

# Anthranilic Acid Assisted Preparation of Fe<sub>3</sub>O<sub>4</sub>-Poly(aniline-co-o-anthranilic acid) Nanoparticles

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**ABSTRACT:** Magnetic Fe<sub>3</sub>O<sub>4</sub>-poly(aniline-co-o-anthranilic acid) nanoparticles were prepared by a novel and simple method: anthranilic acid assisted polymerization. The synthetic strategy involved two steps. First, Fe<sub>3</sub>O<sub>4</sub> nanoparticles capped by anthranilic acid were obtained by a chemical precipitation method, and then the aniline and oxidant were added to the modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles to prepare well-dispersed Fe<sub>3</sub>O<sub>4</sub>-poly(aniline-co-o-anthranilic acid) nanoparticles. Fe<sub>3</sub>O<sub>4</sub>-poly(aniline-co-o-anthranilic acid) nanoparticles exhibited a superparamagnetic behavior (i.e., no hysteresis loop) and high-saturated magnetization ( $M_s = 21.5$

emu/g). The structure of the composite was characterized by Fourier-transform infrared spectra, X-ray powder diffraction patterns, and transmission electron microscopy, which proved that the Fe<sub>3</sub>O<sub>4</sub>-poly(aniline-co-o-anthranilic acid) nanoparticles were about 20 nm. Moreover, the thermal properties of the composite were evaluated by thermogravimetric analysis, and it showed excellent thermal stability. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1666–1671, 2006

**Key words:** anthranilic acid; Fe<sub>3</sub>O<sub>4</sub>; poly(aniline-co-o-anthranilic acid)

## INTRODUCTION

Polyaniline (PANI) is one of the most frequently investigated semiconducting polymers potential for advanced applications such as organic lightweight batteries, electrochromic displays, electroluminescent, biosensor and chemical sensors<sup>1–6</sup> because of its excellent environmental stability, easy synthesis, and reversible acid/base doping/dedoping chemistry;<sup>7–13</sup> but it is sometimes limited in practical applications by its intractable nature due to its insolubility in any known solvent and the film's high brittleness when free standing. A lot of work has been done to overcome this problem by polymerization of aniline derivatives<sup>14–20</sup> with alkyl,<sup>18,20</sup> sulfonic acid group,<sup>14,16,17</sup> or carboxyl group<sup>15</sup> substitution. Some substituted or copolymerized PANI polymers become soluble in solvents such as *N*-methylpyrrolidone or dimethylformamide.<sup>14,18</sup> In addition, with carboxyl groups existing in its backbone, this functional copolymer may act as

a matrix for immobilization of cationic species in solutions at certain pH values, e.g., proteins, enzymes, and metal ions. The intrinsic advantage of using such copolymer-based anionic materials as immobilization matrices is their load-adjustable nature as a result of increasing or decreasing their ionic sites and thus their electrostatic affinity simply by modulating the molar ratio of the monomers in the copolymerization bath. It is therefore of availability to synthesize poly(aniline-co-o-anthranilic acid).

In recent years, there has been increased interest in nanostructures of the conducting polymers, such as nanospheres,<sup>21</sup> nanotubes,<sup>22</sup> nanowires,<sup>23</sup> and nanoparticles,<sup>24</sup> mainly because they will have the advantages of both low-dimensional system and organic conductors.<sup>25</sup> In addition, the multifunctionalized PANI nanostructures have also been synthesized by blending with inorganic electrical, optical, and magnetic nanoparticles to form composite nanostructures.<sup>24,26</sup> Among those inorganic nanoparticles, Fe<sub>3</sub>O<sub>4</sub> nanoparticles have received great attention because of their unique magnetic properties.

Recently, composites of PANI containing Fe<sub>3</sub>O<sub>4</sub> nanoparticles have attracted considerable attention for use in electromagnetic interference shielding,<sup>27</sup> electrochromic device,<sup>28</sup> and nonlinear optical systems.<sup>29</sup> And the preparation of Fe<sub>3</sub>O<sub>4</sub>-PANI composite has been mostly studied through several ways. Nanostructures of Fe<sub>3</sub>O<sub>4</sub>-PANI composite were obtained by a self-assembling process in the presence of  $\beta$ -naphthalene sulfonic acid (NSA) as a dopant.<sup>24</sup> Magnetic

