Study on the Preparation and Properties of Colored Iron Oxide Thin Films

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Abstract. Colored iron oxide thin films were prepared using Sol-gel technique. The raw materials were tetraethyl orthosilicate (TEOS), ethanol (EtOH), iron nitrate, and de-ionized water. Various properties were measured and analysed, including the colour of thin films, surface topography, UV-Visible spectra, corrosion resistance and hydrophobicity. To understand how these properties influenced the structural and optical properties of Fe3O4 thin films, Scanning Electron Microscope (SEM), UV Spectrophotometer and other facilities were employed. Many parameters influence the performance of thin films, such as film layers, added H2O content, and the amount of polydimethylsiloxane (PDMS). When the volume ratio of TEOS, EtOH and H2O was 15:13:1, the quality of Fe(NO3)3·9H2O was 6g, and pH value was 3, reddish and uniform Fe3O4 thin films with excellent properties were produced. Obtained thin films possessed corrosion resistance in hydrochloric acid with pH=1 and the absorption edge wavelength was ~350.2nm. Different H2O contents could result in different morphologies of Fe3O4 nanoparticles. When 1.5 ml PDMS was added into the Sol, thin films possessed hydrophobility without dropping. Coating with different layers, thin films appeared different morphologies. Meanwhile, with the increment of film layers, the absorbance increased gradually.
1. Introduction

As nanosized magnetic metal, Fe reveals unique properties and it has a wide application in many fields, including thin film solar cells, data storage materials, magnetic resonance imaging and so on [1-2]. Silicon is a low cost and ideal material for modifying the surface performance. In the same time, the physical integrity of the underlying core nanocrystals still exists. Silicon coating of oxides can be easily performed using sol-gel technique and it binds to the silica through -OH surface groups [3-5]. The iron oxide is an important inorganic material. Nano-iron oxide has been paid attention by researchers because of its unique nature and application. It can be used for the preparation of catalyst, high-density magnetic recording materials, optical gas sensing materials, functional pigments and so forth. It has wide and potential application in the fields of acoustic, electronics, optics and thermo [6-7]. The performance of materials depends on their composition and microstructure. Therefore, iron oxide with different morphologies has become a hot research point.

PDMS/SiO₂ hybrid material is a hot research point in recent years. The formation of the PDMS/SiO₂ hybrid material could promote the molecule to produce conformational transformation easily, which could eliminate the stress in the gel conversion process. Meanwhile, it could inhibit the embrittlement of the material. PDMS/SiO₂ hybrid material possesses excellent optical and mechanical properties, superior high-temperature and aging resistance. Its outstanding feature is non-toxic [8-10]. Adjusting the PDMS content could control the hardness and elasticity, which could produce bioactive materials.

In 2010, Flora Heshmatpuor et al. [11] in Iran obtained a red and blue gel block by using sol-gel method. They added the inorganic salts respectively containing cobalt ions and iron ions into the solution. The effect of the heat treatment on the film color was discussed. The obtained thin film possessed best properties when the temperature was 600°C, including the uniform color, high transparency and so forth. Nowadays, this technique has been applied in optoelectronic products. For example, the anti-color LCD optical thin films come out in Japan. This product reveals different optical properties according to different colors. Recently, researchers in Tongji University prepared environmentally friendly colored glass with sol-gel technique. They joined one biological stain, such as methylene blue and phthalocyanine blue, as a raw material. On the one hand, obtained colored glass was uniform and transparent. On the other hand, the products could be recycled. However, there are some limitations for the biological stain as the raw material, including high pH value, superior solubility, strong absorption bands in the visible region and high melting point.

In this paper, sol-gel technique was utilized to prepare colored iron oxide thin films and the properties were analyzed. Transparent iron oxide thin film has a wide and significant application in our lives. Recently, the study of such films has become systematic and in-depth. Moreover, the research on iron oxide films develops quickly. Typically, deposited thin film is amorphous and it needs subsequent heat treatment for the crystallization. There exist many factors that affect the crystal structure of thin film, including the substrate material, the chemical properties of the solution, heat treatment conditions and so forth. Sol-gel method possesses many advantages. For example, the process is simple and the experiment cost is not high. And this technique could produce thin films with excellent properties. SEM, UV Spectrophotometer and other experimental apparatus were utilized to analyze the performance of obtained colored iron oxide thin films.
2. Experiments

Reddish iron oxide thin films were prepared by sol-gel method using TEOS and Fe(NO₃)₃·9H₂O as Si and Fe precursors respectively. At first, 15ml TEOS and 13ml EtOH were mixed together in a beaker at the temperature of 25°C. And about 5 drops of diluted hydrochloric acid were added in it until the pH value was regulated to 3. At the same time, 6g Fe(NO₃)₃·9H₂O and certain amount of de-ionized water were blended together in another beaker at room temperature. These two beakers were placed on the JB-3 Magnetism Stirrer for 15min. Then, the solution of the second beaker was added drop wise into the first beaker and the obtained mixed solution was stirred for 2h. After that, certain amount of PDMS was added into this mixed solution, which was then watered bath at 60°C for 2h in an enclosure condition. Two hours later, the obtained Sol system was aged for 24h at room temperature. Then, the Sol was coated on the substrate by dip coating method. Finally, humid Gel was dried for 1h at the temperature of 100°C and then sintered in the muffle at 450°C for 30 min. Iron species, such as Fe₂O₃ nanoparticles, were successfully incorporated in the inner surfaces of mesoporous silica. And the crystallization of iron oxide particles inside the voids would reveal a better performance.

