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Preparation of nano materials by rheological phase reaction method

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Introduction

Green chemistry is a new issue that is the great concerned and expected to achieve in twenty-first century. Although we can get new material of human needs with traditional chemical methods, in many occasions, neither not only use of resources efficiently, but also produce large emissions that will cause serious environmental pollution. Green chemistry is a higher level of chemical, Anastas and Waner [1] proposed the twelve principles of green chemistry. Its main feature is the "atom economy", it means to take full advantage of each raw material atom in the process of acquiring new material transforming, and achieve "zero emissions". Therefore it not only can make full use of resources, but also without producing pollution. Green chemistry can change waste into treasure and improve economic efficiency. Traditional chemical shift towards green chemistry can be seen as chemical from "extensive" to "intensive" changes.

Inorganic synthesis chemistry is a research of inorganic compound of the structure, properties, reactivity and scientific applications. Inorganic synthetic chemistry has been vigorous development with modern experimental methods of updating and developing. There the liquid phase synthesis and solid-phase synthesis of inorganic synthetic chemistry have developed into two main synthesis methods. The advantage of phase synthesis is obvious, because the reaction is carried out in the liquid phase, the reactants is in a highly dispersed state and generally carried out completely and rapidly, the desired product can usually be obtained. But the reaction is affected by many factors and constraints, such as solubility of reactants, solubility of product, chemical equilibrium and pH. Either precipitation method (including direct precipitation, co-precipitation, homogeneous precipitation method and the complex precipitation) or now developed sol-gel method, hydrothermal method (including hydrothermal crystallization method, a hydrothermal synthesis, hydrothermal decomposition, hydrothermal oxidation, hydrothermal precipitation) and the thermal solvent are so on.

Solid-phase synthesis reaction is one of the first used in chemical synthesis reactions; it is particularly suitable for high temperature reactions. In addition to high-temperature solid-phase synthesis, modern solid-phase chemical synthesis also include intermediate temperature and low temperature solid-phase synthesis. Solid-phase reactions include four stages of interface diffusion, reaction, nucleation and growth. Although solid-phase reaction does not have advantage of the above mentioned liquid phase synthesis, it has characteristic of high selectivity, high efficiency and simple technology process, this method is still widely used in production and life.

As it can be seen from the above discussion, the conventional liquid and solid-phase synthesis can be said to be complementary.

Rheological phase reaction

The concept of rheological phase reaction

It is between the liquid state and the solid phase material in nature and everyday life, such as debris, concrete, mud, ink, jam and ceramics slurry. These substances have common nature—rheology properties.

Rheological phase system comes from rheology. It is the study of science of material flow and deformation. Rheological phase refers to a state of disguised rheological properties, it has complex structure or composition in the chemically, properties between solid and liquid in mechanics, or
contains both solid particles and liquid, it can flow or slow flow and forma complex of macro-uniform system.

The rheological phase reaction is chemical reaction with rheological phase joining in the reaction system, it is a kind of soft chemical synthesis method of synthetic combining rheology and chemistry synthesis and is a new green chemical synthesis method.

For example, the simplest solid-solid rheological phase reaction, the solid reactant is fully grinded and uniformity mixed, the reaction is mixed by appropriate means, adding the right amount of water or other solvents substance as a solvent to prepare a solid particles and liquid uniform distribution of matter, the solid particles are completely witted, but the solid and liquid are not layered or become viscous solid and liquid mixture system - rheological phase system, and then control in a proper reaction conditions and closed reaction for a certain time , the reaction is complete to obtain the desired product of a single crystal phase.

**Characteristic of rheological phase reaction method**

The rheological phase reaction method is a process of preparing compounds or materials from a solid–liquid rheological mixture. The solid reactants are fully mixed in the proper molar ratio, and are made up by adding a proper amount of water or other solvents to form a solid–liquid rheological body, in which the solid particles and liquid substances are uniformly distributed. After reaction under suitable experimental conditions, the product is obtained. There are many advantages in the rheological phase system, such as the surface area of solid particles can be efficiently utilized, the contact between solid particles and fluid is close and uniform, and heat exchange is very good. Local overheating can be avoided, and the reaction temperature is easy to be controlled. By means of this method, many functional materials and compounds with novel structures and properties have been obtained.

In the rheological phase reaction process, the surface area of the solid particles can beef festively used, close contact with the fluid, uniform, good heat exchange, does not occur local overheating and the temperature is easy to be adjusted. In this state, the concentration of many substances will behave surplus reaction phenomena and properties. Rheological phase reaction is an energy efficient, pollution reduction and green chemical synthesis route. The advantages of rheological phase reaction show mainly in the following aspects:

1) In the rheological phase system, the solid particles in the fluid distribution, in close contact with the surface that can be effectively used; the reaction can be carried out more fully;
2) We can get pure single compound, the product with the reaction vessel volume ratio is very high, and also avoid to be produced a lot of waste. It is a highly efficient, environmentally friendly, energy-saving, economical and green chemistry;
3) Fluid is good heat exchange and heat stability, it can avoid local overheating and the temperature is easily adjustable;
4) In the rheological phase system, many substances will show the super concentration phenomena and new reaction features, and we can even get some compounds of new structures and specific functions with self-assembled;
5) Functional nano materials and amorphous materials can be easily obtained with rheological phase reaction technology;
6) Even more interesting thing is that we can also get a large single crystal by use of rheological phase reaction method, which has opened up a new way to prepare the single crystal. These characteristics conform to the current requirements of the development of green chemistry community, and thus this method is welcomed by more and more people.
**Rheological phase reaction principle and process**

The rheological phase reaction method is a process of preparing compounds or materials from solid–liquid rheological mixture. That is, the solid reactants are fully mixed in a proper molar ratio, made up by adding a proper amount of water or other solvents to a solid–liquid rheological body, in which the solid particles and liquid substance are uniformly distributed. Then after reaction under suitable conditions, the products are obtained. Under the solid-liquid rheological state, many substances have new reaction properties.

A typical rheological phase reaction must go through the following five steps: dissolution, diffusion, reaction, nucleation and growth. For the rheological phase reaction, reaction steps may be expressed in (1).

\[
\begin{align*}
A_{(a)} + B_{(b)} + nH_2O_{(l)} &\rightarrow A_{(l)} + B_{(l)} + nH_2O_{(l)} \\
\rightarrow C_{(amorphous)} &\rightarrow C_{(crystal nucleus)} \rightarrow C_{(crystal)}
\end{align*}
\]

Thus, the rheological phase reaction through five stages, namely dissolution-diffusion-reaction-growth. But because of the rate at different stages of the reaction system or in the same reaction under different conditions are not the same, the characteristics of each stage are not legible, the total response characteristics show reaction rate only determining step characteristics.

**Rheological phase reaction method of the development process**

Rheological phase synthesis method is developed on the basis of a rheological phase reaction method, originally it was developed and defined a new chemical synthesis method by J. T. Sun professor and his team of Wuhan University in 1998, and this method had successfully synthesized a number of metal salts of aromatic carboxylic acids. Rheological phase reaction method proposed and experienced liquid water film reaction→solid liquid reaction→semi-solid state reaction reaction→rheological phase reaction several stages, and the method has been successfully used to study the preparation of lithium-ion battery electrode materials. Exploring chemical reaction principle in rheological phase reaction state will have important scientific significance for the development of nanomaterials, the rheological phase reaction method of the development process are shown tab.1.

**TABLE 1**
Rheological phase reaction method of the development process

<table>
<thead>
<tr>
<th>Name</th>
<th>Time</th>
<th>Research Scope</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hooke and Newton</td>
<td>17century</td>
<td>Elastic solid and fluid flow</td>
<td>Thematerial of viscoelasticity theory</td>
</tr>
<tr>
<td>Bingham EC</td>
<td>1929year</td>
<td>Object of shape and flow</td>
<td>rheology</td>
</tr>
<tr>
<td>Ju Tang Sun (China)</td>
<td>End of 20 century</td>
<td>Rheology combined with chemical reaction</td>
<td>rheological phase reaction</td>
</tr>
</tbody>
</table>

The reaction conditions are easy to be grasped, and the defects to obtain a single product with other methods to be solved, so that the obtained products are more accurate characterized and this method is recognized quickly by many researchers.
Classification of rheological phase reaction method

This react directly after mixing the reactants flow of water into a disguise and then in a classification of rheological phase reaction. According to different liquid medium used in rheological phase reaction process, the reaction conditions requirements are different sometimes; the corresponding applies to the type of material preparation. Generally it divided into water as a media and an organic solvent as the medium of rheological phase reaction.

Rheological phase reaction with water as the medium

Under the action of external force and the heating, partial dissolution of the reactants begin, where the solvent water in the reaction mass and play the role of the reactor. Different from the pure liquid phase reaction, since the presence of a small amount of solvent water without changing the reaction isotropic and limits, only serve to accelerate the reaction and reduce the reaction temperature. This is because a small amount of solvent water cannot be completely solvated reactants, so the huge impact of liquid phase reaction solvent will not appear on the rheological phase reaction. And since the flow in the heating phase reaction process mainly carried out and the reactants as solvent water formed a uniform flow of disguise, also played a role in uniform heating of the reaction system and the full utilization of surface area.