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and conductive Fe<sub>3</sub>O<sub>4</sub>-PANI nanoparticles with core-shell structure have also been synthesized by Deng et al.<sup>30</sup> Recently, we have also synthesized core-shell Fe<sub>3</sub>O<sub>4</sub>-PANI nanoparticles by aniline dimmer-COOH assistance.<sup>31</sup>

In this study, we prepared magnetic Fe<sub>3</sub>O<sub>4</sub>-poly(aniline-*co-o*-anthranilic acid) nanoparticles by a novel and simple method: anthranilic acid assisted polymerization. Firstly, the Fe<sub>3</sub>O<sub>4</sub> capped by anthranilic acid was obtained by a chemical precipitation method, and then the aniline and oxidant were added to the modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles to prepare well-dispersed Fe<sub>3</sub>O<sub>4</sub>-poly(aniline-*co-o*-anthranilic acid) nanoparticles. Furthermore, the size, structure, and properties of the modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles and resultant composite were characterized by transmission electron microscopic (TEM), Fourier transform infrared (FTIR), X-ray diffraction (XRD) analysis, and so on.

## EXPERIMENTAL

### Materials

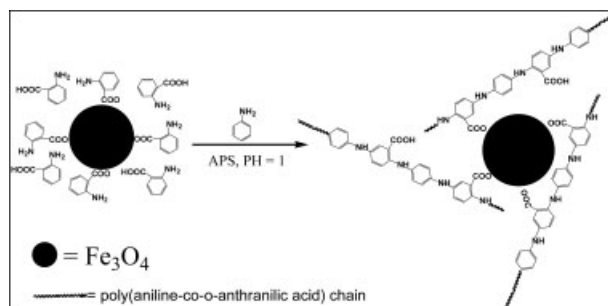
Aniline monomer was distilled under reduced pressure and stored below 0°C. All the other reagents were analytical grade, and used as received without further purification, including anthranilic acid, *N,N'*-dimethylformamide (DMF), ammonium persulfate (APS), FeCl<sub>2</sub> · 4H<sub>2</sub>O, FeCl<sub>3</sub> · 6H<sub>2</sub>O, NH<sub>3</sub> · H<sub>2</sub>O, hydrochloric acid (HCl), and ethanol. Distilled and deionized water was used.

### Synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles capped by anthranilic acid

FeCl<sub>2</sub> · 4H<sub>2</sub>O (0.86 g) and FeCl<sub>3</sub> · 6H<sub>2</sub>O (2.35 g) were dissolved under N<sub>2</sub> in distilled and deionized water (20 mL) under vigorous stirring. As the solution was heated to 60°C, 5 mL NH<sub>3</sub> · H<sub>2</sub>O (28% (w/w)) was added, quickly followed by addition of a solution of anthranilic acid (0.5891 g in 2 mL of ethanol). And the resultant solution was allowed to proceed for 0.5 h at 80°C with constant and vigorous stirring to produce a stable, water-based suspension. (To test the structure and properties of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles capped by anthranilic acid, the resulting mixture was subsequently washed with distilled water and ethanol for several times respectively, and dried under dynamic vacuum at room temperature for 24 h.)

### Synthesis of Fe<sub>3</sub>O<sub>4</sub>-poly(aniline-*co-o*-anthranilic acid) nanoparticles

The suspension of Fe<sub>3</sub>O<sub>4</sub> nanoparticles capped by anthranilic acid was transferred into a 250-mL beaker with stirring at 0–5°C. When the suspension was adjusted to 80 mL and pH = 1 by adding distilled water



**Figure 1** Synthesis of Fe<sub>3</sub>O<sub>4</sub>-poly(aniline-*co-o*-anthranilic acid) nanoparticles by anthranilic acid assisted polymerization.

and dilute hydrochloric acid, aniline (0.4 mL) was added to the above suspension. One minute later, a solution 1.96 g APS in 40 mL 0.1M HCl solution was added to the mixture quickly. After the addition, the resulted solution reacted for another 6 h. During the polymerization, the Fe<sub>3</sub>O<sub>4</sub>-poly(aniline-*co-o*-anthranilic acid) nanoparticles were formed as illustrated in Figure 1. Then the mixture was filtered using a Buchner funnel and water aspirator, and the filter cake was washed with distilled water and ethanol for several times, followed by drying under dynamic vacuum at 40°C for 24 h.

