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Preparation and Characterization of Fe/Sio$_2$ Nanoparticles Composite via Sol-Gel and Chemical Reduction Method

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Abstract— *Fe/SiO$_2$ nanoparticles composite via sol-gel and chemical reduction method was studied in this work. We found that the Fe/SiO$_2$ nanocomposite is studied with various ratios between Fe and SiO$_2$. We found that the Fe nanoparticles are distributed uniformly on the SiO$_2$ support, leading to enhance the surface area of Fe on the SiO$_2$ as well as improve the stability of Fe on SiO$_2$ compared to pure Fe. The results shows the surface area of Fe/SiO$_2$ is about of 50.108 m^2/g, is much larger than the pure Fe (26 m^2/g). The results of this work suggests that the way to synthesis Fe/SiO$_2$ nanocomposite with highly uniform distribution and surface area via sol-gel and chemical reduction method*

Keywords— Fe/SiO$_2$, sol-gel, Stober method, composite, nanoparticle.

I. INTRODUCTION

Fe NPs have shown a high chemical reduction rate on several kinds of contaminants, including toxic metal ions.[1-2] The properties of nanometer-sized magnetic iron particles have been investigated extensively by both experimental and theoretical analysis. On the one hand, these particles show promise for practical applications, such as catalysis, magnetic recording, magnetic fluids, and biomedical applications; on the other hand, their utility has been limited due to easy aggregation and uncontrolled oxidation. [3] The synthesis of Fe NPs with a uniform particle size distribution has been demonstrated using high-temperature thermolysis in oil-based reaction systems [4-5]. However, these reactions were considered harmful because of the involvement of toxic reagents and the high energy consumption. From the viewpoint of practical applications, any method to fabricate Fe NPs must take into account the susceptibility of Fe NPs to oxidation and aggregation owing to the magnetic interaction between the particles. Controlling the oxidation of Fe NPs is particularly important, as oxidation leads to degradation in their magnetic properties [6].

Since Fe NPs are oxidized rapidly in water and air, they exhibit a loss or decrease in magnetism and dispersibility in a biological environment. Therefore, preserving the stability of Fe NPs is considered another challenge for biomedical applications. To prevent the oxidation of Fe NPs, the core-shell structures that are stable, biocompatible and hydrophilic were demonstrated using surface modifications with organic polymers of poly(acrylic acid) [7] poly(ethylene glycol) [8], dendrimers [9], chitosan [10-11] and silica (SiO$_2$) layers. The SiO$_2$ shells provide an electrically-insulting layer that decreases energy loss and additionally prevents the possibility of a decrease in permeability due to Fe oxidation. Li et al. prepared α-Fe nanoparticle/ordered mesoporous silica with the aid of a triblock copolymer using oxidation and reduction reactions [12]. Yang et al. formed Fe-core/SiO2 shell nanoparticles using oleic acid and citric acid as the surface capping agents in an aqueous environment at room temperature. However, in this case, a 400°C reduction treatment was needed to obtain pure Fe/SiO$_2$ nanoparticles without FeO$_x$, increasing the energy uptake.

The aim of this study was to prepare metallic Fe NPs on SiO$_2$ spheres like a nanoparticles composite to prevent iron oxidation and enhance the distribution of Fe on SiO$_2$ using a sol-gel process at low heat treatment conditions and the chemical reduction method. The Fe/SiO$_2$ nanoparticles composite are prepared with various compositions of Fe:SiO$_2$ to find out the good properties for the magnetic nanoparticles composite. The XRD, TEM, BET as well as the magnetic properties of the Fe/SiO$_2$ nanoparticles composite are characterized in detail in this work.

II. EXPERIMENT

1. Materials

Tetraethylorthosilicate (TEOS), potassium borohydride (KBH$_4$, 98%), anhydrous ferric chloride (FeCl$_3$), potassium dichromate (K$_2$Cr$_2$O$_7$), nitrogen (99,9%) and ethanol (99,5%) were all of analyric grade without further purifying. Deionized water was used throughout the study.