In some rheological phase reaction, the solvent from the water as a media in addition to mass and heat transfer effect, but it is often used as reactants or reaction products present. Currently most of the organic acid and metal oxides are used in rheological phase reaction, and it is found that single crystal preparation with this method has tremendous potential.

Organic solvent as the medium of rheological phase reaction

In the preparation of metal oxide, water as the medium due to the reaction product OH formed by the reaction system in the heating drying process, hydrogen or crystal bridge effect may be easy to agglomerate the product. When there are special requirements of the product size or temperature, we often joined partially or completely organic solvents such as ethanolor others as reaction medium. After reaction there generally required repeated washing of the product and dried, compared with water as the medium, organic as medium has more width of the interfacial tension, the apparent viscosity and temperature of the heating operation. The temperature and shear rate of polishing can greatly affect the viscosity, while the viscosity has a direct impact on the solid reactant in a uniform distribution in the medium. Thus in the study, it’s better to start from the medium and the starting rheological properties of the reactants, each component viscoelasticity test, shear rate and temperature influence on the flow system, morphology comprehensive selection of reaction conditions. While an organic solvent as the medium, the cost is higher.

Application of rheological phase reaction

At first, only a few types of compounds are prepared by rheological phase reaction, which may be mainly because various research direction determine the type of compounds prepared. The synthesis of research focuses on Central South University, Wuhan University and its research applications are mainly concentrated on the metal-organic salts, metal oxides and single crystal materials, which
disguise the system with flow super concentration and ease the impact on the defect nucleation. With the advantages of this approach continuing to show a lot, more and more researchers in disguise prepared using the stream and coming out of a lot of material. There include single crystal materials, elemental metal, metal oxide, composite metal oxide, metal organic salt, composite thermoelectric materials, negative temperature coefficient thermostats, advanced electrode materials, polycrystalline soft ferrite materials, inherently conducting polymers (ICPs) and so on.

**Single crystal material**

Since flow disguised system allows a large number of solid particles exist and a high concentration of the dispersed phase within the system, which enable it to prepare some of the less soluble conventional solution reaction difficulty to prepare single-crystal materials. At present, this method has been prepared under relatively mild the acid copper, salicylic acid Ni and other single crystals, and Wuhan University, M. C. Yin [2] had prepared a series of aromatic spindle acid complexes single crystal of novel structure and excellent luminescent properties with the rheological phase reaction system.

**Elemental metal**

Nanosized materials with novel properties present a wide potential application in many fields [3-4]. Constructions of well ordered and realizations of their potential applications have resulted in intensive research for the past few years. The demands of super fine metal powders have increased dramatically in the electronics, biotechnology, powder metallurgy and energy sources fields. Micro-nanostructured nickel with unique morphology, size and structure may exhibit superior functionality or provide new possibilities due to the composite structure, porosity, stability and the inherent properties of nanosized materials. Micro-nanostructured nickel has been prepared as anode materials for Li ion batteries, via a rheological phase reaction method. \( \text{Ni}_2\text{C}_2\text{O}_4\cdot x\text{H}_2\text{O} (x=2 \text{ or } 2.5) \) as precursors are obtained from the solid–liquid rheological mixture of \((\text{NH}_4)_2\text{C}_2\text{O}_4\cdot \text{H}_2\text{O} \) and \( \text{Ni(NO}_3)_2 \). The micro-nanostructured nickel displays an initial discharge capacity of 457 mAh g\(^{-1}\). It also has a remarkable cycling stability with an average capacity fade of 0.17% per cycle from 13th to 50th cycle in 0.01–3.00 V versus Li at a constant current density of 100 mA g\(^{-1}\).

**Metal oxide**

Over the last two decades, research on diluted magnetic semiconductors (DMS) have attracted much interest with the aim of identifying doped semiconducting materials with large magnetic moments and high curie temperature (TC) [5] for potential application in spintronic devices. These devices will use both the spin and charge of carriers [6]. Considerable effort has been devoted to studying wide-band-gap oxide or nitride-based DMS, such as transitional metal-doped \( \text{SnO}_2 \) [7], \( \text{ZnO} \), \( \text{TiO}_2 \) [8], \( \text{In}_2\text{O}_3 \) [9], \( \text{GaN} \), etc., owing to their transparency in the visible region and as well as their magnetic property at or above room temperature [10].

Cao et al [11] used \( \text{H}_2\text{C}_2\text{O}_4\cdot \text{H}_2\text{O} \) and \( \text{ZnO} \) as raw materials, nano meter \( \text{ZnO} \) was prepared with rheological phase reaction method. The optimal preparation conditions were decided by ort hogonaltes. The precursor ( \( \text{ZnC}_2\text{O}_4\cdot 2\ \text{H}_2\text{O} \) ) was synthesized by rheological phase reaction at 60°C. After 3h in 450°C, the precursor decomposed into nano meter \( \text{ZnO} \).

Allemaiaet al [12] reported nanoparticles of a series of arsenic–cobalt mixed valency spinel oxides of theoretical formula \( \text{As}_x\text{Co}_3-x\cdot \text{O}_4 (x=0, 0.005, 0.01, 0.015, 0.024) \) have been successfully prepared by the rheological phase reaction and the pyrolysis method. The products of the precursor at 500°C resulted
in the formation of arsenic-doped cobalt oxide nanoparticles of 48 nm in crystal size. Arsenic-doped cobalt oxide nanoparticles have been successfully synthesized by this method. The line width analysis is consistent with an average crystalline size of \( \approx 45 \) nm. The SEM study shows the ultrafine spherical particles with a homogenous distribution. Upon thermal analysis at 936.34°C arsenic-doped \( \text{Co}_3\text{O}_4 \) nanoparticles could be converted to \( \text{SbCoO} \), \( \text{CoO} \) nanoparticles.

Zhou et al [13] reported that La, Y and Gd salicylate precursor have synthesized with rheological phase reaction method, the resulting solid residue nanoscale powders \( \text{R}_2\text{O}_3 \) was obtained in air at 800°C thermal decomposition, \( \text{R}_2\text{O}_3 \) was substantially spherical nanoparticles; and \( \text{R}_2\text{O}_3 \) median particle size of \( (d_{50}) \) was 19.3 nm (\( \text{La}_2\text{O}_3 \)), 53.8 nm (\( \text{Y}_2\text{O}_3 \)) and 28.6 nm (\( \text{Gd}_2\text{O}_3 \)), the results are consistent to X-ray powder diffraction and scanning transmission electron microscopy.

Polycrystalline soft ferrite materials are attractive for microwave applications, high-quality filters, rod antennas, radio frequency circuits, transformer cores, read/write heads for high speed digital tapes and also sensors, owing to their high resistivity, low magnetic coercivity, low eddy current losses, high Curie temperature and chemical stability. It is interesting that the desired electrical and magnetic properties of soft ferrites can be tailored by controlling the different types and amounts of substituents. Until now, many investigations have been carried out to make further improvements on the electrical and magnetic properties of substituted ferrites. From Rezlescu et al.’s study [14], rare earth ions have limited solubility in the spinel lattice and affect the physical properties of substituted ferrite due to their larger ionic radius. When rare earth ions enter the octahedral (B-site), they can replace \( \text{Fe}^{3+} \) ions at low rare earth ions content.

Jin et al [15] have prepared precursor using nickel acetate, ferric hydroxide and oxalic acid as raw materials by rheological phase reaction methods, nano-nickel ferrite powder can be obtained at different temperatures calcining. Powder was square block, with an average particle size of about 30 nm, distribution, good dispersion. Compared to other methods, the calcination temperature of rheological phase reaction methods is low, you can overcome the defects of particles increase and agglomeration caused in high-temperature calcination.

Hu [16] has prepared silver vanadium oxide of one-dimensional material using a band of particle \( \text{V}_2\text{O}_5 \) sol as vanadium source by rheological phase self-assembly, its length is a few to tens micrometers and diameter 100~400 nm nanofiber gathered into bundles of \( \beta \)-\( \text{AgVO}_3 \), and the reaction can be carried out at a lower temperature.

**Metal organic salt**

Metal organic salt is prepared by rheological phase reaction is one of the important applications, the literature were prepared by flow disguised magnesium phthalate, the result of pure magnesium phthalate, which is a layered structure is monoclinic crystal "will be obtained in the decomposition of nitrogen wake onions, benzophenone compound" more difficult to direct synthesis of these compounds, the magnesium phthalate thermal decomposition in nitrogen for such compounds may be prepared to provide simple and feasible method for green synthesis.

**Advanced electrode materials** [17]

Advanced electrode materials for energy storage and conversion systems, such as high energy density batteries, super capacitors, and fuel cells, have been increasingly focused on by material scientists all over the world in recent years. The transition-metal oxides, such as \( \text{RuO}_2 \), \( \text{MnO}_2 \), \( \text{NiO} \), and \( \text{Co}_3\text{O}_4 \), and transition-metal complex oxides, such as \( \text{LiMn}_2\text{O}_4 \), \( \text{LiCoO}_2 \), \( \text{LiFePO}_4 \), and \( \text{Li}_4\text{Ti}_5\text{O}_{12} \), are some of the most important electrode materials for these systems. Some of these materials have been used for practical
applications; however, there are still increasing requirement to meet advanced development for electrode materials with improved performance. So, it is extreme important to develop alternative electrode materials with a combination of low cost and improved performances.

