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PREPARATION AND CHARACTERIZATION OF FE_2O_3 MICRO-NANO MATERIALS

Shitao Wu[1*] and Guoxi Wu[2]

*[1] College of Light Industry Science and Engineering, Nanjing Forestry University, Nanjing 210037, China;
[2] School of Urban Planning & Landscaping, XuChang University, XuChang, 461000, China.

Email: iebopingzhang@163.com; wgx1217@126.com

ABSTRACT

Micro-nano Fe_2O_3 particles with different morphologies were prepared by a hydrothermal method under different reaction conditions using FeCl3 and ammonia as raw materials. The crystallinity and morphology of the products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. By studying the influence of different pH, reaction temperature, concentration of reaction solution, Ammonia acceleration on the products, the optimum conditions of micro-nano Fe_2O_3 particles were determined. The optical absorption properties of the optimum conditions of micro-nano Fe_2O_3 were characterized by ultraviolet visible near infrared (UV-Vis-NIR) absorption spectrometer.

Keywords: Micro-nano Fe_2O_3; Hydrothermal method; Preparation; Characterization.

1. INTRODUCTION

Nano-particles have quantum size effect, surface effect, small size effect, macro quantum tunneling effect, coulomb blockage effect and dielectric confinement effect. These effects make it different from conventional solids and macro particles in terms of light, magnetism, electricity, heat, mechanical property, physical property and chemical property. It is then destined to have tremendous potential and application prospects in many fields [1]. Micro-nano Fe_2O_3 materials not only have extensive uses and excellent performance like traditional nano materials, but also low cost. Along with constant development of material science and technology, preparation method of nano Fe_2O_3 has been always renewed to meet urgent requirements in the field of new synthetic materials. Methods learn from each other and high-quality nano Fe_2O_3 materials are prepared. To date, researches on nano Fe_2O_3 mainly focus on the following issues: 1), develop new material sources, create new product, invent new technique and enhance product quality [2]; 2), study on the properties of nano Fe_2O_3 [3]; 3), preparation technology of compounding powder of smaller particle size (under 30nm). With the development of studies on nano Fe_2O_3 property, preparation technology and its application, nano Fe_2O_3 is expected to be used in fields of high-permeability soft magnetic ferrite and self-assembly two-dimensional thin film. Research on catalysis and transformation mechanism of electron transfer has guiding function for preparation of other metallic oxide powder.

Micro-nano Fe_2O_3 particles with different morphologies were prepared by a hydrothermal method under different reaction conditions using FeCl3 (FeCl3·6H2O) and ammonia (NH3·H2O) as raw materials. The crystallinity and morphology of the products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively. By studying the influence of different reaction conditions such as pH reaction temperature and concentration of reaction solution on the final products, the optimum conditions of preparation of micro-nano Fe_2O_3 particles were determined. The optical absorption properties of the products prepared under optimum conditions were characterized by ultraviolet visible near infrared (UV-Vis-NIR) absorption spectrometer.

2. NANO FE_2O_3 AND ITS RESEARCH STATUS

Nana Fe_2O_3 is the most stable ferric oxide chemical compound, having n- type semiconductor properties (Eg=2.1eV) [4]. It has well light resistance, weather resistance and magnetism. And it shows good absorptive action to ultraviolet ray. It also has good absorptive flocculation effect [5] and shielding effect to humus acid. So it can be widely used in many important fields of such like flocculants [3], flicker coating, plastic, leather, electron, automotive topcoat, sensor, semiconductor, catalyst and high-magnetic recording materials [6,7]. Plus it is low-cost and non-toxic. Therefore, nano Fe_2O_3 has promising application prospects. Properties of materials to a large extent depend on the size and morphology of particle. Thus synthetic method of Fe_2O_3 with different sizes and morphologies becomes a hot issue in this field. So far, several structures of nano Fe_2O_3 have already been developed.

They are: one-dimensional, discoid, granulate, fusiform, acicular, diamond-like, hollow sphere-like, pipe-in-pipe, hedgehog, tree branch-like and melon shaped [4,8].