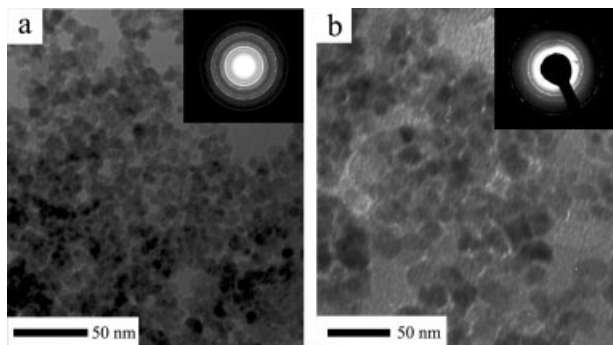
### Characterization

FTIR spectra of KBr powder-pressed pellets were recorded on a BRUKER VECTOR22 spectrometer. UV-vis spectra of Fe<sub>3</sub>O<sub>4</sub> nanoparticles capped with anthranilic acid were performed on UV-2501 PC Spectrometer (Shimadzu) in DMF. Elemental analysis by energy dispersive X-ray (EDX) analysis was done using a scanning electron microscope (SEM, Shimadzu, super-scan SSX-550) coupled to an X-ray detector for EDX analysis. X-ray powder diffraction (XRD) patterns of the product were recorded on a Rigaku D/max 2500/PC powder diffractometer with Cu K $\alpha$  radiation using a tube voltage and current of 40 kV and 200 mA, respectively. TEM experiments were performed on a JEM-3010F electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. The room-temperature magnetization in an applied magnetic field was performed by model JDM-13 vibrating sample magnetometer. A Perkin-Elmer PYRIS 1 TGA was used to investigate the thermal stability of the Fe<sub>3</sub>O<sub>4</sub>-poly(aniline-*co-o*-anthranilic acid) composite in the temperature range from 50 to 900°C under nitrogen protection.

## RESULTS AND DISCUSSION

### Structure, morphology, and properties of Fe<sub>3</sub>O<sub>4</sub> nanoparticles capped with anthranilic acid

The morphology of Fe<sub>3</sub>O<sub>4</sub> nanoparticles capped by anthranilic acid was examined with a transmission



**Figure 2** TEM image of (a)  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid and (b)  $\text{Fe}_3\text{O}_4$ -poly(aniline-co-o-anthranilic acid) nanoparticles synthesized by anthranilic acid assisted polymerization.

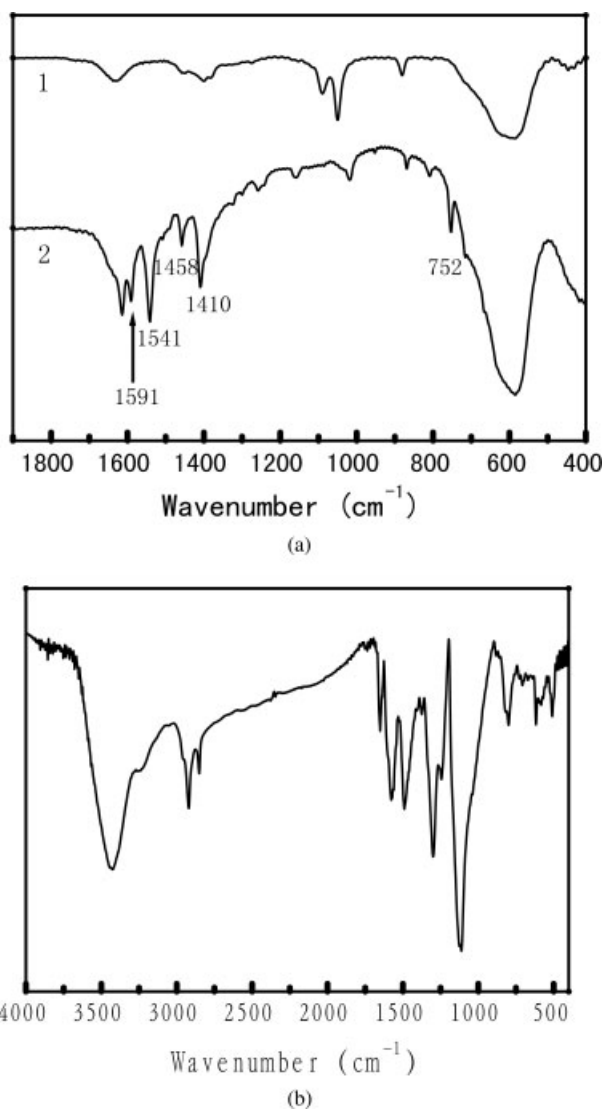
electron microscope (TEM). Figure 2(a) shows the TEM micrograph of  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid. The particles were almost spherical with diameters of about 10 nm. Most of these particles formed aggregates because of the interactions between  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid. The driving forces for the formation of aggregates were considered to be hydrogen bonding, and  $\pi$ - $\pi$  interactions (between the molecules of anthranilic acid). The electron diffraction pattern indicates that the nanoparticles are face centered cubic  $\text{Fe}_3\text{O}_4$  with (220), (311), (400), (422), (511), and (440) planes, the same as that of the pure  $\text{Fe}_3\text{O}_4$ .