Recently, indium oxide (In$_2$O$_3$) has been studied for energy storage and conversion system applications. For example, Zhou et al. [18] have investigated the electrochemical properties of nanostructured In$_2$O$_3$ film in an organic electrolyte for a lithium battery, in which a large reversible capacity of nanostructured In$_2$O$_3$ thin film was found to be 883 mAh g$^{-1}$, corresponding to 8.9 Li per In$_2$O$_3$. Chang et al. [19] have also studied the capacitive performance of In$_2$O$_3$ nanoparticles (include nanospheres and nanorods) in the electrolyte of 1.0 M Na$_2$SO$_4$. This work shows that the performance of In$_2$O$_3$ is influenced by the morphology of In$_2$O$_3$, and the specific capacitance of In$_2$O$_3$ can achieve 105 F g$^{-1}$ for In$_2$O$_3$ nanorods. Prasad et al. [20] reported that nanostructured- and nanorod-shaped three-dimensional In$_2$O$_3$ prepared by a potentiodynamic method has evidently redox capacitive behaviors in 1 M Na$_2$SO$_4$ electrolyte. As a lithium-enriched indium oxide, LiInO$_2$ material should have evident a lithium ion insertion/extraction redox reaction in a suitable electrolyte, which can be applied in the energy storage and conversion devices. However, there are a very few literature reports on the electrochemical properties on the lithium-rich indium oxide (LiInO$_2$) as yet. Herein we report the synthesis of LiInO$_2$ by a very simple rheological phase method and study its electrochemical characteristics in LiOH and Li$_2$SO$_4$ solutions for the first time by means of analyzing cyclic voltammetry (CV) curves.

Conventional LiMnO$_2$ prepared used ion exchange, Lei et al. [21] first try to synthesize monoclinic structure NaMnO$_2$ with rheological phase under air atmosphere, and then obtain a product with layer monoclinic structure by the solvent thermal method at 120 °C. This method is simple more than traditional methods of synthesis process, obtained layer LiMnO$_2$ used as a secondary Lithium-ion battery cathode materials that exhibit good electrochemical charge-discharge cycle performance. He et al. [22] was prepared cubic spinel structure LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with heat treatment at 850 °C for 6 h by the rheological phase reaction method, its particle size was between 0.2 ~0.4μm. Through the relevant tests showed that the synthesis of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ is a high voltage, high-capacity, high rate capability and better performance of lithium-ion battery cathode material.

Li et al. [23] synthesized pinel Li$_2$Mn$_2$O$_4$ used LiNO$_3$ and electrolytic MnO$_2$ as raw material, organic solvents containing hydroxyl and water mixture as dispersant by rheological phase reaction method, relevant test results showed that spinel-type lithium manganese oxide compounds with average valence of Mn 3.5 at the calcination temperature of 760°C, its compound have good electrochemical performance, 4.05 V and 3.95 V two discharge platform, and have a good voltage stability, its initial discharge capacity is 117 mA·h·g$^{-1}$, charge-discharge efficiency is greater than 90%, the discharge capacity is about 102 mA·h·g$^{-1}$ after 20 cycles.

**Preparation example of nanomaterials by rheological phase reaction method**

**Micro-nanostructured nickel** [24]

(NH$_4$)$_2$C$_2$O$_4$·H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O and anhydrous ethanol were all analytical-grade reagents. Solutions were prepared by use of deionized water. (NH$_4$)$_2$C$_2$O$_4$·H$_2$O (48.87 g) was added in 5.0 M nickel nitrate solution [Ni(NO$_3$)$_2$·6H$_2$O (100g), H$_2$O (20 ml)] at 70–90 °C to form a rheological body with viscoelasticity. The rropy rheological body was fully dispersed with an appropriate amount of deionized water added,
then filtered, washed, dehydrated with anhydrous ethanol and dried at 80–90°C to yield NiC$_2$O$_4$·2H$_2$O (Precursor A), the overall yield was 99.76%. The nickel nitrate was added in supersaturated ammonium oxalate solution to give NiC$_2$O$_4$·2.5H$_2$O (Precursor B), the overall yield was 97.98%.

An appropriate amount of nickel oxalate was cased in sealed vessel. The air inside expanded and let out slowly when the thermal decomposition was carried out, which ensured the precursor was saturated with self-atmosphere. The vessel was heated up to 335°C in air furnace with a heating rate of 5°C min$^{-1}$, kept at 335°C for 6 h to give a black sample. The nickel obtained from the Precursor A and B was marked as Ni A and Ni B, respectively.

Fig. 1 presents the TG–DTG–DSC curves of Precursor A (6.223 mg) and B (7.620 mg). The specific temperature and mass losses are labeled on DSC–TG curves. Analysis shows that the molar compositions of Precursor A and B are NiC$_2$O$_4$·2H$_2$O and NiC$_2$O$_4$·2.5H$_2$O, respectively. The DSC peaks closely correspond to the weight changes observed on the TG curves. The thermal decomposition generally proceeds in two steps: dehydration and decomposition of the anhydrous oxalate. The mass loss before 200°C, characterized by a small endothermic peak on DSC curves, is ascribed to the dehydration of adsorptive water. XRD analysis confirms that the final products of thermal decomposition in Al crucible are nickel powders, which is different from the common reports on thermal decomposition of nickel oxalate in air. The thermal decomposition reaction formula of the precursors can be expressed as follows ($x = 2$ or 2.5):

\[ \text{NiC}_2\text{O}_4 \cdot x\text{H}_2\text{O} \rightarrow \text{NiC}_2\text{O}_4 + x\text{H}_2\text{O} \]  

(2)

\[ \text{NiC}_2\text{O}_4 \rightarrow \text{Ni} + 2\text{CO}_2 \]  

(3)

But thermal decomposition behaviors of the two precursors are different: the decomposition rate of Precursor B is twice than that of Precursor A (shown in DTG curves).
FIGURE 1.1
TG–DTG–DSC curves of Precursor A(a) and B(b) in covered Al crucible

Fig. 1.2a shows the XRD patterns of Precursor A and B prepared via rheological phase reaction method. The partial refined crystal lattice parameters calculated by the JADE5.EXE procedure are presented in Tab. 1.2.
TABLE 2
Lattice parameters of Precursor A and B

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Precursor A</th>
<th>Precursor B</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.G.</td>
<td>P2/m(No.10)</td>
<td>P2/m(No.10)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>7.8167(16)</td>
<td>9.8874(40)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>2.6607(6)</td>
<td>4.2409(19)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.9066(11)</td>
<td>6.5671(47)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>122.84</td>
<td>266.13</td>
</tr>
</tbody>
</table>

All characteristic diffraction peaks of two precursors are well indexed to the monoclinic phase of nickel oxalate, with the space group P2/m (No. 10). The broken line in Fig. 1.2a indicates that the two precursors are different from each other. Diffraction relative intensity and peak position of two XRD patterns are different from those reported in the literature (JCPDS File Card No. 25-0581). XRD patterns and lattice parameters of the products are given in Fig 1.2b and Tab. 1.3.

TABLE 3
Lattice parameters of Ni_A and Ni_B

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ni_A</th>
<th>Ni_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.G.</td>
<td>Fm3m(225)</td>
<td>Fm3m(225)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.5232(1)</td>
<td>3.5245(1)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>43.73</td>
<td>43.78</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>D_cal(gcm⁻³)</td>
<td>8.9150</td>
<td>8.9058</td>
</tr>
</tbody>
</table>

In order to get an accurate lattice parameters silicon element (internal standard) is added to compensate for sample displacement error (Fig. S4 and Fig. S5, Supplementary Information). Results show that lattice parameters and the position of main peaks of face centered cubic nickel are well consistent with the standard file (JCPDS File Card No. 04-0850), proving the sole existence of nickel particles. No sign of the formation of oxides species could be observed in Fig.1.2b. All diffraction peaks are very sharp, which indicates that the high crystallinities of the products.
FIGURE 1.2
XRD patterns of oxalate nickel precursors (a) and nickel products (b)

Particle sizes and morphology changes throughout the thermal decomposition are shown in Figs.1.3 and 1.4 SEM and TEM observations. The particles size and morphology of the Precursor A and B are obviously different from each other. The Precursor B consists of mono dispersed quadrate crystals with the particle sizes of 0.6–1.0µm (Fig.1.3b1). The Precursor A consists of many irregular block crystals with the particle sizes of 0.1–0.2µm (Fig.1.3a1). After thermal decomposition, Precursor A changes into close-grained spherical heteromorphy with the average particle sizes about 0.1µm (Fig.1.2a2 and Fig.1.3a3). The product Ni B with the average particle sizes about 0.5nm keeps the quadrate
morphology of the Precursor B and the single quadrature crystal still consists of many nano spheres with the average particle sizes about 20nm (Fig. 1.3b₂ and Fig. 1.4b₂). The results from SEM and TEM images agree well with the observations from the XRD and electrochemical measurements.