In the past few years, researches on nano materials have been developed very fast. Current preparation methods of nano Fe_2O_3 include dry methods and wet methods [9]. Dry methods include resistance heating method, electric arc method, plasma method, pulse current method, high-frequency induction heating method, laser ablation method and sputtering method; and wet methods include hydrothermal method, sol-gel method, hydrolysis method, micro-emulsion method, electrochemical process and method of precipitation [10, 11]. Products from dry methods are well-quality and this sort of method has short technical process and good operating environment. Under this method, particles are equally distributed, superfine and finely spread. However, despite of all these advantages, its processing is difficult technically. It has high requirements to the materials and structure of equipment. Raw materials in wet methods are easy to get and can be used directly (only proper purification treatment needed). Particles are controllable and operation is easy to handle. Thus wet methods are highly attached importance. Their application is especially common in industrial production. Hydrothermal method in wet methods is easy to operate, plus its reaction conditions are simple to handle. So it is a relatively simple preparation method in terms of technical equipment. But how to prepare nano Fe_2O_3 with good size and morphology is still a key issue in promoting its application in many fields. Studies discovered that concentration of reaction solution, reaction temperature, dropping speed of ammonia and pH values of reaction solution all have huge impact on the crystallinity and morphology of the products. Hence with the best reaction temperature, dropping speed of ammonia and pH values being determined, cost of production can be largely reduced.

This thesis adopts hydrothermal method to compound products by altering reaction conditions like reaction temperature, dropping speed of ammonia and pH. Through examinations of sample products, the optimum synthesis conditions are determined. And the absorptive character of the products prepared under optimum conditions were characterized by ultraviolet visible near infrared (UV-Vis-NIR) method.

3. EXPERIMENT

3.1 Reagent and instrument

Principal reagents used in this experiment are listed in table 1 and instruments in table 2.

Table 1. Principal reagents used in this experiment

Name of the reagent	Molecular formula	Reagent purity	manufacturer
Strong ammonia	$NH_3 \cdot H_2O$	analytically pure	Tianjin Kaitong Chemical Reagent Co., Ltd
FeCl3	$FeCl_3 \cdot 4H_2O$	analytically pure	Tianjin Kemiou Chemical Reagent Co., Ltd
anhydrous ethanol	C_2H_5OH	analytically pure	Sinopharm Chemical Reagent Co., Ltd

Table 2. Principal instruments used in this experiment

Name of instrument	Type	manufacturer
electronic balance	BS/BT	Beijing Sartorius co., LTD.
Heating fraction model (voltage adjusting and temperature controlling)	DF-101S	Gongyi Yuhua Instrument co., LTD.
Numerical control ultrasonic cleaner	KQ-300DE	Kunshan Ultrosonic Instrument co., LTD
thermostatic blast oven	ZFD-5040	Shanghai Zhicheng Analyrical Instrument Manufacturing co., LTD
vacuum drying chamber	DZF-6021	Shanghai Yihen Scientific Instrument co., LTD
High-speed tabletop centrifuge	GT16-3	Beijing Era Beili Centrifuge co., LTD
X-ray powder diffractometer	D8-ADVANCE	Brucker AXS, Germany
ultraviolet visible near infrared (UV—Vis—NIR) absorption spectrometer	Cray5000	Agilent, USA
scanning electron microscopy	EVOLS 15	ZEISS, Germany
agate mortar	12 cm	Shanghai Longtuo Equipment co., LTD

3.2 Experimental procedures

Fetch certain amount of FeCl3 and dissolve it in 20mL distilled water under stirring condition. Once dissolution completed, controll different pH and dropping speed of ammonia. And when the dropping procedure is done, solution is transferred to the reaction still immediately with different reaction temperatures and times controlled as well. When the experiment is done, colorless and transparent solution can be observed obviously and there is red sediment at the bottom of the reaction still. Centrifugalize and wash (use deionized water and anhydrous ethanol, three times each) the sediment. Then put it in the constant-temperature vacuum drying oven to conduct natural cooling and grinding. Products are prepared.

3.3 Characterization of products

Use X-ray diffractometer (XRD, Bruker, Cu) to analyze the purity and crystallinity of products under such conditions: voltage 40kV, electric current 40mA, scanning speed 0.2º.S-1 and scanning angle 20º~90º. Then use scanning electron microscopy (SEM, ZEISS) to observe its morphology. Finally use ultraviolet visible near infrared (UV-Vis-NIR) absorption spectrometer to characterize the absorptive features of products made under optimum conditions.