The FTIR spectra of  $\text{Fe}_3\text{O}_4$  nanoparticles with and without anthranilic acid assistance are shown in the Figure 3(a). Compared with  $\text{Fe}_3\text{O}_4$  nanoparticles without anthranilic acid, new peaks appear at 752, 1410, 1458, 1541, and 1591  $\text{cm}^{-1}$ . The peak at 752  $\text{cm}^{-1}$  can be assigned to the out-of-plane bending of C—H in the 1,4-disubstituted benzenoid rings. The peaks at 1458, 1541  $\text{cm}^{-1}$  can be assigned to the stretching vibration of benzene rings. And the peaks at 1410 and 1591  $\text{cm}^{-1}$  are the characteristic peaks of carboxyl group salt form. This indicates the presence of the anthranilate around the  $\text{Fe}_3\text{O}_4$  nanoparticles. The UV-vis spectra of  $\text{Fe}_3\text{O}_4$  nanoparticles with and without anthranilic acid assistance are shown in the Figure 4. Compared with  $\text{Fe}_3\text{O}_4$  nanoparticles without anthranilic acid, new absorption appears at 336 nm in the  $\text{Fe}_3\text{O}_4$  nanoparticles with anthranilic acid assistance, which is associated with a  $\pi$ - $\pi^*$  electronic transition of the benzenoid ring<sup>32</sup> of anthranilic acid. The characteristic EDX elemental analytical data represented in Figure 5 demonstrate the presence of C, N, O, and Fe, supporting the formation of  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid. Since the samples of  $\text{Fe}_3\text{O}_4$  nanoparticles capped with anthranilic acid were washed repeatedly with ethanol which can dissolve anthranilic acid completely, all of the above data strongly indicate that there are some interactions between  $\text{Fe}_3\text{O}_4$  nanoparticles and anthranilic acid.

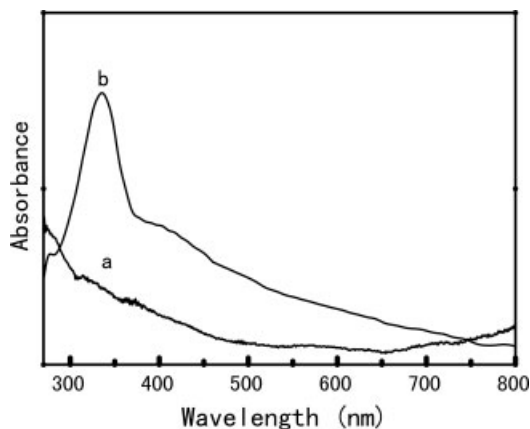
The XRD patterns of  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid are shown in Figure 6(a). The diffraction peaks of the  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid were measured to be  $2\theta = 30.20, 35.46, 43.14, 53.42, 57.24, \text{ and } 62.72^\circ$ , which can be assigned (220), (311), (400), (422), (511), and (440). These data are in good agreement with that of  $\text{Fe}_3\text{O}_4$ .<sup>33</sup> According to Scherrer's<sup>34</sup> equation:

$$\beta = k\lambda D \cos \theta$$

where  $\lambda$  is the X-ray wavelength;  $k$ , the shape factor;  $D$ , the average diameter of the crystals in angstrom;  $\theta$ , the Bragg angle in degree; and  $\beta$  is the line broadening measured by half-height in radian. The value of  $k$  depends on several factors, including the miller index of the reflecting plane and the shape of the crystal. If



**Figure 3** FTIR spectra of (a) (1)  $\text{Fe}_3\text{O}_4$  nanoparticles and (2)  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid, and (b)  $\text{Fe}_3\text{O}_4$ -poly(aniline-co-o-anthranilic acid) nanoparticles.