FIGURE 1.3
SEM images of PrecursorA(a₁) and NiA(a₂), PrecursorB(b₁) and NiB(b₂)
In recent years, remediation of contaminated environments using nanoscale elementary metals, metal oxides, and their composites has drawn much attention due to their smaller particle size, larger specific surface area, higher density of reactive surface sites, and greater intrinsic reactivity of surface sites. Compared with zero-valent iron (ZVI), nano zero-valent iron (NZVI) has a larger specific surface area and higher reactivity.

Nevertheless, NZVI particles prepared using traditional methods tend to agglomerate rapidly in water via Van der Waals and magnetic attraction forces, forming particles with diameters ranging from several microns to several millimeters, or even larger. In addition, conventional NZVI particles may react fast with the surrounding media (e.g. dissolved oxygen, water and other oxidizing agents), resulting in rapid loss in reactivity.

To prevent nanoparticle agglomeration, various particle stabilizing approaches have been reported. He et al. [26] developed a new strategy for stabilizing palladized iron nanoparticles by using sodium carboxymethyl cellulose (NaCMC) as a stabilizer. The stabilized nanoparticles exhibited markedly increased stability against aggregation, chemical reactivity, and soil transport. He and Zhao [27] prepared a new class of starch stabilized bimetallic nanoparticles to degrade polychlorinated biphenyls (PCBs). The starch-encapsulated nanoparticles at 1 g/L were able to transform over 80% of PCBs in less than 100 h, as compared to only 24% with non-encapsulated Fe-Pd nanoparticles. Choi et al. [28] developed granular activated carbon impregnated with reactive iron/palladium bimetallic nanoparticles.

Chemicals of analytical grade or higher were used in this study, including FeSO$_4$·7H$_2$O, KBH$_4$, K$_2$Cr$_2$O$_7$, NaCMC. All the reagents were prepared with millipore deionized water. All solvents were degassed and saturated with N$_2$ before use.

The encapsulated ZVI nanoparticles were prepared in water by reducing Fe(II) to Fe(0) using KBH$_4$ in the presence of NaCMC as a stabilizer. Briefly, FeSO$_4$·7H$_2$O and KBH$_4$ were mixed by grinding in a molar ratio of 1:2. The solid mixture was added to a NaCMC solution to obtain a rheological body, and then the mixture was transferred into a three-necked round-bottom flask. The reaction was conducted under continuous stirring at room temperature under the continuous purge of nitrogen gas. The resulting solid product was collected by filtration, washed with deionized water and ethanol, and finally...
dried under vacuum. The reaction involved is as follows:

\[ \text{Fe}^{2+} + 2\text{BH}_4^- + 6\text{H}_2\text{O} \rightarrow \text{Fe}^0 + 2\text{B(OH)}_3 + 7\text{H}_2 \quad (4) \]

As shown in Fig. 1.5, the XRD patterns of C-NZVI after three days of aging indicated the presence of the body-centered cubic α-Fe (110 and 220) (2θ = 44.83° and 65.22°, respectively). The presence of K⁺ (2θ = 30.12°, 31.24°) derived from the potassium residue after washing introduced by KBH₄ during the synthesis of C-NZVI. In addition, the characteristic diffraction peaks of iron oxide (2θ = 35.46°, 43.12°, 53.50°, 56.98°, and 62.64°) were weak, suggesting the prepared C-NZVI has a strong antioxidant activity.

FIGURE 1.5
XRD of C-NZVI particles

FIGURE 1.6
TEM image of C-NZVI particles
The TEM image (Fig. 1.6) demonstrated that NZVI particles were encapsulated into the microspheres by CMC and were isolated from each other. CMC has been successfully used as an effective stabilizer in the preparation of nanoparticles such as Ag nanoparticles and superparamagnetic iron oxide nanoparticles. Like starch, CMC is also low-cost and environmentally friendly compound. CMC and starch have similar macromolecular skeletons. However, CMC carries carboxylate groups in addition to hydroxyl groups. Hence, CMC can interact with iron nanoparticles more strongly and stabilize the nanoparticles more effectively.

**Preparation of ZnO nanoparticles** [29]

Zn$_{1-x}$Cu$_x$O($x=0.010$, 0.015, 0.020 and 0.025) was synthesized by a rheological phase method. Stoichiometric quantities of the raw materials, zinc acetate (ZA) (Zn(CH$_3$COO)$_2$·2H$_2$O)(>99%; Merck, Darmstadt, Germany), cupric acetate (CA)(Cu(CH$_3$COO)$_2$·4H$_2$O) (Merck;>99%) and oxalic acid (OA) (H$_2$C$_2$O$_4$·2H$_2$O) (Merck; >99.5%), were used as precursors. The reaction between a 0.1 M solution of ZA and 0.15 M solution of OA gave the maximum amount of intermediate product compared to other precursor ratios[30]. Initially, 0.01 M of ZA and y M($y=0.00010$, 0.00015, 0.00020 and 0.00025) of CA were stirred in 50 ml of deionized water until the solution becomes transparent. Cu and Zn oxalate were prepared by slow addition of oxalic acid with constant stirring for 12 h at room temperature. The precipitate was dried at 90°C for a few minutes. To obtain Cu-doped ZnO nanocrystalline powder, the dried powder was heated in an open atmosphere for 1 h.

To determine the appropriate calcination temperature, TG–DT analyses of the synthesized Zn–Cu oxalate powders with different Cu concentrations were performed. One DT–TGA curve (other not shown) for 2.0% Cu concentration, heated at 10°C/min up to 600°C in a nitrogen atmosphere with alumina as reference, is shown in Fig. 1.7. The DTA peaks closely correspond to the weight changes observed on the TG curves. As seen in Fig. 1.1, the DTA curve can be divided into two steps. The initial step from 120 to 160°C is endothermic and due to weight loss of 18–22%, arising from dehydration of the oxalate precursors and formation of anhydrous oxalate. A similar type of endothermic reaction was noted by Pillai et al. [31], Shen et al. [32] and Guo et al. [33], who prepared pure ZnO powder by decomposition of zinc oxalate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O). The anhydrous oxalate is stable up to approximately 370°C and it then decomposes in the next step. This step is an exothermic process with the DTA peak at 420°C, indicating a weight loss of around 41% due to decomposition of the anhydrous oxalate precursors and the formation of Zn$_{1-x}$Cu$_x$O. Since there is no appreciable change in weight above 430°C, the calcination temperature of the powder was optimized at 430°C. The colour of the as-synthesized samples is slightly brownish.
Crystallinity of the synthesized Zn$_{1-x}$Cu$_x$O powder was examined initially by XRD. The sharp XRD peaks of the as-prepared powder, as shown in Fig. 1.8, confirm the formation of crystalline Zn$_{1-x}$Cu$_x$O. The absence of peaks corresponding to cupric or cuprous oxide suggests that the Cu is present as a dopant element. Particle sizes of the synthesized powder are shown in Fig. 1.9 and the size distribution is shown in Fig. 1.10. The particles sizes obtained from SAXS measurements were comparable to those calculated from the Scherrer relation [34], as modified by Krill et al. [35]. Maximum proportional error analysis showed that the particle size obtained from SAXS is more accurate than that calculated from the Scherrer relation.
FIGURE 1.8
XRD pattern of ZnO nano-crystalline powder doped with (a) 1%, (b) 1.5%, (c) 2% and (d) 2.5% Cu. Curves are shifted vertically to improve clarity.

FIGURE 1.9
Small angle X-ray profile of particle size for (a) 1%, (b) 1.5%, (c) 2% and (d) 2.5% Cu doping.
FIGURE 1.10
Particle size distribution as measured from small angle X-ray scattering for (a) 1%, (b) 1.5%, (c) 2% and (d) 2.5% Cu doping

Compositional analyses were initially performed by EDX, where it was found that the doping concentrations were close to the nominal concentrations in the precursor materials. An EDX spectrum is shown in Fig. 1.11. Binding energies of the Zn3p, Zn3s and Cu2p levels were measured by XPS; those of the Zn3p and 3s state are shown in Fig.1.12. The higher binding energy of these two states is due to chemical bonding between zinc and oxygen (935.3eV). Binding energy of the Cu2p3/2 state (Fig.1.13), which is larger than the binding energy of Cu2p3/2 state in +1 valence, determined the valency state of Cu to be +2[36,37,38]. Therefore, the valence state of Cu in the as-prepared samples was assigned to be divalent (3d9; S=1/2) [39].
FIGURE 1.11
Energy dispersive X-ray analysis for 2% Cu-doped ZnO

FIGURE 1.12
X-ray photoelectron spectrum for the Zn 3s and 3p state
Polycrystalline spinel ferrites are widely used in many electronic devices. These are preferred because of their high electrical resistivity, chemical stability, mechanical hardness, and reasonable cost. The use of ferrites for certain application depends on their electrical and magnetic properties, which in turn are sensitive to the preparation condition as well as the type and amount of substitution.