2. Preparation of iron nanoparticles coated with silica (Fe/SiO$_2$)

Fe/SiO$_2$ nanoparticles composites were prepared by th sol-gel method combining with chemical reduction method without using any surfactant together with stabilizer. The process includes two steps: the 1st step is the synthesis of SiO2 nano size by the sol-gel method and the 2nd step is the preparation of Fe/SiO2 by chemical reduction method using the KBH4 as reductant agent at room temperature. The detail process is described as the **Fig. 1 and Fig. 2.**

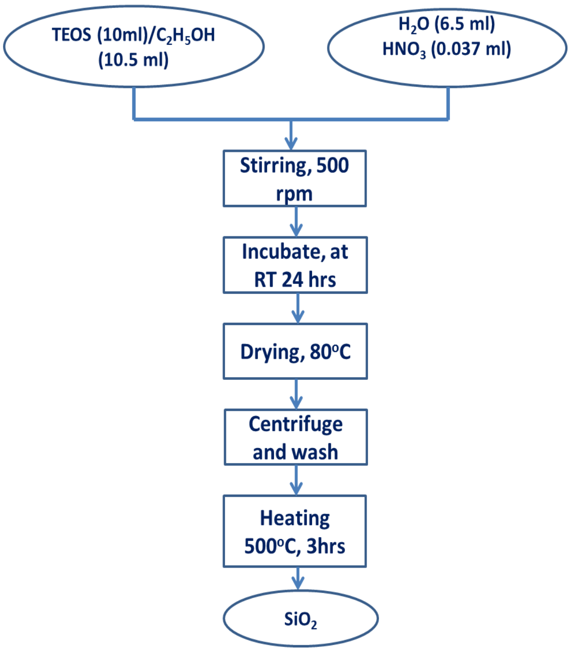


Fig.1:The 1st step to synthesis the SiO_2

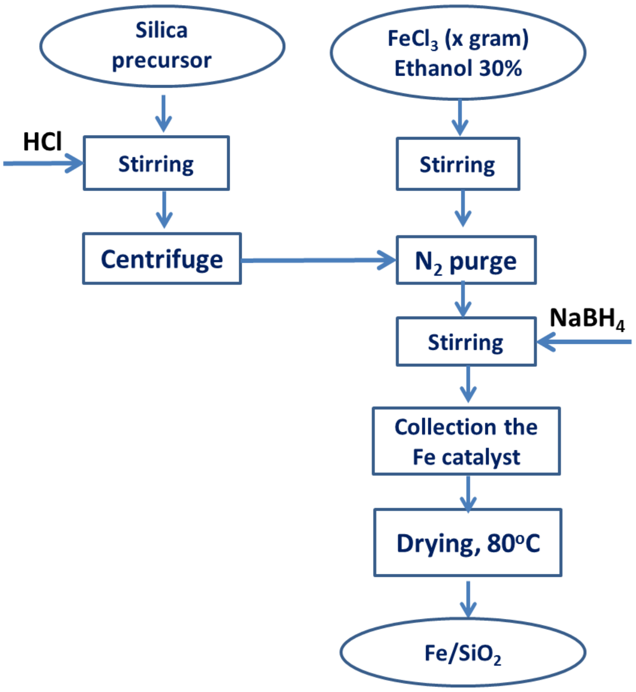


Fig.2: The 2nd step to synthesis the Fe/SiO_2 nanoparticle composite

3 Characterization of Fe/SiO_2

X-ray diffraction (XRD) patterns of the specimens were recorded using an X-ray diffractometer (D8 Phaser, Bruker) equipped with a Cu Ka radiation source (1.5406 Å) and nickel filter. Microstructure analysis was performed with a transmission electron microscope (TEM, JEE 420-JEOL). The magnetic properties at room temperature were investigated using a vibrating sample magnetometer (MicroSense Easy VSM Sofware 9.13L). In addition, specific surface area of Fe/SiO_2 nanoparticles were measured by the Brumauer – Emmett – Teller (BET) method using Quantochrome NOVA 11.0.

III. RESULT AND DISCUSSION

The Fe/SiO_2 nanocomposite is studied with various ratios between Fe and SiO_2 (see the table 1)

Table1: The samples of Fe/SiO_2 with various ratio of Fe:SiO_2

No.	Sample	Fe:SiO2
1	F1S1	1:1
2	F2S1	2:1
3	F3S1	3:1

The color of Fe/SiO_2 nanocomposite could be observed clearly from the Figure 3. It can be seen that the F1S1 sample for the black color compared to other ratios, and the brown color of Fe/SiO2 sample could be observed clearly for the sample with the Fe:SiO_2=3:1 This result may be understood due to the high amount of Fe in the Fe/SiO_2 nanocomposite leading to oxidize easily to form the oxide Iron, resulting in the brown color formation. Therefore, the ratio of Fe:SiO_2 was selected to measure XRD, TEM, BET and Magnetic properties.

