

# Hydrothermal Synthesis of Leaf-shaped Ferric Oxide Particles onto Multi-walled Carbon Nanotubes (MWCNTs) and Its Catalysis for the Electrooxidation of Ascorbic Acid

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Ferric oxides, hydrothermally prepared from potassium ferricyanide ( $K_3Fe(CN)_6$ ), were artificially immobilized onto multi-walled carbon nanotubes (MWCNTs) to catalyze the electrooxidation of ascorbic acid (AA). Images of SEM (scanning electron microscopy) revealed that the obtained ferric oxide particles were leaf-shaped particles, as has never been reported so far. Results obtained from EDS (electron diffraction spectroscopy) and XRD (X-ray diffraction) demonstrated that iron element exists in the produced particles and the prepared ferric oxide particles are  $\alpha$ - $Fe_2O_3$  rather than other types of ferric oxides. The catalysis of ferric oxides-coated MWCNTs for the electrooxidation of ascorbic acid (AA) was detected by cyclic voltammetry (CV), and enhanced oxidation peak current of AA was observed on a ferric oxides/MWCNTs ( $Fe_2O_3$ /MWCNTs)-modified graphite electrode when compared to the oxidation peak current of AA on a MWCNTs-modified graphite electrode, which strongly supported the proposition developed by Professor R.G. Compton. FT-IR spectra indicated that there are some interactions between ascorbic acid and ferric oxides, which probably is beneficial to the electrooxidation of ascorbic acid.

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**Keywords:** Ferric oxides; Potassium ferricyanide; Multi-walled carbon nanotubes(MWCNTs); Ascorbic acid

## 1. INTRODUCTION

Since the simple preparation technique of carbon nanotubes (CNTs) was developed by Iijima [1], many research works on CNTs were carried out with an intention to explore the novel application of CNTs. Generally, CNTs are grouped as single-walled CNTs, denoted as SWCNTs, consisting of a single tube of "rolled up" graphite sheet, and multi-walled CNTs, assigned as MWCNTs, having several concentric tubes of graphite fitted one inside the other. Till now, many advantages of CNTs

have been exhibited. Of them, electrocatalysis for the electrochemical process is thought to be the main contribution of CNTs when used in electrochemistry [2]. But for its catalysis mechanism, several explanations are proposed, for example, the modification of CNTs could augment the electrode surface[3], behaving like a metallic conductor that allows CNTs to increase the conductivity between electrolyte and electrode[4], “defects” on CNTs should be responsible for its electrocatalysis for the electron transfer process[5]. Recently, Professor Compton[6] proposed two mechanisms to interpret the catalysis of CNTs: one is the defects existing on CNTs; the other is the metal element wrapped in CNTs. These two inconsistent propositions intrigued us to keep on probing the catalysis of CNTs, here, MWCNTs were employed.

Iron oxides, as the main superparamagnetic material, can offer a great potential applications in different fields such as ferrofluids, color imaging, magnetic refrigeration, detoxification of biological fluids, magnetically controlled transport of anti-cancer drugs, magnetic resonance imaging and magnetic cell separation[7], therefore, many methods were developed to prepare iron oxides, such as electron beam deposition[8], sputter deposition[9], alkaline treatments[10], electrochemical deposition[11]. Among these developed methods, thermal decomposition route [12] is the frequently selected method due to its simple manipulation. Hydrothermal treatment of iron salt could generate iron oxides when the applied conditions are appropriate, for example, Wang group reported the synthesis and magnetic properties of  $\text{Fe}_3\text{O}_4$  in which  $\text{Fe}(\text{CN})_3 \cdot 9\text{H}_2\text{O}$  was utilized as the iron-contained precursor[13]. Professor Musić discussed the effects of urotropin on the chemical and microstructural properties of Fe-oxide powders prepared by the hydrolysis of aqueous  $\text{FeCl}_3$  solutions [14]. Obviously, the doped iron element in CNTs should exist in the form of iron oxides, thus, preparing ferric oxide is the first step in this work. To the best of our knowledge, till now, there is no paper reporting the preparation of iron oxide through the hydrothermal process of ferricyanide.