The morphology and size of the colored iron oxide thin films were determined by Field Emission Scanning Electron Microscopy (SEM) (Hitach, S-4300). To investigate the absorbance, a UV-spectrophotometer (U-3010) was employed. The absorption spectrum is between 300 and 800nm. And other properties of Fe₂O₃ thin films were analyzed by other facilities.

3. Results and discussion

3.1 The obtained colored iron oxide thin films

Fig. 1 shows the macroscopical image of obtained colored iron oxide thin films, which were prepared in a suitable sol viscosity by dip coating technique. The volume of TEOS, EtOH and H₂O was respectively 15 ml, 13 ml and 1 ml, the quality of Fe(NO₃)₃·9H₂O was 6g, and pH value was 3. From Fig. 1, it could be seen that the obtained thin films were transparent and uniform with reddish color. The sol viscosity plays a significant role in the forming of thin films. In the initial stage of sol aging, the sol viscosity was smaller than 2 cp. Under this situation, it was hard to form thin films on the glass slide. Meanwhile, the film thickness was so small that there existed apparent color interference fringes. The sol became larger than 5 cp in the later stage of sol aging, which would result in thin films with large thickness. This could produce apparent bubbles in the coating because the small bubbles on the surface of coating solution could not evaporate freely when the viscosity is too large.

![Fig. 1](image_url) The macroscopical image of obtained colored iron oxide thin films
3.2 The surface morphology of obtained colored iron oxide thin films

Figure 2 illustrates the FESEM images of colored iron oxide thin films produced by sol-gel method. As shown in Fig. 2, the surface was even and thin films were uniform. There was no crack and the bottom of thin films was connected together. What is more, the nanoparticles were distributed narrowly and uniformly, and the shape was regular. It could be found that the average nanoparticle size was ~ 55nm at the sintering temperature of 450°C. However, some island particles were distributed randomly on the surface of thin films. Through analysis, these particles are probably SiO₂ particles with small degree of polymerization. This phenomenon corresponds to the film formation process in the film nucleation growth theory, indicating that the film growth process on the substrate is essentially a heterogeneous nucleation and crystal growth process.

![Fig. 2 FESEM images of colored iron oxide thin films](image)

3.3 The effect of added H₂O content on the morphology of Fe₂O₃ nanoparticles

As shown in figure 3, there were three different morphologies of Fe₂O₃ nanoparticles. The morphology of Fe₂O₃ nanoparticles was spherical without adding de-ionized water. When 2 ml de-ionized water was added into the sol system, the shape of Fe₂O₃ nanoparticles became ellipsoidal and tetrahedral. However, the Fe₂O₃ nanoparticles were transferred to block-shaped ones with 6 ml H₂O. It was concluded the H₂O is a significant element for the preparation of colored iron oxide thin films, and adding varying amounts of de-ionized water could produce different morphologies of Fe₂O₃ nanoparticles. This could prove that de-ionized water has large influence on the anisotropic growth of Fe₂O₃ nanoparticles, which would cause different morphologies.
Fig. 3 Different morphologies of Fe$_3$O$_3$ nanoparticles with H$_2$O adding amount of a) 0 ml, b) 2 ml and c) 6 ml

3.4 The optical absorption of iron oxide thin films

Fe$_3$O$_4$/SiO$_2$ thin films are important silicon-based light-emitting materials because of the surface plasmon resonance of metal particles and local field enhancement effect. This kind of thin films possess excellent nonlinear optical properties in special wavelength range, including strong absorption, high nonlinear coefficient and fast response [12-13]. Study on the visible-near infrared light absorption of thin films, especially the effect of applied electric field on absorption, could help deepen the understanding of complex band structure of thin films, field-assisted photoemission mechanism and photoelectric conversion. When the beam shines in the composite thin films, energy is exchanged because of the interaction. Incident light in the thin films decays due to the optical absorption. Light intensity attenuation complies with the Bouguer-Lambert law [14-15]. The absorption spectrum between 300 and 800 nm was shown in figure 4 displayed the absorption edge wavelength of this sample, which was 350.2nm. This proves that obtained thin films possess excellent UV absorption performance.