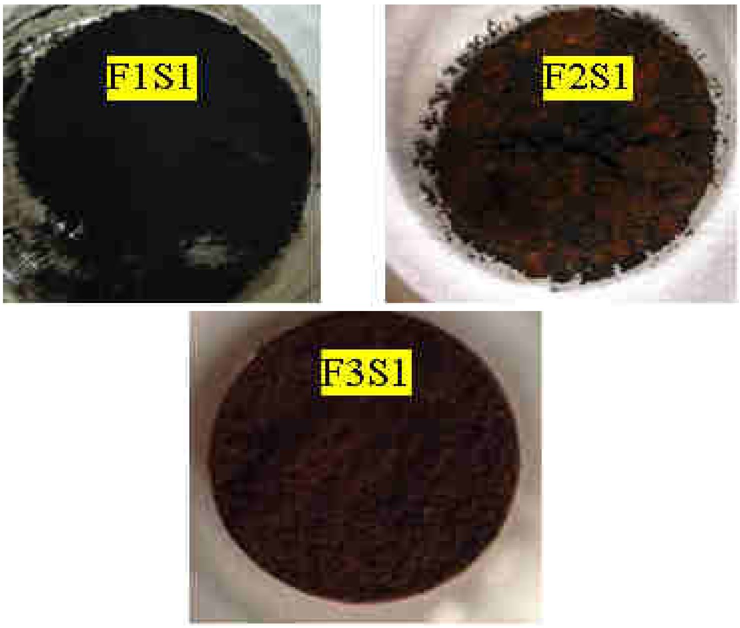


Fig.3: The color of Fe/SiO_2 with various ratio of Fe:SiO_2

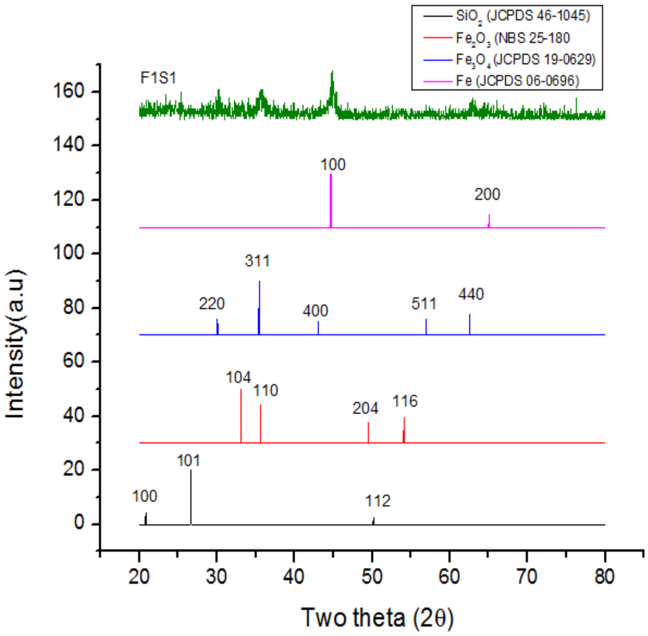
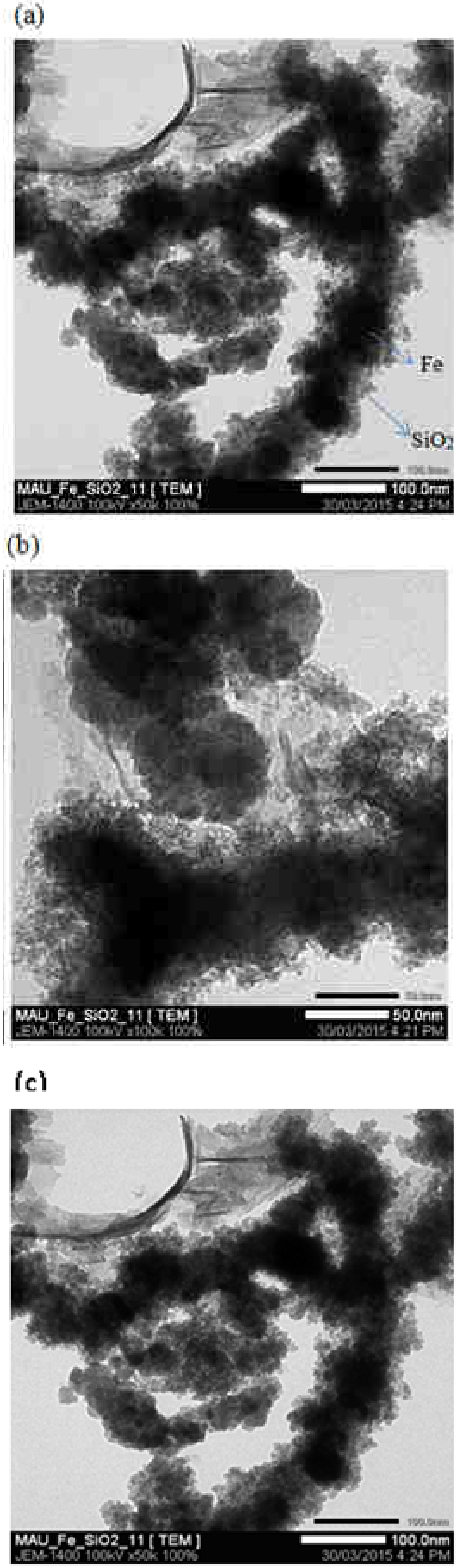