The key roles of ascorbic acid (AA) in biological bodies[15] has induced extensive research on itself, among these researches, developing a rapid method to determine the concentration of AA in biological systems was regarded as the main work in electrochemistry. Howbeit, on the conventional electrodes, the oxidation of AA showed poor reproducibility, low selectivity and sensitivity, thus, much interest focused on the utilization of mediators and modified electrodes to catalyze the oxidation of AA. For instance, Zhang described the electrocatalytic oxidation of AA on a polyaniline film synthesized in the presence of  $\beta$ -naphthalenesulfonic acid [16]. Besides, quinine groups [17], TCNQ[18], nickel pentacyanonitrosylferrate[19], amino acids [20] and functionalized self-assembled monolayer of 4-aminothiophenol [21] were all employed to modify the electrode surface to catalyze the oxidation of AA.

In this work, based on our previous work on MWCNTs [22-24], potassium ferricyanide was first hydrothermally decomposed onto MWCNTs to form the ferric oxide-modified MWCNTs, and then, some direct characterization techniques, such as, SEM, EDS and XRD were used to feature the obtained samples to be  $\alpha$ - $\text{Fe}_2\text{O}_3$ , lastly, after numerous attempts, under proper conditions, the ferric oxides-immobilized MWCNTs showed an obvious catalysis for the electrooxidation of AA. The interaction between AA and ferric oxide was also testified by the FT-IR spectra. This preliminary work not only presented a novel way to prepare leaf-shaped ferric oxide particles, but also demonstrated that under some proper conditions, iron oxides, here,  $\alpha$ - $\text{Fe}_2\text{O}_3$ , have catalysis for the oxidation of AA,

which is consistent with the proposition developed by Professor Compton. Developing a novel modified electrode, i.e., Fe<sub>2</sub>O<sub>3</sub> /MWCNTs-modified electrode, for the oxidation of AA is the main contribution of this work.

## 2. EXPERIMENTAL PART

### 2.1. Chemicals

Potassium ferricyanide(K<sub>3</sub>Fe(CN)<sub>6</sub>) and all other employed reagents were all purchased from Tianjin Chemical Reagent Co., Ltd(China). Multi-walled carbon nanotubes (L.MWNTs-1020, outer diameter: 10-20nm, length: 5-15 $\mu$ m) with a purity of more than 95% were purchased from Shenzhen Nanotech Port Co., Ltd (China). All other chemicals were used as received without further purification and all aqueous solutions were prepared using redistilled water.

### 2.2. Hydrothermal synthesis of ferric oxides onto MWCNTs

First, 20ml of  $5 \times 10^{-3}$  M K<sub>3</sub>Fe(CN)<sub>6</sub> aqueous solution was mixed with 5mg of MWCNTs, and then the mixture was transferred into a home-made autoclave. And this well sealed autoclave was placed in a SRJX-8-13 box-type furnace equipped with KSY 12-16 furnace temperature controller at room temperature, subsequently, the temperature of furnace was enhanced to the desired value within 20 min and kept for 2 h to fulfill the hydrothermal process.

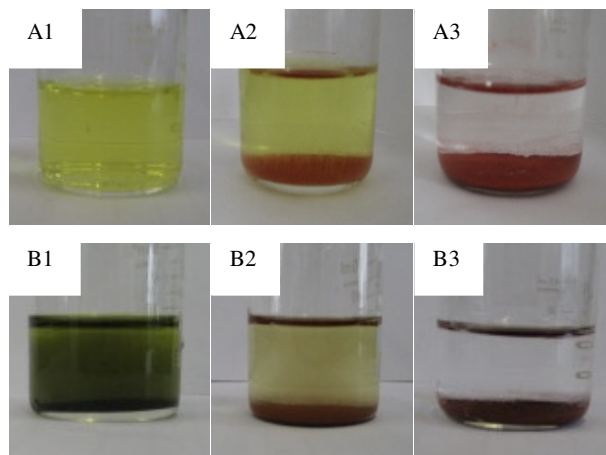
### 2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer (Germany) with Cu K $\alpha$  as the radiation source ( $\lambda=0.154$ nm). Electron diffraction spectroscopy (EDS) was recorded on a WD-8 X-ray energy instrument (Japan). FT-IR spectrum was recorded on a fourier transform infrared spectrometry (1730, P-E, USA). Scanning electron microscopy (SEM) was performed on a Hitachi S-570 microscope (Japan) operated at 20kV. Electrochemical measurements for the samples were all carried out on a CHI 660B electrochemical workstation (Shanghai Chenhua Apparatus, China).