The rare-earth ions that can be isotropic or anisotropic due to the great variation in the f electron orbital contribution to magnetic interactions are becoming the effective additives for the improvement of ferrite properties. The substitution of rare-earth elements in spinel ferrites is promising to manipulate magnetic coupling, as reflected in the decrease of hyperfine field as well as Curie temperature to increase the sensitivity, and may bring about important modifications in structure and electrical and magnetic properties of the ferrites.

The nanocrystalline Zn$_{0.6}$Cu$_{0.4}$Cr$_{0.5}$Gd$_x$Fe$_{1.5-x}$O$_4$ ($x=0.00, 0.02, 0.04, 0.06, \text{ and } 0.08$) were synthesized by a rheological phase reaction method. As shown in the flowchart (Fig.1.14), stoichiometric quantities of Fe(NO$_3$)$_3$·9H$_2$O, Cu(NO$_3$)$_2$· 3H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, Cr(NO$_3$)$_3$·6H$_2$O, Gd(NO$_3$)$_3$·6H$_2$O and H$_2$C$_2$O$_4$·2H$_2$O were well-mixed and a proper quantity of absolute ethanol was added into the mixture to prepare the rheological bodies. Precursors were prepared from the rheological bodies in a 50 ml teflon-lined stainless autoclave at 120°C for 48 h. The resulting solid products were collected by filtration, washed with deionized water and ethanol, dried at 60°C for 12 h and finally calcined at 900°C for 2 h in air.
FIGURE 1.14
A general flowchart of the synthesis process

Fig. 1.15 shows the TGA curves of $\text{Zn}_{0.6}\text{Cu}_{0.4}\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_4$ precursor measured with a heating rate of 10°C/min in air, indicating the multistep weight loss with increasing temperature up to 800°C. It can be seen that the first small fraction of weight loss from room temperature to about 130°C is mainly due to the expulsion of absorbed water in the precursor. Obvious weight loss has been found in the temperature range of 140–260°C because of the complete dehydration and the formation of anhydrous oxalate. The weight loss in the range of 260–330°C is attributed to forming carbonate by decomposition of the oxalates. The weight loss in the range of 330–400°C is corresponded to the formation of oxides by decomposition of the carbonate. The final step started at 400°C is related to the solid–solid interaction of oxides to form a $\text{Zn}_{0.6}\text{Cu}_{0.4}\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_4$ ferrite.
Zn–Cu–Cr ferrite has a cubic spinel structure, which belongs to the space group \((Fd3m)\). The group theory predicts the following modes in spinel: \(\Gamma = A_{1g}(R) + E_g(R) + F_{2g}(in) + 3F_{2g}(R) + 2A_{2u}(in) + 2E_u(in) + 4F_{1u}(IR) + 2F_{2u}(in)\), where (R), (IR), and (in) represent Raman-active vibrations, infrared-active vibration, and inactive modes, respectively. Fig.1.16(a) shows the Raman spectrum of Zn–Cu–Cr ferrite prepared by a rheological phase reaction method. There are five Raman active modes \((A_{1g} + E_g + 3F_{2g})\) observed at ambient conditions in this study. The peaks at 668 and 560 cm\(^{-1}\) are attributed to the characteristics of the tetrahedral sites \((\text{AO}_4)\), which reflects the local lattice effect in the tetrahedral sublattice, other peaks at 195, 320, and 489 cm\(^{-1}\) correspond to the characteristics of the octahedral sites \((\text{BO}_6)\), which reflects the local lattice effect in the octahedral sublattice. These results are consistent with the previously reported studies. The IR spectrum of the as-prepared Zn–Cu–Cr ferrite is shown in Fig.1.16(b). It is found that the peaks at 561 and 461 cm\(^{-1}\) are intrinsic vibration of the tetrahedral and octahedral sites, respectively. The broad peak at 3430 cm\(^{-1}\) and the peak at 1632 cm\(^{-1}\) correspond to the stretching and bending modes of the hydroxyls, respectively. These results confirm the formation of cubic spinel-phase structure. Fig.1.17 shows the XRD patterns of Gd-substituted Zn–Cu–Cr ferrites obtained by a rheological phase reaction method. All patterns show diffraction lines corresponding to cubic spinel structure (JCPDS card number 77–0013) with no extra lines, indicating the formation of single-phase spinel. The peaks appeared at \(2\theta = 18.3, 30.2, 35.5, 37.3, 43.3, 53.5, 57.1\) and \(62.7^\circ\) can be assigned to scattering from the \((111), (220), (311), (222), (400), (422), (511),\) and \((440)\) planes of the spinel crystal lattice, respectively.
FIGURE 1.16
(a) Raman and (b) IR spectra of the as-prepared Zn–Cu–Cr ferrite
FIGURE 1.17
XRD patterns of the as-prepared Zn$_{0.6}$Cu$_{0.4}$Cr$_{0.5}$Gd$_{x}$Fe$_{1.5-x}$O$_4$ ferrites: (a) x = 0.00, (b) x = 0.02, (c) x = 0.04, (d) x = 0.06, and (e) x = 0.08

TABLE 4
X-ray diffraction data for Zn$_{0.6}$Cu$_{0.4}$Cr$_{0.5}$Gd$_{x}$Fe$_{1.5-x}$O$_4$

<table>
<thead>
<tr>
<th>composition</th>
<th>a (Å)</th>
<th>r (variant)(Å)</th>
<th>volume(Å$^3$)</th>
<th>dx(g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$<em>{0.6}$Cu$</em>{0.4}$Cr$<em>{0.5}$Fe$</em>{1.5}$O$_4$</td>
<td>8.385</td>
<td>0.969</td>
<td>589.5</td>
<td>5.37</td>
</tr>
<tr>
<td>Zn$<em>{0.6}$Cu$</em>{0.4}$Cr$<em>{0.5}$Gd$</em>{0.02}$Fe$_{1.48}$O$_4$</td>
<td>8.387</td>
<td>0.975</td>
<td>590.0</td>
<td>5.42</td>
</tr>
<tr>
<td>Zn$<em>{0.6}$Cu$</em>{0.4}$Cr$<em>{0.5}$Gd$</em>{0.04}$Fe$_{1.46}$O$_4$</td>
<td>8.391</td>
<td>0.981</td>
<td>590.8</td>
<td>5.45</td>
</tr>
<tr>
<td>Zn$<em>{0.6}$Cu$</em>{0.4}$Cr$<em>{0.5}$Gd$</em>{0.06}$Fe$_{1.44}$O$_4$</td>
<td>8.397</td>
<td>0.986</td>
<td>592.1</td>
<td>5.49</td>
</tr>
<tr>
<td>Zn$<em>{0.6}$Cu$</em>{0.4}$Cr$<em>{0.5}$Gd$</em>{0.08}$Fe$_{1.42}$O$_4$</td>
<td>8.409</td>
<td>0.992</td>
<td>594.6</td>
<td>5.51</td>
</tr>
</tbody>
</table>

The lattice parameter and X-ray density for samples are given in Table 1.4. It is observed that the lattice parameter increases with increasing Gd substitution. The increase in lattice parameter with increasing Gd content can be explained on the basis of the ionic radii. The samples under investigation have the chemical composition Zn$_{0.6}$Cu$_{0.4}$Cr$_{0.5}$Gd$_{x}$Fe$_{1.5-x}$O$_4$. Therefore, the mean ionic radius of the variant ions for composition (Gd$_x$Fe$_{1.5-x}$) can be written as $r_{\text{variant}} = x r_{\text{Gd}^3} + (1.5-x) r_{\text{Fe}^3}$, where $r_{\text{Gd}^3}$ is the radius of Gd$^{3+}$ ion (0.938 Å) and $r_{\text{Fe}^3}$ is the ionic radius of Fe$^{3+}$ ion (0.6459 Å). The observed increase in $r_{\text{variant}}$ with the Gd content leads to the expansion of unit cell. X-ray density ($d_x$) is calculated using the formula $d_x = 8M/Na^3$ where M, N, and a are the molecular weight, Avogadro’s number, and lattice parameter, respectively. It can be seen that X-ray density increases with increasing Gd content, which was attributed to the increase in molecular weight in spite of the increase in the volume since the atomic weight of Gd$^{3+}$ ion (157.25 amu) is larger than that of Fe$^{3+}$ (55.85 amu).
FIGURE 1.18
AFM images of the as-prepared Zn$_{0.6}$Cu$_{0.4}$Cr$_{0.5}$Gd$_x$Fe$_{1.5-x}$O$_4$ ferrites: (a) $x = 0.00$ and (b) $x = 0.06$

The morphology and particle sizes of the obtained samples has been studied by AFM. The typical AFM images of the Gd-substituted Zn-Cu-Cr ferrites are displayed in Fig.1.18. It indicates that the ferrite particles obtained are agglomerated to some extent, due to the relative higher calcination temperature and interaction between magnetic particles. The particle sizes of the sample Zn$_{0.6}$Cu$_{0.4}$Cr$_{0.5}$Fe$_{1.5}$O$_4$ are in the range of 80-90 nm. It can be found from Fig.1.5(b) that the particle sizes of Gd-substituted ferrite sample are smaller than that of pure Zn-Cu-Cr ferrite, which is in agreement with the results of literature.