Fig.4: *XRD pattern of the prepared Fe:SiO_2 =1:1 nanocomposite*

Figure 4 shows the XRD pattern of the prepared Fe:SiO_2 =1:1 nanocomposite. The XRD pattern demonstrated that SiO_2 were amorphous phase because of absencing of peaks corresponding to silica despite coating outside. Moreover, in **Fig. 4** we can see that the dominant Fe peak was observed for Fe:SiO_2 at $2\theta=44,68^o$, some weak peaks at 35.5^o and 30.1^o are corresponding to Fe_3O_4 iron oxide. The diffraction peak at $44,68^0$ is rather clearly due to the existing of α-Fe particles (JCPDS card no. 06-0696).

The morphology of Fe/SiO_2 sample was examined by TEM measurement in **Figure 5.** It can be seen that the dark sphere was attributed to Fe and the gray shell can be attributed with SiO_2. The Fe nanoparticles are distributed uniformly on the SiO_2 support, leading to enhance the surface area of Fe on the SiO_2 as well as improve the stability of Fe on SiO_2 compared to pure Fe.



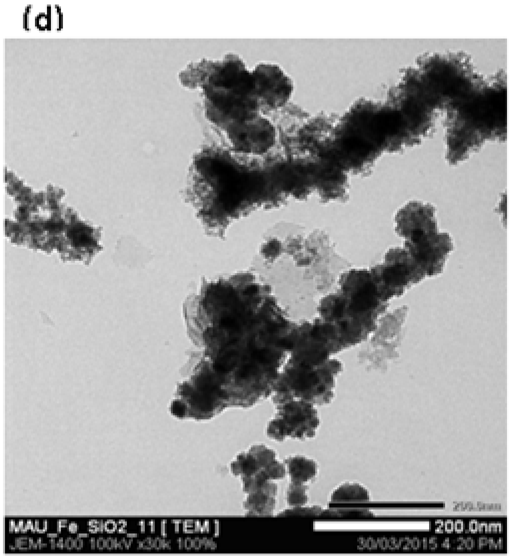
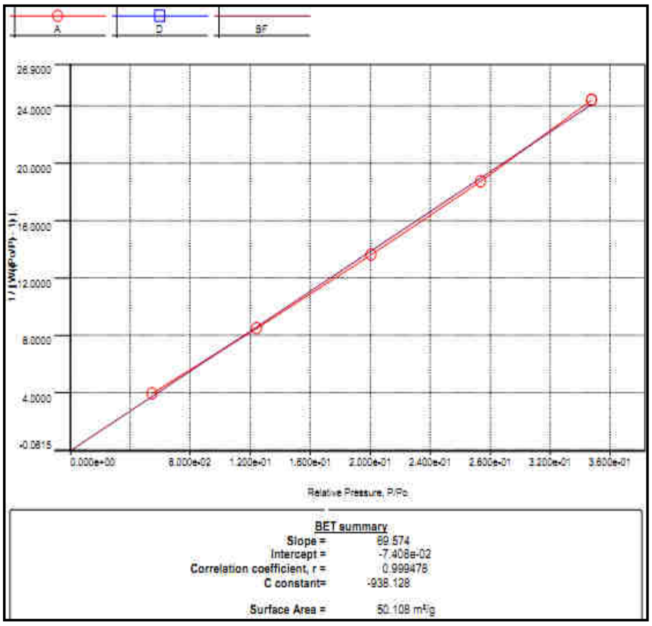


Fig.5: TEM measurement of Fe:SiO_2 sample, (a)- (d) overview and high resolution image.