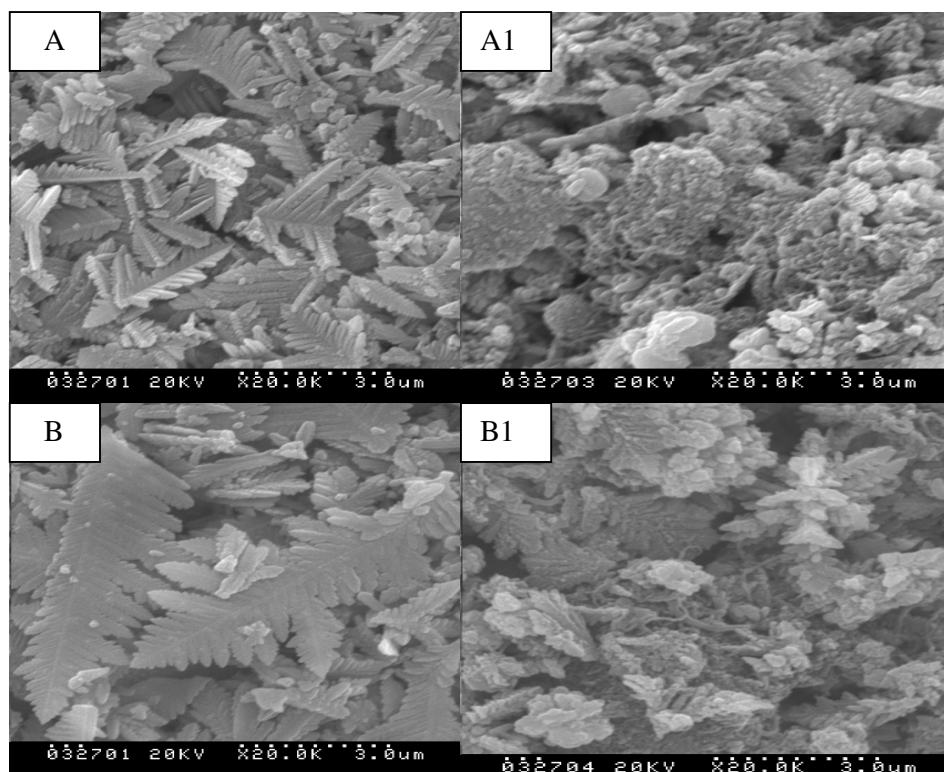
## 3. RESULTS AND DISCUSSION

Fig.1 is the digital photos for the as-prepared samples. In the absence of MWCNTs, as shown by A2, after the hydrothermal process, some red-brown particles are formed at the bottom of the beaker, and as the temperature was promoted to 200 $^{\circ}$ C, more particles are observed, as shown by A3, indicating that the higher temperature is beneficial to the preparation of samples. In the presence of MWCNTs, as shown by B1, B2 and B3 in Fig.1, the color of as prepared samples was altered

correspondingly. Generally, red-brown particles should be  $\text{Fe}_2\text{O}_3$  rather than  $\text{Fe}_3\text{O}_4$  since  $\text{Fe}_3\text{O}_4$  is black. This visible phenomena strongly demonstrate that it is feasible to generate the ferric oxide particles by this hydrothermal process of  $\text{K}_3\text{Fe}(\text{CN})_6$  as has never been reported so far.