**Tb$^{3+}$ doped luminescence zinc** [41]

The bivalent metal and rare earth salicylates were generally prepared by reaction of metal chloride with ammonium salicylate aqueous solution or by reflux, vaporization and crystallization of metal carbonates in salicylate acid aqueous solution. The monosalicylate salts can be obtained by thermal decomposition of these salicylate salts at 150-350°C. The studies on luminescence property of Tb(Sal)$_3$(Sal=HOC$_6$H$_4$CO$_2$) have been carried out. The Tb$^{3+}$-doped lanthanum, zinc and alkali earth metal phthalates have better luminescence properties than pure terbium complexes. But the luminescent behavior of Tb$^{3+}$-doped salicylate hasn’t been reported. The Tb$^{3+}$-doped alkali earth metal salicylates mainly send out the blue luminescence of the salicylate group, the luminescence efficiency of Tb$^{3+}$ions is very low and its thermal stability is not satisfactory. The salicylic acid and zinc oxide were analytical reagent grade, and terbium carbonate was prepared in the laboratory. The ZnO, salicylic acid and Tb$_2$(CO$_3$)$_3$ were fully mixed in 1:2:x and 1:1:x (x=0.0005-0.075) mole ratios, and the rheological bodies were made with a proper quantity of water. Zn(Sal)$_2$:Tb and α-Zn Sad:Tb were synthesized from the rheological bodies in a closed container at 70-90°C for 1-2 h. b-Zn Sad:Tb was obtained by thermal decomposition of Zn(Sal)$_2$:Tb at 280°C for 4-5 h under an inert atmosphere.

The data of powder X-ray diffraction and IR spectra indicate that the crystal structures and co-ordinate structures of α- and b-Zn Sad:Tb 0.01 are consistent with neat ones. Both are monoclinic, the lattice parameters of α-Zn Sad:b$_{0.01}$ are a=1.1655,b=0.5359,c=0.4999 nm,β=98.65° and Z=2; for the β-Zn Sad:Tb$_{0.01}$ a=2.4425,b=0.7004,c=0.7615nm,β=93.88° and Z=8. The OCO group co-ordinates with the zinc atoms by bidentate bridging, and the hydroxyl oxygen atom also co-ordinates with the two zinc atoms by
bridging. The co-ordination number of zinc is four. The co-ordination structure of zinc with oxygen atoms is a deformed tetrahedron in α-ZnSad:Tb 0.01, but near plane tetragon in β-ZnSad:Tb 0.01. The neat Zn(Sal)₂ generated strong blue luminescence when excited by ultraviolet light. The excitation and emission spectra are shown in Fig. 1.19 (curve 1 and 2). The excitation peak at 317 nm corresponds to the S₁ ₁, π * excited state of the -C₆H₄OH group and the shoulder at 340 nm to the S₁n, π * excited state. The emission band at 425 nm could be assigned to the transition emission from the T₁ ₁, π *, to the ground state and the shoulder at 400 nm to the transition emission from T₁n, π * to the ground state. Zn(Sal)₂:Tb emitted green luminescence under ultraviolet light excitation. The excitation and emission spectra of Zn(Sal)₂:Tb₀.₀₁ are shown in Fig. 1.19 (curve 3–6). The emission bands at 488, 543, 582, 619 nm correspond to the ⁵D₄→⁷F₃(j=6, 5, 4, 3) transitions of Tb³⁺ ions. The broad band at 430 nm is due to the transition emission from the T₁ ₁, π *, and T₁n, π * to the ground state of the -C₆H₄OH group. The excitation band which generated luminescence of Tb³⁺ ions is at 352 nm (curve 3), its long wavelength side obviously exceeds the region of the n, π * transition excitation band of the -C₆H₄OH group, and should be assigned to the n', π '* transition of the CO₂ group. This is because the OCO group co-ordinate with the two zinc atoms by bidentate bridging, and ap-conjugation system is formed in OCO group. The energy of the n', π '* excited state could also be transferred to Tb³⁺ ions efficiently. The excitation bands of the π, π * and n, π * transitions of the -C₆H₄OH group (curve 5) are the same as those of Zn(Sal)₂ and there is little difference in the emission intensity. It is suggested that the energy of the π, π * and n, π * excited states of the-C₆H₄OH group can't be transferred to Tb³⁺ ions efficiently.

**FIGURE 1.19**

Excitation spectra (1,λₑₓ=425 nm; 3,λₑₓ=543 nm; 5,λₑₓ=430 nm) and emission spectra (2 and 6, λₑₓ=317 nm; 4,λₑₓ =352 nm) of Zn(Sal)₂ (1, 2) and Zn(Sal)₂:Tb₀.₀₁ (3–6)

Fig. 1.20 shows the excitation and emission spectra of b-ZnSad and ZnSad:Tb 0.01:Inb-ZnSad: Tb, an obvious splitting of the emission band from the ⁵D₄→⁷F₃ transition of Tb³⁺ ions was found, a shoulder appeared at 542 nm and the strongest peak shifted to 547 nm. The broad excitation band at 340 nm which brought the luminescence of Tb³⁺ ions showed an apparently blueshift compared with Zn(Sal)₂:Tb 0.01. The luminescence of Tb³⁺ ions mainly depended on the energy transfer of the
π, π* and n, π excited states of the -OC₆H₄- group to Tb³⁺ ions, as a result of the co-ordination of a hydroxyl oxygen atom with metal atoms directly. But the luminescent intensities of β-ZnSad and β-ZnSad:Tb0.01 are very weak. The reason for that is the two zinc atoms coordinated with a hydroxyl oxygen atom are at the symmetry axis of two (OC₆H₄CO₂)²⁻ ions, and the two zinc atoms coordinated with an OCO group too. In this structure, the energy of the excited states is easily transferred each other through resonance and is quenched.

FIGURE 1.20
Excitation spectra (1 and 5, λₑₓ = 440 nm; 3, λₑₓ = 547 nm) and emission spectra (2, λₑₓ = 335 nm; 4, λₑₓ = 340 nm) of β-ZnSad (broken line) and β-ZnSad:Tb₀.₀₁ (solid line)

α-ZnSad and α-ZnSad:Tb₀.₀₁ have very strong blue violet and green luminescence under excitation with ultraviolet light, and the excitation and emission spectra are shown in Fig.1.21. For α-ZnSad, the excitation band at 345 nm corresponds to the S₁ n, π* state and the shoulder at 320 nm to the S₁ π, π* state. The emission peak at 388 nm is due to the transition of the T₁ n, π* to the ground state. Its relative intensity is twice as strong as that of Zn(Sal)₂ and 4.7 times as that of β-ZnSad. But the transition emission of the T₁ π, π* to the ground state is too weak to observe an apparent emission peak at 425 nm. It is revealed that in α-ZnSad the energy of both S₁ n, π* and S₁ π, π* states of Sad²⁻ can be transferred to the T₁ n, π* state through intersystem crossing, then to the ground state to produce luminescence.
For α-ZnSad:Tb \(_{0.01}\), the 345 nm excitation band which generates emission of Tb\(^{3+}\) ions is in the same position as the \(S_1\pi,\pi^*\) and \(5\Pi,\Pi^*,\Pi^*\) band of α-ZnSad. The intensities of the broad emission band (curve 4) and the corresponding excitation band (curve 5) of Sad\(^{2-}\) ions were decreased more than 50% compared to that of α-ZnSad. But the emission intensity of Tb\(^{3+}\) ions was 3.5 times as much as that of Zn(Sal)\(_2\):Tb\(_{0.01}\), and five times of β-ZnSad:Tb \(_{0.01}\). It is suggested that the energy of the \(\pi,\pi^*,\pi^*\) and \(n,p^*\) excited states can be transferred to Tb\(^{3+}\) ions efficiently in α-ZnSad to send out the characteristic emission of Tb\(^{3+}\) ions. Table 1.1 reveals the relationship between the emission intensity and Tb\(^{3+}\) ion concentration in α-ZnSad:Tb. The luminescence intensity of Tb\(^{3+}\) ions increases with an increase of Tb\(^{3+}\) ion concentration, but the intensity of transition emission of Sad\(^{2-}\) ion from the \(T_2\pi,\pi^*\) to the ground state decreases gradually. When Tb\(^{3+}\) ion concentration is 15 mol%, the emission intensity of the \(^{5}D_{4}\rightarrow^{7}F_{j}\) tends to be saturated. The excitation and emission spectra of α-ZnSad:Tb \(_{0.15}\) are shown in Fig.1.22.
FIGURE 1.22
Excitation (1, λ<sub>Ex</sub> = 543 nm) and emission (2, λ<sub>E</sub> = 352 nm) spectra of α-ZnS:α-Tb<sub>0.15</sub>

In the excitation spectrum, besides the strong excitation band of the π, π* and n, π* of the salicylate group at 320 (shoulder) and 352 nm, a directly stimulated excitation band of Tb<sup>3+</sup> ions appeared at 381 nm, and could be assigned to the SD3 energy level. But when the sample was excited by 381 nm light, the ⁵D<sub>4</sub>→⁷F<sub>j</sub> emission couldn’t be detected. A similar phenomenon is observed in Tb<sup>3+</sup>-doped zinc phthalate [8].