4. RESULTS AND DISCUSSION

4.1 Influences of different solution concentration to micro-nano Fe_2O_3 preparation

Figure 1 is the XRD figure of products prepared under different solution concentration conditions (all other conditions remain the same). All diffraction peaks in a curve correspond to standard PDF card (Number 01-089-0599) of Fe_2O_3. All diffraction peaks in b curve correspond to standard PDF card (Number 01-089-8104) of Fe_2O_3. And all diffraction peaks in c and d curves correspond to standard PDF card (Number 00-002-0915) of Fe_2O_3. That explains that the product obtained is pure Fe_2O_3. To conclude, different solution concentrations have no effects on the purity of the products.

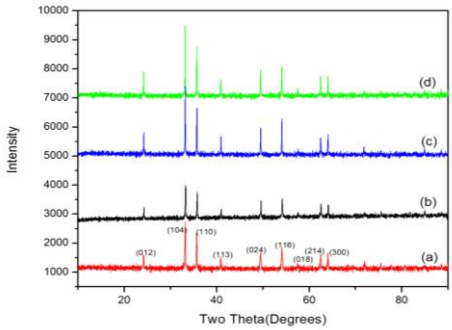
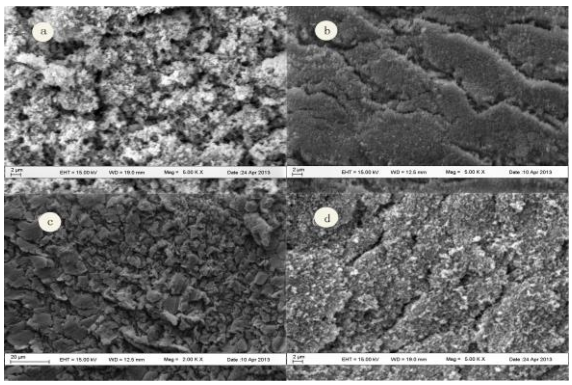


Figure 1. The XRD figure of products prepared under different solution concentrations

Figure 2 is the SEM figure of products prepared under different solution concentration conditions (all other conditions remain the same). From the figure it can be seen that products demonstrated in a are fine particles, particle size distribution is not equal, being 0.1~1μm; products in b are small spherical particles, particle size distribution is relatively equal, being approximately 0.1μm; products in c have no concrete morphologies; products in d are granules with unequal particle size distribution, being 0.5~2μm. That explains that solution concentration has great impact on the morphology of products. Relatively speaking, products' particle size distribution is uniform when raw material is 0.01mol, so the morphology is fine. Therefore, this experiment chooses 0.50 mol·L-1 as the optimum concentration of reaction solution.

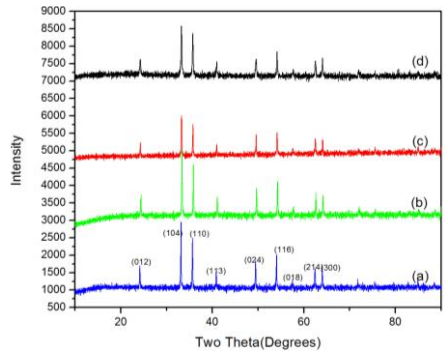


(a)0.25 mol·L-1 (b)0.50 mol·L-1 (c)0.75 mol·L-1 (d)1.00 mol·L-1 (a)0.25 mol·L-1 (b)0.50 mol·L-1 (c)0.75 mol·L-1 (d)1.00 mol·L-1

Figure 2. The SEM figure of products prepared under different solution concentrations

4.2 Influences of different dropping speed of ammonia to Micro-nano Fe_2O_3 preparation

Figure 3 is the XRD figure of products prepared under different dropping speed of ammonia conditions (all other conditions remain the same). From the figure it can be seen that all diffraction peaks in a curve correspond to standard PDF card (Number 01-089-0915) of Fe_2O_3. All diffraction peaks in b, c and d curves correspond to standard PDF card (Number 01-089-8104) of Fe_2O_3. That explains that the product obtained is pure Fe_2O_3. To conclude, different dropping speeds of ammonia have no effects on the purity of the products.