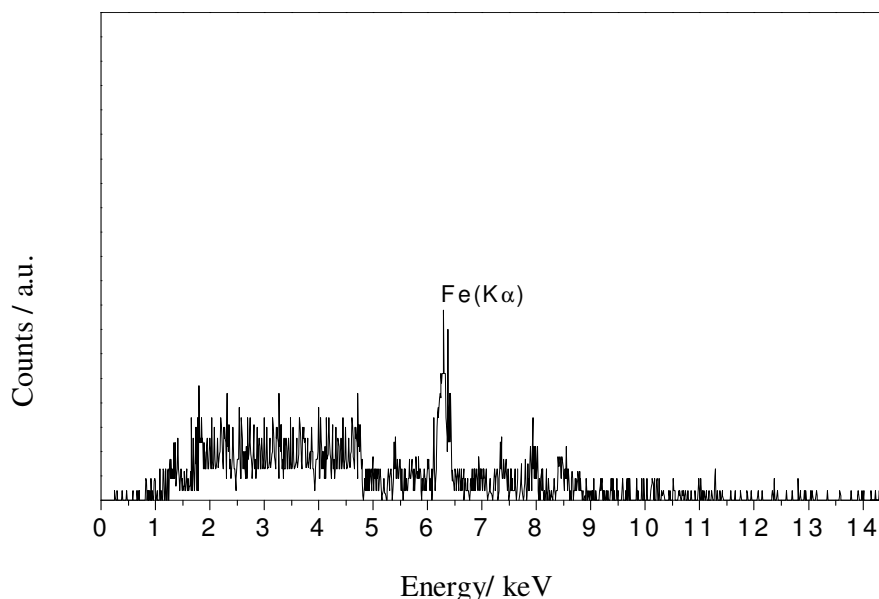


**Figure 1.** Digital photos for the as-prepared samples. A1:  $5 \times 10^{-3}$  M  $\text{K}_3\text{Fe}(\text{CN})_6$  aqueous solution, A2: samples obtained after 2h hydrothermal synthesis at 150 °C; A3: obtained after 2h hydrothermal synthesis at 200 °C. B1: mixture of  $5 \times 10^{-3}$  M  $\text{K}_3\text{Fe}(\text{CN})_6$  aqueous solution and 5 mg MWCNTs; B2: after 2h hydrothermal synthesis at 150 °C; B3: after 2h hydrothermal synthesis at 200 °C



**Figure 2.** SEM images for the resultant samples. A: Leaf-shaped  $\text{Fe}_2\text{O}_3$  obtained at  $150^\circ\text{C}$  A1: mixture of  $\text{Fe}_2\text{O}_3$  oxides and MWCNTs obtained at  $150^\circ\text{C}$ . B: Leaf-shaped  $\text{Fe}_2\text{O}_3$  obtained at  $200^\circ\text{C}$  B1: mixture of  $\text{Fe}_2\text{O}_3$  and MWCNTs obtained at  $200^\circ\text{C}$ .

Fig.2. shows the images of the as-prepared ferric oxides, in which leaf-shaped ferric oxide particles were clearly exhibited. To the best of our knowledge, this is the first time to report the leaf-shaped ferric oxide particles though ferric oxide particles with many shapes have been reported [25]. Interestingly, as the hydrothermal temperature was increased from  $150^\circ\text{C}$  ( shown by Fig. A in Fig.2) to  $200^\circ\text{C}$ ( shown by Fig. B in Fig.2), particles with larger size are observed. When MWCNTs were introduced, as shown by A1 and B1 in Fig.2, less leaf-shaped ferric oxide particles with well-shaped structure was produced, suggesting that MWCNTs have greatly affected the crystal growth of ferric oxides, probably there is an interaction between MWCNTs and ferric oxides, leading to the destroyed crystal structure of ferric oxide particles. We must *admit that* the obtained ferric oxide particles does not belong to nanoparticles since the particles obtained at  $150^\circ\text{C}$  is about  $1\mu\text{m}$  in length and those particles obtained at  $200^\circ\text{C}$  is about  $3.2\mu\text{m}$  in length.

