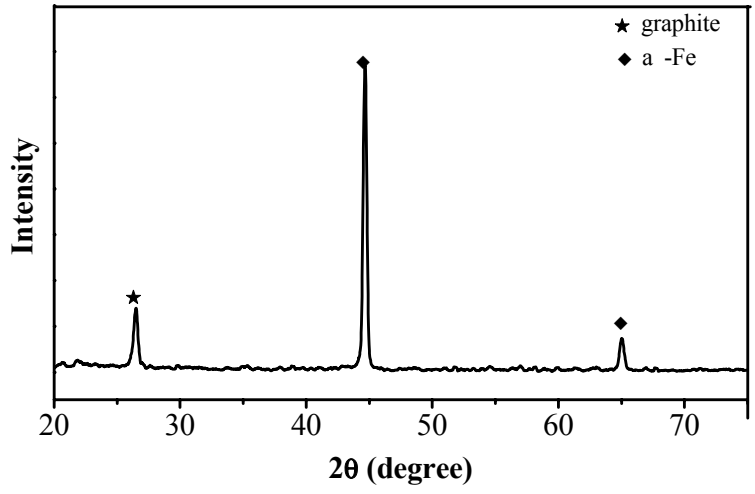

Fig. S5 XRD pattern of the carbon nanosheets.

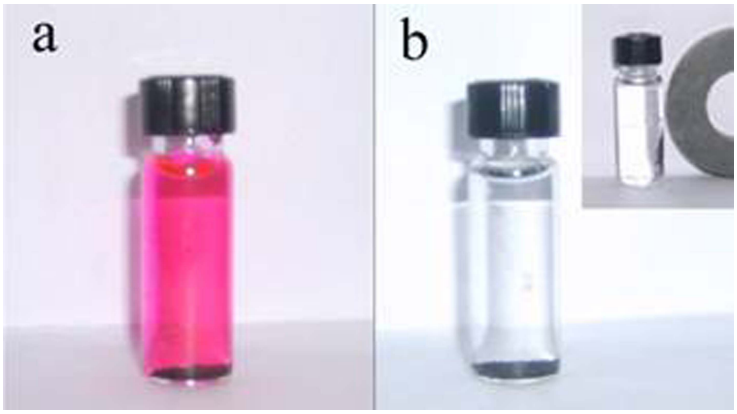

Fig. S6 The photos of the RhB aqueous solution before (a) and after (b) adsorption reaction, respectively. The solids used in here derives from PAWBA-$[Fe(CN)_6]^{3-}$., i.e. carbon capsule-magnetic particles composites.

Table S1 Adsorption and desorption of RhB.

	Adsorption [mg/g]	Desorption [%]
The first time	6.6	93.2
The second time	6.2	91.5

Table S2 The amount of Fe in the resins and products.

Resin Source	The amount of absorbed Fe in the resins (m mol/g)	The content of Fe in the products (%)
PAWBA	1.4	28.1
PSSBA	1.2	25.3
PAWAC	4.1	57.8

Table S3 The data of carbon material balance.

Resin source	The amount of carbon in the original resins-metal ion composites (%)	The conversion of carbon (%)	The require amount of ion-exchange resins for 1 g carbon nanomaterials (g)
PAWBA	42.8	56.0	4.2
PSSBA	67.9	41.3	3.6
PAWAC	23.6	57.3	7.4