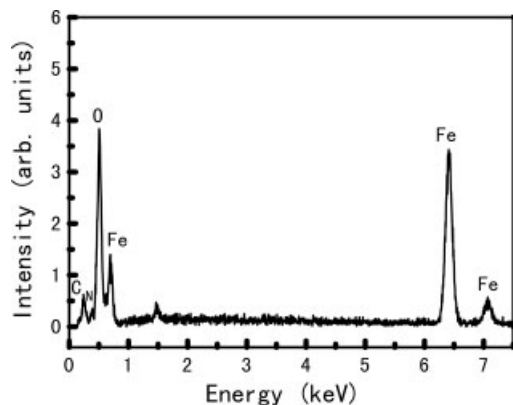
**Figure 4** UV-vis spectra of (a)  $\text{Fe}_3\text{O}_4$  nanoparticles and (b)  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid.

the shape is unknown,  $k$  is often assigned a value of 0.89. When the reflecting peak at  $2\theta = 62.72^\circ$  is chosen to calculate the average diameter, the average size of the  $\text{Fe}_3\text{O}_4$  is about 9.5 nm, which is consistent with the results of TEM.

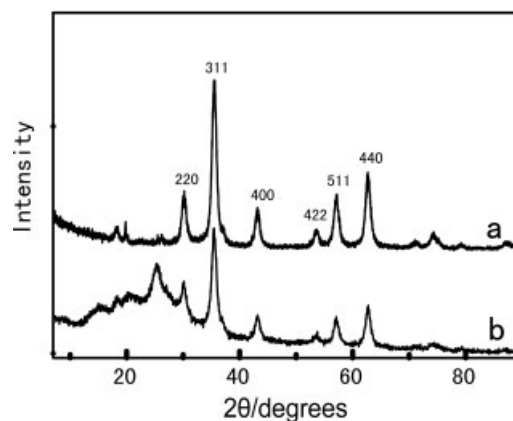
The magnetic properties of  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid were investigated using a vibrating sample magnetometer. Typical magnetization curve as a function of applied field at room temperature (298 K) is shown in Figure 7. There is no pronounced hysteresis loop, which indicates that both the retentivity and the coercivity of the particles are zero. This observation is consistent with superparamagnetic behavior.

#### Structure, morphology and properties of $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) nanoparticles

Figure 2(b) shows the TEM micrograph of  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) composite. We can see that most of the resulting  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) composite is in the form of nanopar-



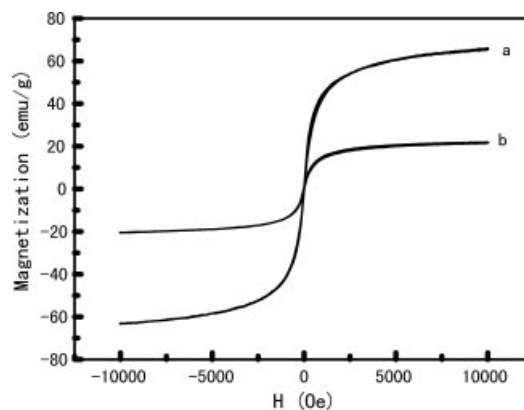
**Figure 5** EDX elemental analysis for  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid.



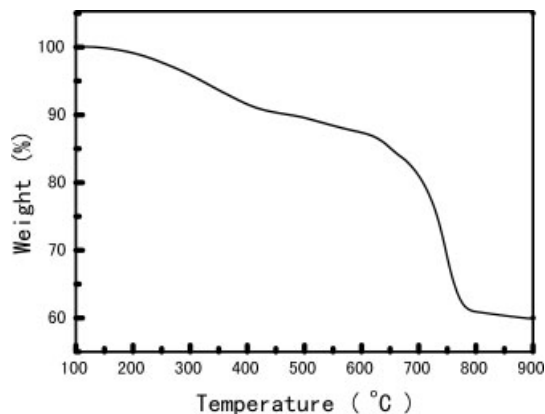
**Figure 6** XRD scattering patterns of (a)  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid and (b)  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) nanoparticles.

ticles with diameter about 20 nm, which was bigger than that of  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid. It indicates that the polymerization of anthranilic acid and aniline is carried out on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid. In addition, TEM image proves that there is no apparent aggregation among the  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) nanoparticles, which indicates that the  $\text{Fe}_3\text{O}_4$  nanoparticles are well dispersed with the anthranilic acid assistance. The electron diffraction pattern of the  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) nanoparticles is similar to that of the pure  $\text{Fe}_3\text{O}_4$ .