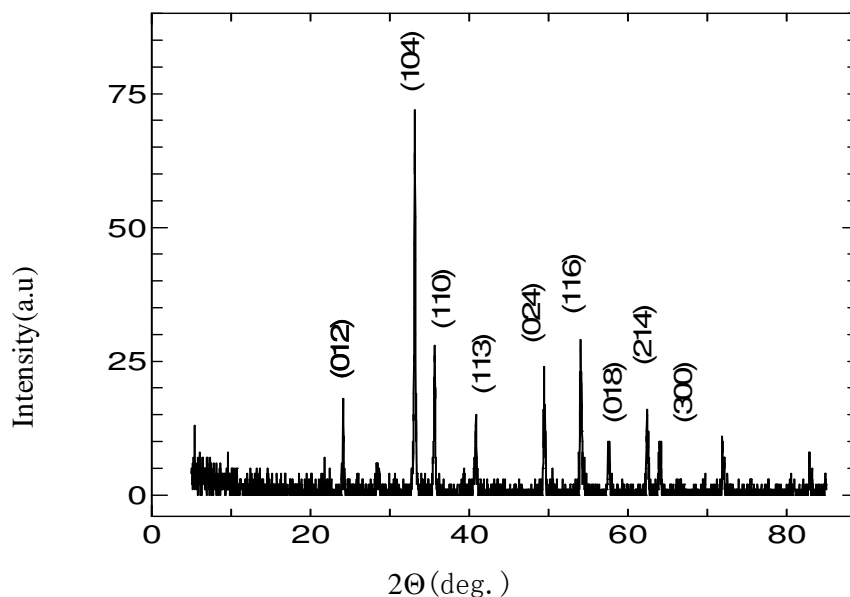


**Figure 3.** EDS spectrum for the as-prepared mixture of MWCNTs and ferric oxide particles obtained at  $150^\circ\text{C}$

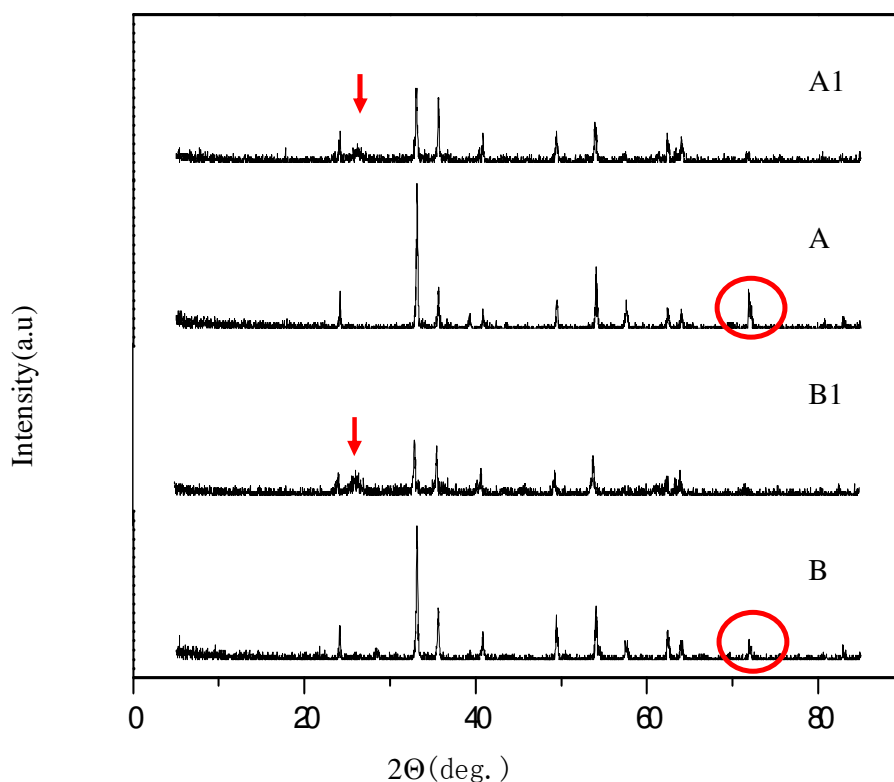
EDS spectra, as shown by Fig.3, clearly demonstrates that for the as-prepared samples, i.e., mixture of  $\text{Fe}_2\text{O}_3$  and MWCNTs that obtained at  $150^\circ\text{C}$ , except for the diffraction peak of iron, no other evident diffraction peaks were observed, suggesting that no impurities were introduced into the resultant samples. EDS spectra (not shown here) for the samples obtained at  $200^\circ\text{C}$  is similar to Fig.3 very well.

XRD plots, as illustrated by Fig.4 revealed that the obtained red-brown particles (samples A2 in Fig.1) are  $\alpha\text{-Fe}_2\text{O}_3$  (JCPDS 33-664), according with the former literature very well.<sup>25</sup> XRD plots for the red-brown particles obtained at  $200^\circ\text{C}$  are very similar to the plots in Fig. 4, implying that in the absence of MWCNTs, this hydrothermal process of  $\text{K}_3\text{Fe}(\text{CN})_6$  mainly yielded  $\alpha\text{-Fe}_2\text{O}_3$ . As reported

previously, hydrothermal synthesis has been widely employed in the preparation of ferric oxide. For example, Rockenberger [26] reported the surfactant-capped nanocrystals of transition metal oxides by thermal decomposition method, and Sun [27] published its work on the preparation of monodisperse magnetite nanoparticles by high-temperature solution-phase reaction of  $\text{Fe}(\text{acac})_3$  in phenyl ether. To the best of our knowledge, there is no paper reporting the hydrothermal decomposition of potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) to produce  $\alpha\text{-Fe}_2\text{O}_3$ .