(a) 1 s·drop-1 (b) 10 s·drop-1 (c)30 s·drop-1 (d) 60 s·drop-1

Figure 3. The XRD figure of products prepared under different dropping speed of ammonia

Figure 4 is the SEM figure of products prepared under different dropping speed of ammonia conditions (all other conditions remain the same). From the figure it can be seen that products demonstrated in a are granules, particle size distribution is not uniform with reunion phenomenon, being 0.1~0.5μm; products in b are also granules, particle size distribution is not uniform either with reunion phenomenon, being approximately 0.1~1μm; products in c are granules as well, particle size distribution is equal, being approximately 0.1μm; products in d are granules with reunion phenomenon, being about 0.5μm. That explains that different dropping speeds of ammonia have great impact on the morphology of products. Relatively speaking, when dropping speed of ammonia is 30 s·drop-1, the dispersion is uniform, the particle size is even and the morphology is good. Thus, this experiment chooses 30s·drop-1 as the optimum dropping speed of ammonia.

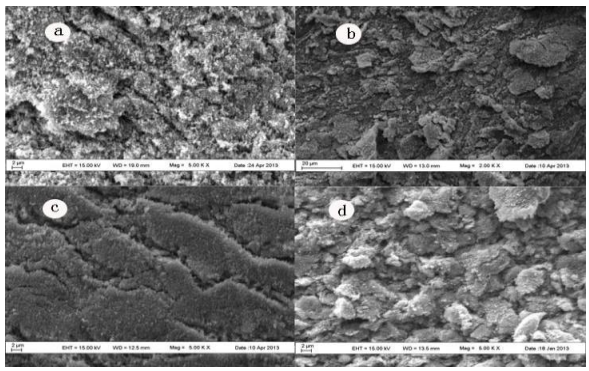
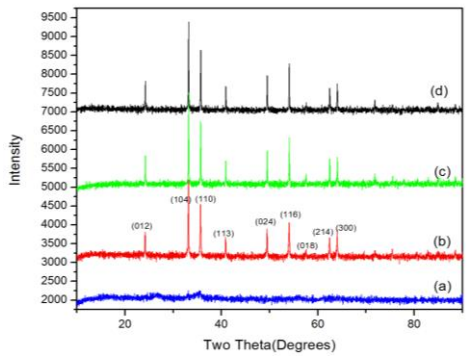


Figure 4. The SEM figure of products prepared under different dropping speed of ammonia

4.3 Influences of different reaction temperatures to Micro-nano Fe_2O_3 preparation

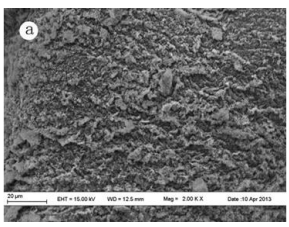
Figure 5 the XRD figure of products prepared under different reaction temperature conditions (all other conditions remain the same). From the figure it can be seen that all diffraction peaks in a curve cannot correspond to standard PDF card of Fe_2O_3. All diffraction peaks in b and c curves correspond to standard PDF card (Number 01-089-0915) of Fe_2O_3. All diffraction peaks in d curve correspond to standard PDF card (Number 00-002-8104) of Fe_2O_3. That reveals the fact that products in a curve are not pure Fe_2O_3 and products in b, c and d are pure. Different reaction temperatures have influences on the purity of products. Products are pure when reaction temperature is not lower than 180 ℃ and when it is lower than 180 ℃, energy obtained by the molecules in reaction process is less, reaction molecule is not active. Thus hydrolysis is not complete in short time, and then no pure products can be acquired consequently.



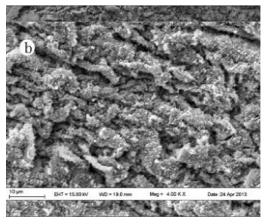
(a) 1 s drop-1 (b) 10 s drop-1 (c)30 s drop-1(d) 60 s drop-1 (a) 160 ℃ (b) 180 ℃ (c) 200 ℃ (d) 230 ℃

Figure 5. The XRD figure of products prepared under different reaction temperatures

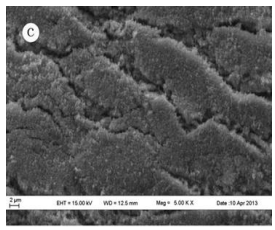
Figure 6 is the SEM figure of products prepared under different reaction temperature conditions (all other conditions remain the same). From the figure, products in a are granules, particle size distribution is not uniform with reunion phenomenon, being 1~2μm; products in b are also granules, particle size distribution is not uniform either, being 0.5~1μm; products in c are small spherical particles, particle size distribution is equal, being approximately 0.1μm. It explains that different reaction temperatures have huge impact on the morphology of products. Relatively speaking, products prepared under 230 ℃ reaction temperature are dispersed uniformly with even particle size and good morphology. Therefore, 230 ℃ is selected to be the optimum reaction temperature in this experiment.



