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FASILE SYNTHESIS OF MESOPOROUS CARBON COMPOSITES FROM IRON-CONTAINING RESORCINOL-FORMALDEGIDE RESINS

Carbon encapsulated iron nanoparticles are an important class of nanomaterials because of their interesting size-dependent properties and plentiful application potential in a wide range of technologies, including magnetic data storage, magnetic separation, catalysis, ferro-fluids, biomedicine, etc.

In the present study, we investigated the development of carbon nanocomposites via carbonization of resorcinol–formaldehyde resin/Fe compounds. The Fe-polymer precursors were prepared using 5 g resorcinol, 7.5 g formaldehyde (37 % aqueous solution) and 2 g $Fe(C_5H_7O_2)_2$ (sample was denoted as RF-$Fe(ac)_2$) or 4.5 g of $Fe(C_5H_7O_2)_3$ (denoted as RF-$Fe(ac)_3$) using aqueous alcoholic solution (12.5 ml H_2O:12.5 ml Isopropanol) via sol–gel method. Then they were dried at room temperature, ground and dried at 90 °C for 10 h. Carbonization of the samples was carried out in a tubular furnace under argon atmosphere upon heating from room temperature to 800 °C at a heating rate of 5 °C/min and kept at the maximum temperature for 2 h. The effects of the starting composition on the textural and structural characteristics of the Fe-containing carbon composites are discussed. Such composite materials were characterized by N_2 sorption, Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM).

In order to determine the crystal structure and the phases of the particles, the as-made metal particles were analyzed by the XRD of Co K_α radiation. Figure 1a shows the patterns of an iron particle sample. Note that three phases were identified. One is bcc α-Fe, another is fcc γ-Fe, and the carbide phase was found. In addition, an intensive diffraction peak at 2θ=30.55° observed on the XRD patterns that attributed to graphite plane (002). Since most carbides of ferromagnetic materials are either nonmagnetic or weakly magnetic, it is desirable to further develop this process where the elemental metal nanoparticles are carbon-coated without the formation of any carbides.

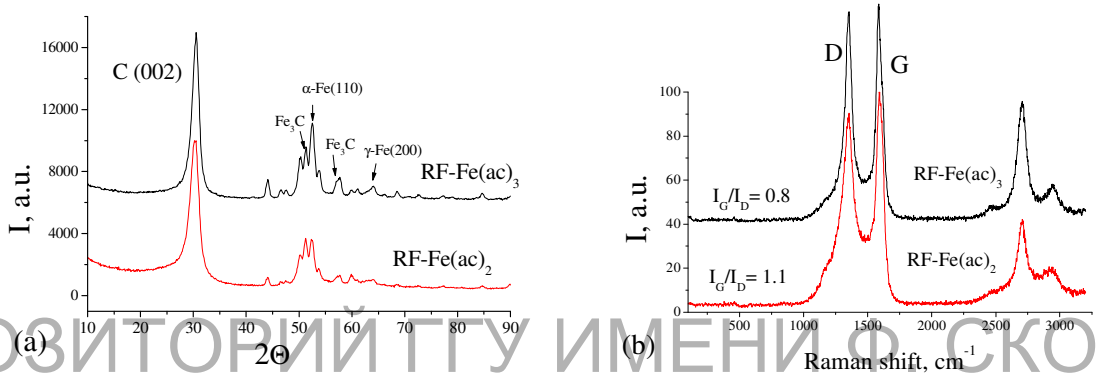

Figure 1 – XRD patterns of chars (a) and Raman spectra of Fe/C nanocomposites (b)

The crystallinity of the carbon was further examined by Raman characterization technique (Fig. 2b). The spectra show distinct D bands (1350 cm^{-1}) and G (1600 cm^{-1}), which are well-known characteristics of graphitic materials. The intensity ratio of these bands (I_G/I_D) is higher in the RF-$Fe(ac)_2$ sample that demonstrates that the overall crystallinity of carbon has enhanced during the process. The high intensity of the G band shows that the amount of graphitized and well-organized carbon exceeds the amount of amorphous and disordered carbon in our samples, enabling their functionalization. Besides, both samples have a distinct 2D (2700 cm^{-1}) band (Fig. 1b), which indicates very good crystallinity of the material.

Figure 2 shows SEM images of Fe-doped chars. Note that the as-made materials consist of only dense agglomerates of irregular shapes without any additional carbon formations.