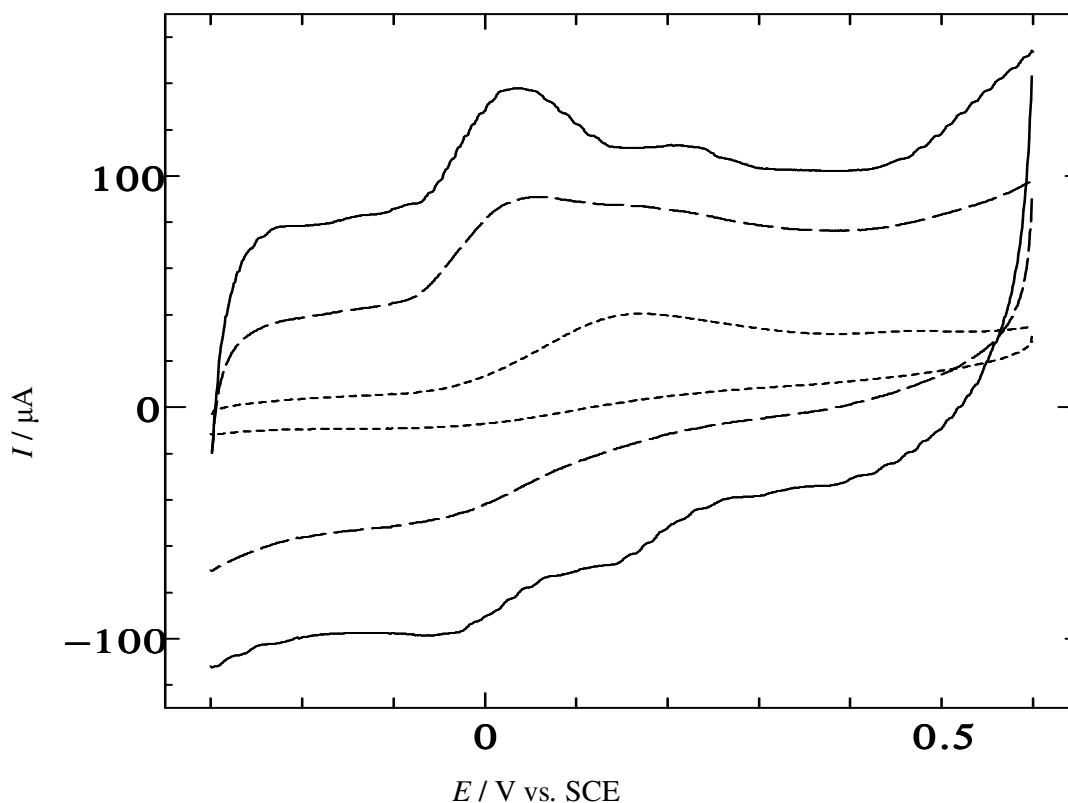


**Figure 4.** XRD patterns for the leaf-shaped ferric oxides obtained at 150°C



**Figure 5.** XRD patterns for the obtained samples. A1: mixture of  $\text{Fe}_2\text{O}_3$  and MWCNTs obtained at  $150^\circ\text{C}$ ; A: Leaf-shaped  $\text{Fe}_2\text{O}_3$  obtained at  $150^\circ\text{C}$ ; B1: mixture of  $\text{Fe}_2\text{O}_3$  and MWCNTs obtained at  $200^\circ\text{C}$ ; B: Leaf-shaped  $\text{Fe}_2\text{O}_3$  obtained at  $200^\circ\text{C}$

The total XRD patterns for the prepared samples were illustrated in Fig.5. It can be seen that as MWCNTs were introduced, typical crystal face of C (002) for MWCNTs was exhibited at  $26.4^\circ$ , as shown by the red arrow, according with the reported data very well [28], and the diffraction peak at  $72.3^\circ$  was thoroughly suppressed when MWCNTs were introduced, as shown by the circled peaks in Fig.5. The attenuated peak strongly indicated that MWCNTs influenced the crystal structure of ferric oxides.