The molecular structure of resulting  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) nanoparticles was characterized by FTIR spectroscopy [Fig. 3(b)] and XRD. The main peak at  $3425\text{ cm}^{-1}$  is attributed to N—H stretch vibration. The peaks at  $2920$  and  $2850\text{ cm}^{-1}$  can be assigned to the O—H stretch vibration. The peaks at  $1651\text{ cm}^{-1}$  corresponds to the C=O stretch vibration.



**Figure 7** Magnetization versus applied magnetic field at room temperature for (a)  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid and (b)  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) nanoparticles.



**Figure 8** TGA thermograms of  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) nanoparticles in  $\text{N}_2$ .

The peaks at  $1577$  and  $1491\text{ cm}^{-1}$  can be assigned to the stretching vibration of a quinone and benzene rings, respectively. The peak at  $1300\text{ cm}^{-1}$  is attributed to C—N stretching vibration of a secondary aromatic amine. The peak at  $1111\text{ cm}^{-1}$  is from the N=Q=N (Q is quinoid ring) stretching mode. The out-of-plane bending of C—H in the 1,4-disubstituted benzene ring is reflected in the  $798\text{ cm}^{-1}$  peak.

Figure 6(b) shows the XRD pattern of the  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) nanoparticles. The main peaks are at  $2\theta = 30.15, 35.45, 43.20, 53.50, 57.10,$  and  $62.75^\circ$ , which is in good agreement with the XRD peaks of pure  $\text{Fe}_3\text{O}_4$ <sup>33</sup> and  $\text{Fe}_3\text{O}_4$  nanoparticles capped by anthranilic acid. However, a broad peak centered at about  $25^\circ$  is observed in the Figure 6(b), which is the characteristic peaks of the diffraction by poly(aniline-*co-o*-anthranilic acid).

Figure 7(b) shows the dependence of the magnetization on the applied magnetic fields for  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) nanoparticles at room temperature. The saturated magnetization ( $M_s$ ), remnant magnetization ( $M_r$ ) and coercive force ( $H_c$ ) are estimated to be  $M_s = 21.5\text{ emu/g}$ ,  $M_r = 0$ , and  $H_c = 0$ , respectively. No hysteresis loop (i.e.,  $M_r = 0$  and  $H_c = 0$ ) is observed, indicating a superparamagnetic behavior. This superparamagnetic behavior is similar to that of  $\text{Fe}_3\text{O}_4$  nanoparticles. Thus, it is reasonable to believe that the  $\text{Fe}_3\text{O}_4$  nanoparticles in the  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) composite contribute to the superparamagnetic behavior.

A Perkin-Elmer PYR1 TGA was used to investigate the thermal stability of the  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) composite in the temperature range from  $50$  to  $900^\circ\text{C}$  under  $\text{N}_2$ . Firstly, the sample was heated from  $50$  to  $120^\circ\text{C}$ , and maintained at  $120^\circ\text{C}$  for  $10\text{ min}$  to evaporate the residual solvent, and then cooled to  $100^\circ\text{C}$  at a rate of  $20.0^\circ\text{C min}^{-1}$ , then heated again to  $800^\circ\text{C}$  at a rate of  $10.0^\circ\text{C min}^{-1}$ . The first weight loss ranging from  $160$  to  $450^\circ\text{C}$  is believed to be

due to the elimination of acid dopant ( $\text{HCl}$ ),<sup>35</sup> —COOH groups, —COO<sup>−</sup> groups,<sup>36</sup> and oligomers.<sup>37</sup> The subsequent weight loss ranging from  $600$  to  $800^\circ\text{C}$  is assigned to the thermal decomposition of PANI backbone chains,<sup>38</sup> which is more higher than that of PANI.<sup>37</sup> The TGA results of the composite show that the  $\text{Fe}_3\text{O}_4$  nanoparticles can improve the thermal stability of the poly(aniline-*co-o*-anthranilic acid).

## CONCLUSIONS

A novel and simple method was used to prepare well-dispersed  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) nanoparticles. The structure and morphology of the composite was characterized by FTIR, XRD, and TEM, which indicated that the  $\text{Fe}_3\text{O}_4$ -poly(aniline-*co-o*-anthranilic acid) nanoparticles were about  $20\text{ nm}$  and well dispersed. Furthermore, it was proved that the obtained composite possesses the superparamagnetic behavior and excellent thermal stability.

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