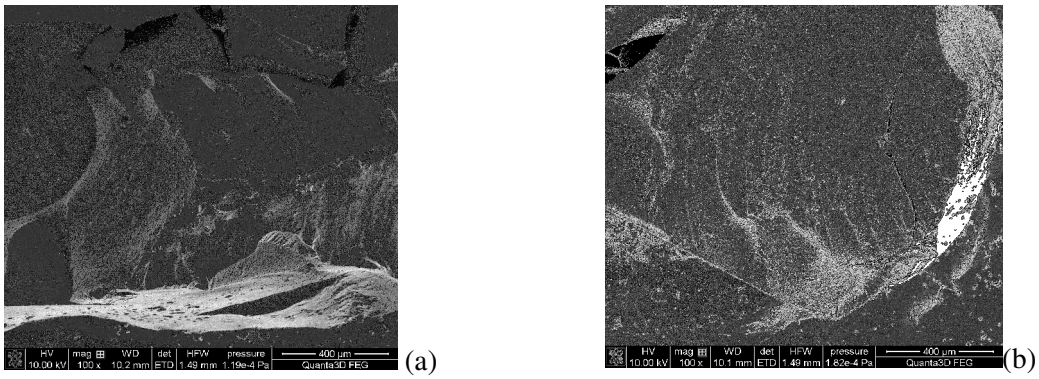

Figure 2 – SEM images of the RF-$Fe(ac)_3$ (a) and RF-$Fe(ac)_2$ (b)

The pore structures of the samples were analyzed based on the low-temperature nitrogen adsorption. The Me@C samples exhibited the type IV isotherms (H2 type of hysteresis loops) (Fig. 3)

according to IUPAC classification. Capillary condensation occurs in the relative wide range of pressure at p/p_0 = 0.45–1.0 indicating a mesoporous character of the materials and the almost complete absence of microspores is observed (i.e. carbon phase is morphologically similar to soot). According to the pore size distributions, the main contribution into the textural porosity of the Fe/C nanocomposites is due to mesopores (Table 1, S_{meso} and V_{meso} at 1 < R < 25 nm). The specific surface area of the nanocomposites is 320.6 and 173.2 m^2/g for RF-Fe(acac)$_2$ and RF-Fe(acac)$_3$, respectively.

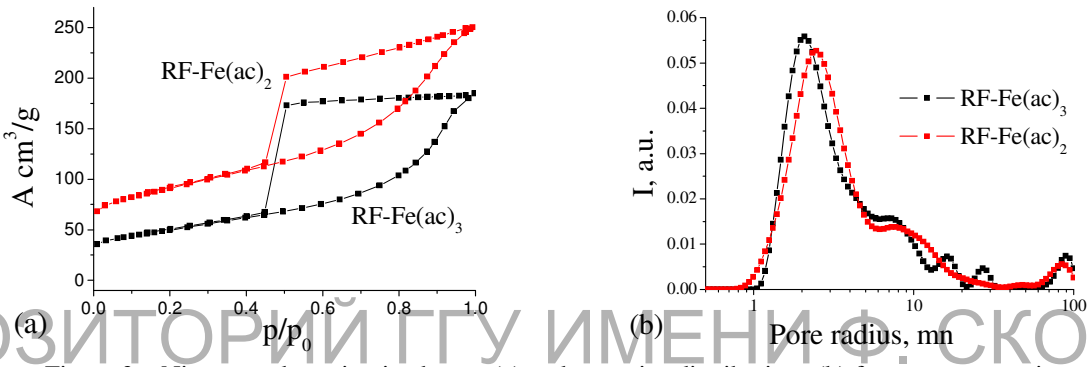

Figure 3 – Nitrogen adsorption isotherms (a) and pore size distributions (b) for nano-composites

Table 1 – Textural characteristics of Fe-doped chars

Sample	S_{BET}, m^2/g	S_{micr}, m^2/g	S_{meso}, m^2/g	S_{macr}, m^2/g	V_p, cm^3/g	V_{micr}, cm^3/g	V_{meso}, cm^3/g	V_{macro}, cm^3/g	Δw
RF-Fe(acac)$_2$	320.6	0	320.0	0.6	1.157	0.01	1.101	0.046	0.13
RF-Fe(acac)$_3$	173.2	0	172.9	0.3	1.166	0.01	1.105	0.051	0.46

Note: Nanopores (S_{nano}, V_{nano}) at radius or half-width R < 1 nm, mesopores (S_{meso}, V_{meso}) at 1 nm < R < 25 nm, and macropores (S_{macro}, V_{macro}) at 25 nm < R < 100 nm; Δw is a criterion showing the deviation of the pore model from the real pore in respect to the specific surface area.

Iron-doped carbon composites were synthesized by a simple one-pot procedure through carbonization of resorcinol-formaldehyde polymers containing Iron(II)- or Iron(III) acetylacetonate. The structural and textural characteristics of the as-made materials were investigated. The XRD results indicate that all chars consist of several phases, namely, iron, carbon, and metal carbides. Raman spectroscopy analysis detected the highly ordered graphitic nature of the carbon.

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