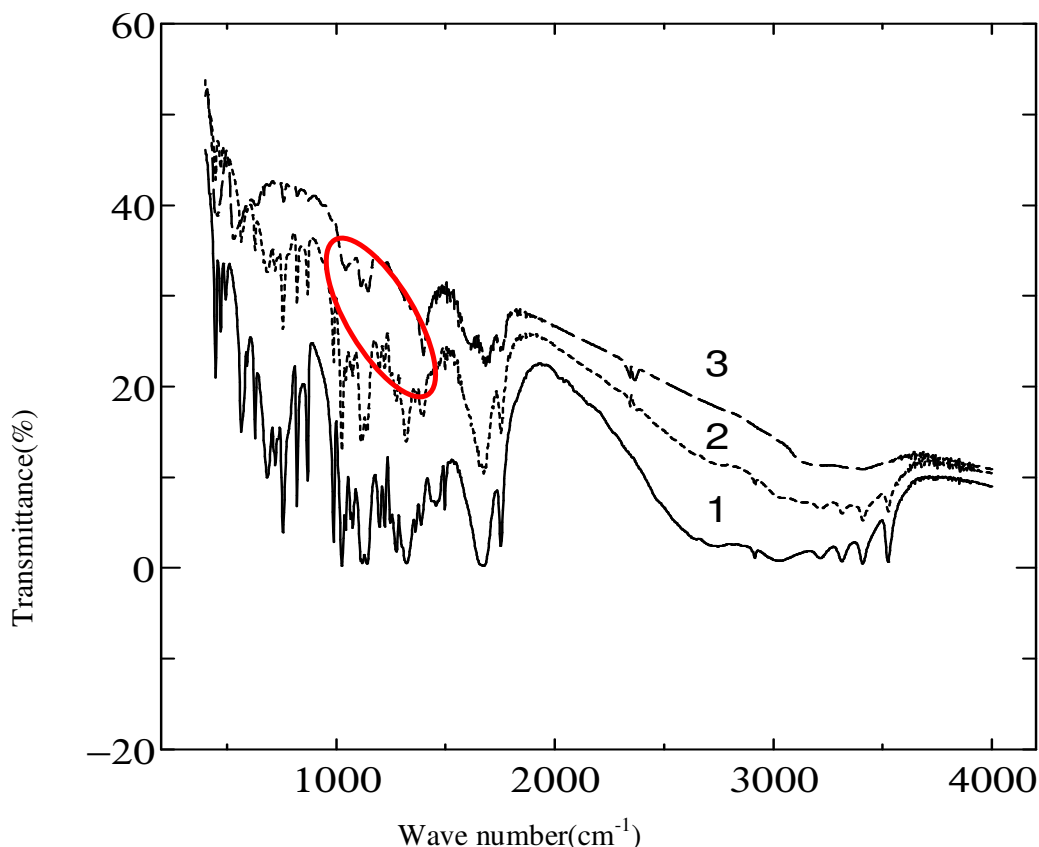
**Figure 6.** Cyclic voltammograms(CVs) for the electrooxidation of AA on the modified graphite electrode in PBS(phosphate buffer solution,  $\text{pH}=6$ )containing  $5 \times 10^{-3}\text{M}$  AA at  $50\text{mV/s}$ ; dotted line: obtained on a graphite electrode; dashed line: obtained on the MWCNTs-modified graphite electrode; solid line: on the  $\text{Fe}_2\text{O}_3/\text{MWCNTs}$ -modified graphite electrode.