The Fe:SiO_2 sample also was measure surface area by Brunauer–Emmett–Teller (BET) measurement. The results shows the surface area of Fe/SiO2 is about 50.108 m^2/g, is much larger than the pure Fe (25 m^2/g) [13] from the previous research. This result could be concluded that the Fe is dispersed uniformly on the SiO_2 support.



BET summary
Slope = 89.574
Intercept = -7.408e-02
Correlation coefficient, r = 0.999478
C constant= -938.128
Surface Area = 50.108 m²/g

Fig.6: The BET surface area of Fe/SiO_2 (Fe:SiO_2=1:1)

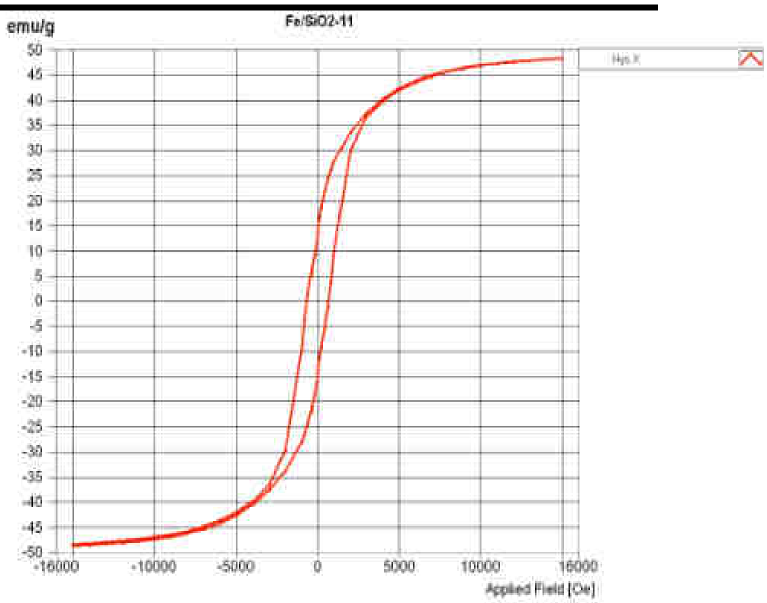


Fig.7: The magnetization hysteresis loops of Fe/SiO_2 with Fe:SiO_2=1:1 (denoted sample F1S1) at room temperature

Fig. 7 shows the magnetization hysteresis loops of Fe/SiO_2 (Fe:SiO_2=1:1) sample at room temperature using a VSM in an applied field -1300 kA/m ≤ H ≤ 1300 kA/m. The coercivity (H_c) value of the prepared Fe/SiO_2 (Fe:SiO_2=1:1) was around Hc= 651,43 (Oe) > 10 (Oe), Mr = 13,713 (emu/g). The saturation magnetization value (M_s) was about 48,517 (emu/g). Compared with bulk Fe (M_s = 220 emu/g), the M_s value of F1S1 sample was reduced. The magnetzation discrepancy in magnetization value beween bulk and our nanoparticles could be attributed to the small particle size effect. It it known that the saturation magnetization value of nanoparticles is smaller than that of corresponding bulk materials [14-18].

IV. CONCLUSION

In conclusion, Fe/SiO_2 nanoparticles were synthesized by sol-gel and chemical reduction method a simple method. The Fe/SiO_2 nanocomposite is studied with various ratios between Fe and SiO_2. We found that the Fe nanoparticles are distributed uniformly on the SiO_2 support, leading to enhance the surface area of Fe on the SiO_2 as well as improve the stability of Fe on SiO_2 compared to pure Fe. The results shows the surface area of Fe/SiO_2 is about 50.108 m^2/g, is much larger than the pure Fe (26 m^2/g).

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