Fig. 4 Absorption spectra of colored iron oxide thin films
3.5 The hydrophobic property of thin films

The hydrophobic materials can be applied in the field of self-cleaning, micro-fluid system and many other fields. Non-wetting means the liquid surface adhesion on solid is smaller than the cohesion. In this case, liquid cannot spread on the solid surface and it tends to shrink into a spherical one on the contact surface [16-17].

Organic silicone polymers own -O-Si-O-Si- chain and -CH3 side chain, which could provide with a hydrocarbon surface. This will form a layer of insoluble waterproofing thin films on this surface. The contact angle increases between water and substrate interface and it appears the “capillary effect”, whose nature is to reduce the surface tension of thin films in order to prevent the water from inflowing into them. PDMS has a low surface energy and its -CH3 is a common hydrophobic group. In this experiment, a simple method was made according to the principle of hydrophobic testing. The glass slide was placed on a horizontal table and 20 drops of de-ionized water were dropped wise on the central area of the surface of thin films added with certain amount of PDMS. The surface spread of water was recorded by a camera. Then the hydrophobic property of thin films was analyzed due to the size of the contact angle. As shown in figure, 20 drops of water were congregated together, showing a regular spherical. For thin films added with PDMS, the gravity of thin films to the water molecule is smaller than the gravitational force between water molecules. Then the molecular density of the adhesion layer is less than the density of water molecules, which results in the gravitation between the molecules within the adhesion layer. In this case, water shows the trend of contraction and there appears a non-wetting phenomenon. From figure 5, the contact angle was ~100°. Therefore, it is concluded that thin films added with suitable PDMS content possess hydrophobic properties.

![Image](image_url)

Fig. 5 The water on the surface of iron oxide thin films and the contact angle

3.6 The corrosion resistance of thin films

Figure 6 shows the corrosion situation of the film surface. Si-based coating possesses chemical stability and acid corrosion resistance. In the experiment, three substrates coating with thin films were soaked in the solutions with 40 ml volume, including hydrochloric acid with pH=1, ethanol, and NaOH solution with pH=10, which were shown in Fig. 6 respectively from left to right. After 40 days, they were fetched out and it was found from Fig. 6 that the glass substrate in the hydrochloric acid had no apparent change. In the ethanol, glass substrate had no any change. However, the surface of glass became pale with a lot of traces, and a part of the coatings dropped. It is concluded that iron oxide thin films possess corrosion resistance in hydrochloric acid with pH=1.
3.7 The coating layers

3.7.1 The effect of coating layers on the morphology of thin films
Multi-layers of coating could improve the wear resistance of thin films. However, the viscosity becomes large when there are several layers of coating. Figure 7 shows the surface of thin films when there are several layers of coating. From Fig. 7 (a), the surface was even and there was nearly no crack. It could reduce reflection and had good transparency. The property of thin films is excellent. Fig. 7 (b) shows the surface of thin films when there were two layers of coating and there existed much regular crack. The property of thin films is good. Fig. 7 (c) illustrates the surface of thin films when there were three layers of coating and there existed much irregular crack. The property of thin films is not good. Figure 7 (d) shows the surface of thin films when there were four layers of coating. It was not even and there existed much irregular crack and the coatings appeared several layers. The property of thin films is not good.

3.7.2 The effect of coating layers on the absorption of thin films
Figure 8 shows the UV-visible spectra of colored iron oxide thin films coated with different layers, including 4-layer film, 3-layer film, 2-layer film and 1-layer film. It can be seen that the absorbance value increased with the increase of the film layers. In the multi-layer structured thin films, the
interface has some impact on the optical absorption of thin films. On the one hand, reflection happens on the film surface. On the other hand, the visible light would vibrate at the interface and it could cause interference if the film is not too thick. When the film layers increase, more reflection is produced on the surface of thin films. Thus, the light absorption rate increases along with it. Transparent metal-Au, Pt, Cu and Ag-thin films are not only excellent reflector of infrared light, but also reflector of visible light. The reason is the free carrier concentration of them is ~1020cm⁻¹ [18-19]. The films should be so thin that they could increase the transparency of visible light region and maintain the strong reflectivity of infrared light region.

![Absorbance vs Wavelength](image)

**Fig. 8** The UV-visible spectra of colored iron oxide thin films coated with different layers of a) 4, b) 3, c) 2 and d) 1

4. Conclusions

Even and reddish iron oxide thin films with excellent performance are prepared when the volume ratio of TEOS, EtOH and de-ionized is 15: 13: 1. However, different H₂O amounts could lead to different morphology of iron oxide nanoparticles. The absorption edge wavelength of colored iron oxide thin films is 350.2nm and the absorbance increases with the increase of coating layers. The coating layer also influences the morphology of thin films. The band angle of Si-O bond in the structure of PDMS makes thin films possess superior performance. And obtained thin films possess corrosion resistance in hydrochloric acid with pH=1. When 1.5 ml PDMS is added into the Sol system, thin films possess hydrophobility.

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