(a) 180 ℃



(b) 200 ℃

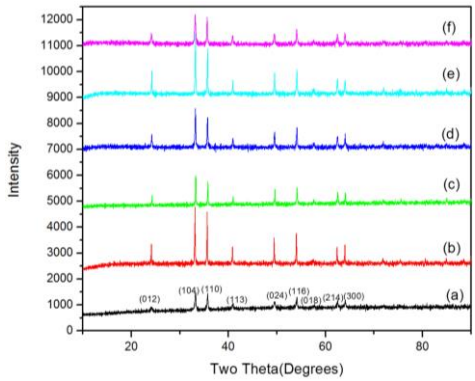


(c) 230 ℃

Figure 6. The SEM figure of products prepared under different reaction temperatures

4.4 Influences of different pH values to Micro-nano Fe_2O_3 preparation

Figure 7 is the XRD figure of products prepared under different pH values (all other conditions remain the same). All diffraction peaks in a curve correspond to standard PDF card (Number 089-8103) of Fe_2O_3. All diffraction peaks in b curve correspond to standard PDF card (Number 01-089-8104) of Fe_2O_3. And all diffraction peaks in c, d, e and f curves correspond to standard PDF card (Number 00-002-0915) of Fe_2O_3. It illustrates that the products are pure Fe_2O_3.



(a) pH=3 (b) pH=6 (c) pH=7 (d) pH=8 (e) pH=9 (f) pH=10

Figure 7. The XRD figure of products prepared under different pH values

The results above show that pH of solution has no effect on the purity of products. Figure 8 is the SEM figure of products prepared under different pH conditions (all other conditions remain the same). From the figure it can be seen that when pH=3, products are mostly spherical-like particles, particle size distribution is not uniform, being 1~3μm; when pH=6, products are still mostly spherical-like particles, particle size distribution is not uniform, being 0.1~1μm; when pH=7, products are fine particles, particle distribution is uniform, being approximately 0.1μm; when pH=8, morphology of the products is not obvious, reunion phenomenon is very strong; when pH=9, products are small ellipsoidal particles, particle size distribution is uniform,

being 1.5~3μm; when pH=10, products are also fine particles, particle size distribution is not uniform, being 0.1~1μm. That concludes that the particle size of known products becomes small and then turn large along with the rise of pH; and when pH=9, products are small ellipsoidal particles, particle size distribution is uniform, being 1.5~3μm. This morphology is better than that of other groups with different pH values. So pH=9 is the optimum reaction pH. Because pH value influences the hydrolysis extent of Fe3+, in weak acid environment (pH<7), one-time nucleation in reaction system is not complete, growing rate of particle is faster than forming rate of crystal nucleus. Repeated nucleation results in multi-granularity particle generation. That must lead to unequal particle sizes and irregular morphologies. In weak alkaline environment (pH≥7), the hydrolysis is complete. At this moment, nucleation rate in the system is faster than growing rate of the nucleus. It is easy to generate particles with uniform particle sizes. Thus, with pH values being between 7~10, nano Fe_2O_3 particles with small particle sizes and narrow particle size distributions can be prepared.

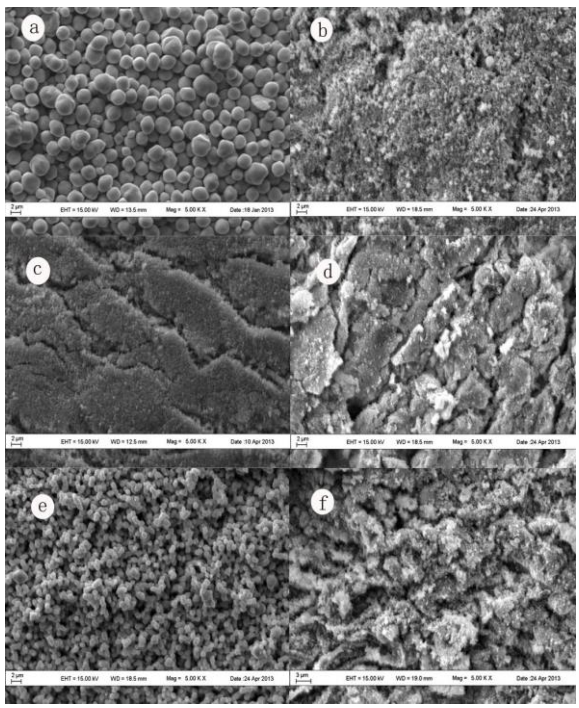
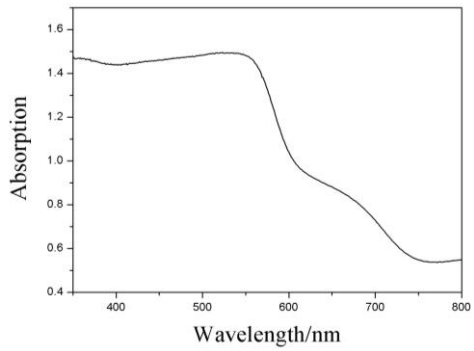