**Negative temperature coefficient ceramic materials** [42]

Negative temperature coefficient thermistors are extensively used in various industrial and domestic fields for temperature measurement, compensation, control and suppression of inrush current, owing to their interesting electrical properties. Nickel manganite (NiₓMn₃₋ₓO₄) with the spinel-type crystal structure is a commonly used material for these thermistors. The semiconducting mechanisms of nickel manganite have been explained by small polaron hopping between localized Mn<sup>3+</sup> and Mn<sup>4+</sup> states in octahedral B-sites under the assistance of thermal activation.

Ni<sub>₀.₉</sub>Mn<sub>₂.₁₋ₓ</sub>Mg<sub>x</sub>O<sub>₄</sub>(0 ≤ x < 0.3) powders were synthesized by RPR-UR method, using analytical reagent MnO₂, NiO, MgO and H₂C₂O₄·2H₂O as starting materials. The metal oxides in their weight proportion with appropriate quantity of water were mixed and irradiated by the 40 kHz ultrasonic waves (Kunshan Ultrasonic Instrument Co., Ltd. KQ-700DE) at the power of 100 W for 30 min. Then oxalic acid was introduced to form rheological phase mixture with constant stirring and irradiating ultrasonic waves for 2 h at 30°C. The prepared precursor was desiccated at 100°C for 12 h and then calcined in an alumina crucible at 700°C for 2 h. Subsequently, the powders were pressed into a disk shape of 10 mm in diameter and 1 mm in thickness, and sintered at 1200°C for 2 h under air atmosphere to form ceramic bodies. The opposite-sides of ceramics were coated with silver-palladium conductive using a screen printer (ATMA Tung Yuan M/C Ind (Kunshan). Co. Ltd.) and heated at 750°C for 20 min.

The TG/DSC analysis curve of the as-prepared Ni<sub>₀.₉</sub>Mn<sub>₂.₁₋ₓ</sub>Mg<sub>x</sub>O<sub>₄</sub> oxalate precursor is shown in Fig.1.23. Two obvious decomposition steps of weight loss are observed in the TG curve, accompanied with an
endothermic peak and a sharp exothermic peak on the DSC curve. This can be attributed to dehydration of crystallization water and the complex decomposition of anhydrous oxalates, respectively. Hereafter, there is no obvious weight loss. It suggests that the decomposition reaction has been completed. An exothermic peak at 677°C indicates the crystallization of spinel phase, which is further confirmed by XRD analysis. The other samples have similar trend via TG/DSC analysis, so the Ni$_{0.9}$Mn$_{1.9}$Mg$_{0.2}$O$_4$ materials is only presented in the text.

![Simultaneous TG/DSC curve of Ni$_{0.9}$Mn$_{1.9}$Mg$_{0.2}$O$_4$ sample](image)

**FIGURE 1.23**
Simultaneous TG/DSC curve of Ni$_{0.9}$Mn$_{1.9}$Mg$_{0.2}$O$_4$ sample

XRD patterns of calcined Ni$_{0.9}$Mn$_{2.1-x}$Mg$_x$O$_4$ (0≤x≤0.3) powders are shown in Fig. 1.24. The diffractograms of all the samples show the presence of single-phase cubic spinel structure with no extra peaks corresponding to any other phase. The average crystallite sizes of Ni$_{0.9}$Mn$_{2.1-x}$Mg$_x$O$_4$ (x=0, 0.1, 0.2, 0.3) samples by the Debye-Scherrer formula are 47.3nm, 53.9nm, 54nm and 49.9nm, respectively, confirming that the synthesized powders are nanocrystalline in nature.
FIGURE 1.24
XRD patterns of Ni$_{0.9}$Mn$_{2.1-x}$Mg$_x$O$_4$ (0≤x≤0.3) samples calcined at 700°C

SEM micrographs of Ni$_{0.9}$Mn$_{2.1}$O$_4$ and Ni$_{0.9}$Mn$_{1.9}$Mg$_{0.2}$O$_4$ samples sintered at 1200°C are shown in Fig. 1.25. The microstructure of the samples revealed well-packed grains. It can be seen that the grain sizes of the as-sintered samples decreased with increasing of Mg content in the Ni$_{0.9}$Mn$_{2.1-x}$Mg$_x$O$_4$ system.

FIGURE 1.25
SEM micrographs of (a) Ni$_{0.9}$Mn$_{2.1}$O$_4$ and (b) Ni$_{0.9}$Mn$_{1.9}$Mg$_{0.2}$O$_4$ samples sintered at 1200°C

To study the contribution of different effects, the Col–Cole analysis for the Ni$_{0.9}$Mn$_{2.1-x}$Mg$_x$O$_4$ has been performed in Fig. 1.26(a). High frequency on the real axis (Z') contains grain resistance (R$_g$) while low frequency contains R$_g$ and grain boundary resistance (R$_{gb}$), which provides the bulk value due to
presence of grain boundary contribution. It also pointed out that the $R_{gb}$ increases with an increase in the Mg content. This is mainly attributed to the dragging effect between Mg\textsuperscript{2+} and grain boundaries, which increases the energy for the movement of grain boundary and retards the grain growth.

Relationship between electrical resistivity and temperature is shown in Fig.1.26(b). A linear relation dependence of ln$\rho$versus$1/T$ obeys the well-known exponential law described by the Arrhenius expression. This indicates that the samples possess the NTC thermistor characteristics. As the concentration of Mg increased from 0.0 to 0.3, the room temperature resistivity $\rho_{25}$, the material constant $B_{25/50}$ and the activation energy $E_a$ for Ni$_{0.9}$Mn$_{2.1-x}$Mg$_x$O$_4$ thermistors increased from 2499 to 4728Ω·cm, 3872 to 3961 K and 0.334 to 0.341 eV, respectively. Compared with the conventional method, the obvious increase in the resistance tolerance of the Ni$_{0.9}$Mn$_{2.1-x}$Mg$_x$O$_4$ ceramics prepared by RPR-UR method with $x=0$, 0.1, 0.2 and 0.3 was 0.91%, 0.27%, 0.40% and 0.49%, respectively. The resistance tolerance was 3.25%, 2.74%, 5.17% and 7.08%, respectively, by the conventional method. The effects of Mg doping on the structural and electrical properties were consistent with another report. Similar results were obtained in Mn$_{1.4}$Ni$_{1.2}$Co$_{0.4}$-xMg$_x$O$_4$. That is to say, as the amount of Mg dopants increased, the amount of Mn\textsuperscript{3+}/Mn\textsuperscript{4+} ions on octahedral sites responsible for hopping and conductivity is decreased, and the resistivity increased. This indicates that the electrical properties of the NTC thermistors can be controlled by changing the composition.

**FIGURE 1.26**

Electrical properties of Ni$_{0.9}$Mn$_{2.1-x}$Mg$_x$O$_4$ samples: (a) the Cole–Cole analysis and (b) relationship between electrical resistivity and temperature

_Inherently conducting polymers (ICPs) [43]_

Inherently conducting polymers (ICPs) are attractive materials, because they cover a wide range of functions from insulators to metals and retain the mechanical properties of conventional polymers. The considerable electrochemical and physicochemical properties result in conducting polymers having various practical applications, such as corrosion protection coatings, electrocatalysts, chemical sensors, rechargeable batteries, light-emitting diodes (LEDs), and electromagnetic interference (EMI) shielding.
Among the conducting polymers, polyaniline (PANI) has received a great deal of attention in recent years due to its easy synthesis, good environmental stability, and high electrical conductivity. Organic–inorganic nanocomposites with an organized structure provide a new functional hybrid between organic and inorganic materials. Novel properties of these nanocomposites can be derived from the successful combination of the characteristics of individual constituents into a single material. Recently, many interesting research studies have focused on the PANI/transition metal (TM) oxide nanocomposites to obtain the materials with synergetic or complementary behavior between polyaniline and inorganic nanoparticles, including PANI/TiO\textsubscript{2}[44], PANI/SnO\textsubscript{2}[45], PANI/ZnO[46], PANI/Fe\textsubscript{3}O\textsubscript{4}[47], PANI/Co\textsubscript{3}O\textsubscript{4}[48], and PANI/NZFO[49]. Ferrite with a spinel structure that is formed by a nearly close-packed fcc array of anions with holes partly filled by the cations can be represented by the formula AB\textsubscript{2}O\textsubscript{4}, where A represents metallic ions located in A interstitial (tetrahedral) sites and B metallic ions located in B (octahedral) sites. Due to the large electronegativity of oxygen, the ionic type of bond prevails in almost all oxide spinels. Soft spinel ferrite \(\text {MFe}_2\text{O}_4\), \(\text {M} = \text{Co, Ni, Zn, Mn, etc.}\) nanoparticles have been intensively investigated due to their remarkable magnetic and electrical properties and wide practical applications in ferrofluids, magnetic drug delivery, magnetic high-density information storage, and microwave absorbance. Based on the above considerations we were motivated to design and fabricate a new class of functional materials combining conducting PANI with magnetic ferrite, which may find their potential applications in microwave absorbing and magnetoelectric devices.