As reported by Professor Compton, partly, the catalysis of carbon nanotubes for electrochemical electron transfer process was attributed to the doped metal element in carbon nanotubes, such as iron. In the following work, the artificially prepared ferric oxide immobilized on multi-walled carbon nanotubes, noted as  $\text{Fe}_2\text{O}_3/\text{MWCNTs}$ , was modified on a graphite electrode, and then the obtained electrode was employed to the electrooxidation of AA. After numerous attempts, the

satisfied results are illustrated in Fig.6, where the solid line corresponds to cyclic voltammograms (CVs) obtained at a  $\text{Fe}_2\text{O}_3/\text{MWCNTs}$ -modified graphite electrode, while the dashed curve corresponds to CVs recorded at the MWCNTs-modified graphite electrode, and the dotted line is the CVs measured on the bare graphite electrode. Here, the electrooxidation of AA on the graphite electrode is clearly observed, according with the former report very well[29], after being modified by MWCNTs, an enlarged current peak was exhibited, for instance, on the bare graphite electrode the oxidation peak current for AA is about  $41.18\mu\text{A}$ , while for MWCNTs-modified graphite electrode, the oxidation peak current was promoted to be about  $91.05\mu\text{A}$ , the oxidation peak potential for AA was negatively shifted from  $0.16\text{V}$  for the bare graphite electrode to  $0.05\text{V}$  when coated by MWCNTs, suggesting that MWCNTs could act as a catalyst for the electron transfer of AA, consistent with the previous report[30]. To our surprise, for the  $\text{Fe}_2\text{O}_3/\text{MWCNTs}$ -modified graphite electrode, the oxidation peak current of AA was dramatically enhanced to be about  $138.05\mu\text{A}$  though its peak potential was only negatively shifted for  $20\text{mV}$  when compared to the MWCNTs-modified graphite electrode. The solid line in Fig.6 at least reveals that an appropriate amount of ferric oxide coated on the MWCNTs could catalyze the electrooxidation of AA.

Obviously, there are many factors affecting the catalysis of ferric oxides for the electrooxidation of AA, for example, the molar ratio of ferric oxides to MWCNTs, the amount of ferric oxides and so on. In this preliminary work, we only showed the satisfied CVs, more detailed discussion will be addressed in the further work.





**Figure 7.** FT-IR spectra of samples, line1: ascorbic acid; line2: mixture of MWCNTs and ascorbic acid; line 3: mixture of ferric oxide and ascorbic acid.

Fig.7 presents the typical FT-IR spectra for the as-prepared samples. Line 1 is the FT-IR spectrum for the pure ascorbic acid, consistent with the report very well [31], while as MWCNTs were introduced, as shown by line 2, no novel peaks were observed except for the suppressed peak intensity. Interestingly, as ferric oxide particles were mixed with AA, as shown by line 3, the absorption peak at  $1000\text{ cm}^{-1}$  was greatly attenuated, suggesting that there should be an interaction between AA and ferric oxides.

Recently, Kong [32] group prepared magnetic multi-walled carbon nanotubes (M-MWCNTs) by introducing  $\text{Fe}_2\text{O}_3$  nanoparticles into the nanotubes, and thought that horseradish peroxidase could be adsorbed in the M-MWCNTs films via electrostatic interaction, hydrophobic interaction and nonspecific interactions. Tsodikov [33] probed the catalysis of ferric oxide towards the 3, 4-dichlorobutene-1 isomerization and benzenealkylation, and suggested that ferric oxide possesses two types of defects: one is the cation vacancies and the other is the anion vacancies caused by non-stoichiometric structure, which is responsible for the catalysis of ferric oxide. Thus, based on the published papers and our experiment, we believe that there must be an interaction between ferric oxide and ascorbic acid though we are unable to present the direct proofs in this preliminary work.

#### 4. CONCLUSIONS

In this work, for the first time, leaf-shaped ferric oxides were prepared by the hydrothermal process of potassium ferricyanide ( $K_3Fe(CN)_6$ ) onto the multi-walled carbon nanotubes (MWCNTs) to catalyze the electrooxidation of ascorbic acid. Results obtained from SEM, EDS and XRD all strongly demonstrated that  $\alpha-Fe_2O_3$  was generated by this mild process. Also, the obtained CVs, corresponding to the electrooxidation of ascorbic acid, verified that the oxidation peak current of ascorbic acid was enhanced by the modification of  $Fe_2O_3$ /MWCNTs to some extent though the oxidation peak potential was not much negatively shifted. Our results strongly supported the proposition, developed by Professor R. G. Compton, that the catalysis of carbon nanotubes (CNTs) was partly attributable to doped metal element in carbon nanotubes. Summarily, preparing leaf-shaped ferric oxide particles onto the multi-walled carbon nanotubes and initiating the investigation of the catalysis of ferric oxide-MWCNTs composite for ascorbic acid are the main contributions of this preliminary work.

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