Figure 8. The SEM figure of products prepared under different pH values

To sum up, the optimum experimental conditions are: concentration of reaction solution is 0.50 mol·L-1, reaction temperature is 230 ℃, dropping speed of ammonia is 30 s·drop-1 and pH is 9.

4.5 Characterization of products' ultraviolet visible near infrared (UV-Vis-NIR) absorption

To determine the optical property of compounded Micro-nano Fe_2O_3 materials, we conducted feature characterization of ultraviolet visible near infrared (UV-Vis-NIR) absorption to Micro-nano Fe_2O_3 prepared under optimum conditions. Results are shown in figure 9.



(a)pH=3 (b) pH=6 (c) pH=7 (d) pH=8 (e) pH=9 (f) pH=10

Figure 9. Products' ultraviolet visible near infrared (UV-Vis-NIR) absorption spectrum

From figure 9 it can be observed that the light absorption regions of products include UV region and visible region. And they keep extending. Especially in UV region and the whole visible region, the absorption is strong. Through calculation based on the figure above, absorption edge λg is about 660 nm. And then through Eg=1240/λg (λg is the absorption edge) the product band gap can be calculated as 1.9eV. Therefore, the band gap value of Micro-nano Fe_2O_3 prepared in this way is lower than that mentioned in the literature (2.1 eV) [2].

This experiment uses FeCl3, ammonia as raw materials and hydrothermal method to prepare stable Micro-nano Fe_2O_3 materials with well-distributed particle sizes after which XRD is adopted to analyze purity degree and SEM is used to observe the morphology and size. Pure micro-nano scale Fe_2O_3 is acquired. This preparation method is simple and quick. The raw material FeCl3 transforms completely into Fe_2O_3 after reaction. Use ratio of raw material reaches 100%. The current developmental requirements are matched. The diameter of products compounded by hydrothermal method in this experiment is approximately 0.1~4μm. By studying the influences of pH, reaction temperature and concentration of reaction solution on products, the optimum experimental conditions are determined: pH is 9, reaction temperature is 230 ℃, concentration of reaction solution is 0.50 mol·L-1 and dropping speed of ammonia is 30 s·drop-1. Due to the different morphologies, particles have different features. And the production output also varies from different compounding conditions. Compounding methods need to be selected in line with specific situations.

The outer electrons of the nano materials produce separated electronic energy levels, and there are great differences between each energy level. The UV-Visible absorption spectrum is an absorption spectrum produced by electron energy level transition after UV or visible light irradiation with a certain frequency. Generally the spectral lines of Nano materials' UV-vis absorption spectroscopy are not separated, but overlapped and relatively close to a spectral line with a certain width. It is because at the same time of electron transition, molecular vibrational or rotational energy levels will also absorb photon and lead to electron transition, and the absorption spectra produced and the electronic absorption spectra overlap each other. The band gap of semiconductor materials can be estimated by the test analysis of UV-vis absorption spectroscopy.

Because different materials have different molecules and atoms, and the molecular structure is also different, the

absorption of light energy is accordingly different. Thus, each material has its unique spectral absorption curve. It is the basis of qualitative and quantitative analysis of the UV-vis Spectrophotometer to determine the content of the material by the absorbed dose rate.

Through UV visible diffuse reflectance spectra, the optical properties of the Fe_2O_3 were analyzed, and the band gap of the optical properties was about 1.9 eV. The compounded Micro-nano Fe_2O_3 materials have strong absorption to ultraviolet and visible light.

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