Aniline was distilled twice under reduced pressure and stored below 0°C. Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}·2H\textsubscript{2}O, and ammonium peroxydisulfate (APS, (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) were all of analytical purity and used without further purification. Preparation of NZFO NPs NZFO NPs were prepared by a rheological phase reaction method. Stoichiometric amounts of Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, and H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}·2H\textsubscript{2}O were mixed thoroughly and then were ground in an agate mortar for 30 min. The mixture was transferred into a 50-mL Teflon-lined stainless autoclave, and an appropriate amount of absolute ethanol was added to form a rheological state mixture. The autoclave was sealed and maintained in a furnace at 120°C for 48 h and then was cooled to room temperature naturally. The resulting solid product was collected by filtration, washed with deionized water and ethanol, and finally dried at 60°C for 12 h. The as-prepared precursors were calcined at 900°C for 2 h in air.

PANI/NZFO NCs were prepared by in situ polymerization of aniline in the presence of NZFO NPs. In a typical procedure, a certain amount of NZFO NPs were added to 35 mL of 0.1 M HCl solution containing 1 mL of aniline monomer and stirred for 30 min. The 2.49 g of APS in 20 mL of 0.1 M HCl solution was then slowly added dropwise to the suspension mixture with constant stirring. The polymerization was allowed to proceed for 12 h at room temperature. The nanocomposites were obtained by filtering and washing the suspension with deionized water and methanol and dried under vacuum at 60°C for 24 h. The nanocomposites with different content of NZFO NPs were synthesized by modulating mass ratios of aniline monomer to NZFO NPs at 9:1 (PANI/NZFO-1) and 4:1 (PANI/NZFO-2), respectively. Fig.1.27 illustrates the polymerization process for PANI=NZFO NCs. It is known that the surface charge of metal oxide is positive below the pH of point of zero charge (PZC), whereas it is negative above that. Because the surface of magnetite has PZC of pH≈6, it is positively charged in acidic conditions. Therefore, adsorption of an amount of the anions may occur and compensate for the positive charges on NZFO NPs surface. Meanwhile, the specific adsorption of these anions on the NZFO NPs surface may also take place. In this approach, aniline monomers are converted to cationic anilinium ions in acidic conditions. Thus, the electrostatic interactions appear between anions adsorbed on the NZFO NPs surface and cationic anilinium ions. The aniline monomers electrostatically complexed to the NZFO NPs.
surface are then polymerized by ammonium persulfate as an oxidizing agent at room temperature.

**FIGURE 1.27**
Formation process of PANI/NZFO NCs

Fig.1.28 shows XRD patterns of the NZFO NPs obtained by a rheological phase reaction method. The observed diffraction peaks are perfectly indexed to cubic spinel Fig.1.1.Formation process of PANI/NZFO NCs. Conducting Polymeric Nanocomposites phase (JCPDS card No. 52-0278), and no impurities are detected in the XRD patterns. The sharp diffraction peaks indicate good crystallinity of the as-prepared product. In addition, the electron diffraction (ED) pattern shown in the upper right inset of Fig.1.28 can be well indexed to (111), (220), (311), (222), (400), (422), (511), and (440) of cubic spinel structure, which is consistent with the results of XRD.

**FIGURE 1.28**
XRD patterns of the as-prepared NZFO NPs

Fig.1.29 shows the XRD patterns of PANI/NZFO NCs. It is clearly seen that the characteristic peaks of PANI centered at around 2θ=20.1, 25.1 and NZFO located at 2θ=30.2, 35.6, 37.2, 43.3, 53.4, 57.1, and
62.6 appear in the XRD patterns of the nanocomposites. Also, the intensities of the characteristic peaks of PANI become weaker after introducing the NZFO NPs into the polymer matrix, revealing that the crystallinity of PANI in the nanocomposites is much lower than that of pristine PANI.

![XRD patterns of PANI/NZFO-2 NCs (a), PANI/NZFO-1 NCs (b), and PANI (c)](image)

**FIGURE 1.29**
XRD patterns of PANI/NZFO-2 NCs (a), PANI/NZFO-1 NCs (b), and PANI (c)

The FTIR spectra measurement was carried out to study the molecular structure of the nanocomposites. Fig.1.30 shows the FTIR spectra of PANI/NZFO NCs. For the pristine PANI, the characteristic peaks observed at 1571 and 1493 cm⁻¹ relate to the C=C stretching of the quinoid rings and benzenoid rings, respectively. The peaks at 1297 and 1242 cm⁻¹ are attributed to the C-N stretching modes of the benzenoid ring. The broad peak appearing at 1134 cm⁻¹ is assigned to the C-H in-plane bending modes. The peak at 802 cm⁻¹ refers to the C-H out-of-plane bending modes. As shown in Figs. 1.30(b) and 30(c), the FTIR spectra of PANI/NZFO NCs are almost identical to that of the pristine PANI; moreover, the characteristic peak for NZFO NPs at around 618 cm⁻¹ in the spectrum indicates the presence of NZFO in the PANI/NZFO NCs [50].
Fig. 1.31 displays UV-Vis absorption spectra of PANI/NZFO NCs. For the pristine PANI, two characteristic absorption bands at around 346 and 605 nm can be observed in Fig. 1.31(a), which correspond to the p-p transition of the benzenoid ring and charge transfer from the benzenoid rings to the quinoid rings, respectively. It is interesting to note that the absorption peak at 346 nm corresponding to the pristine PANI has a red shift in the spectrum of PANI/NZFO NCs. These results suggest that there may be interaction between NZFO NPs and PANI molecular chains [51].
FIGURE 1.31
UV-Vis spectra of PANI (a), PANI/NZFO-1 NCs (b), and PANI/NZFO-2 NCs (c)

The surface morphology of PANI=NZFO NCs was investigated by means of SEM. Fig.1.32(a) gives the SEM micrograph of the NZFO synthesized by a rheological phase reaction method, indicating that the sample consisted of a large quantity of quasi-spherical nanoparticles with size ranging from 80 to 100 nm. Due to the Fig.1.30. FTIR spectra of PANI (a), PANI/NZFO-1 NCs (b), and PANI/NZFO-2 NCs (c). Conducting Polymeric Nanocomposites relatively higher annealing temperature and interaction between magnetic particles, some degree of agglomeration appears unavoidable. Fig. 1.32(b) shows the SEM micrograph of PANI=NZFO NCs, suggesting that the fine PANI particles are deposited on the surface of NZFO NPs.

FIGURE 1.32
SEM micrographs of NZFO NPs (a) and PANI=NZFO-1 NCs (b)
Fig. 1.33 shows the conductivity of PANI=NZFO NCs at room temperature. It is observed that NZFO NPs have a significant influence on the conductivity of PANI/NZFO NCs. The conductivity of PANI/NZFO NCs greatly decreases with increasing content of NZFO NPs. These results can be considered as follows: (1) the insulating behavior of NZFO NPs in the nanocomposites; (2) from XRD study, the introduction of NZFO NPs would weaken the crystallinity of PANI; (3) a certain interaction between NZFO NPs and PANI chains further leads to destruction of the conjugated degree, continuity, and regularity of the polymer chains.

![Conductivity of PANI, PANI=NZFO-1 NCs, and PANI=NZFO-2 NCs](image)

**FIGURE 1.33**
Conductivity of PANI, PANI=NZFO-1 NCs, and PANI=NZFO-2 NCs

The magnetization measurements for PANI=NZFO NCs were carried out using a vibrating sample magnetometer (VSM) at room temperature under an applied magnetic field. Fig. 1.34 shows the magnetic hysteresis loops of PANI/NZFO NCs. It is clearly seen that the magnetic parameters such as saturation magnetization (MS) and coercivity (HC) determined by the hysteresis loops for the NZFO NPs decrease after polyaniline coating. The decrease in MS of PANI/NZFO NCs with decreasing NZFO NPs content shows that the NZFO NPs are responsible for the magnetic behavior of the nanocomposites; furthermore, it is interesting to note that the values of MS of PANI/NZFO NCs are not proportional to the mass fraction of magnetic component in the PANI/NZFO NCs, due to a possible charge transfer between the NZFO surface and PANI, analogous to the corrosion protection of metals by depositing PANI [52].
Magnetic properties observed for magnetic materials are a combination of many anisotropy mechanisms, such as magnetocrystalline anisotropy, surface anisotropy, and interparticle interactions. An effective anisotropy constant, $K_{\text{eff}}$, is expressed as [53]:

$$K_{\text{eff}} = K + K_s + K_{sh} + K_{in} \quad (5)$$

Where $K_s$ is the constant of surface anisotropy, $K_{sh}$ is the constant of shape anisotropy, and $K_{in}$ is the (positive) constant of supplementary anisotropy that reflects nanocrystallite interactions. It is known that the surface anisotropy results from low coordination symmetry for spin–orbit couplings at the surface of nanoparticles and decreases upon coating; moreover, the interparticle interactions decrease when magnetic particles are coated with the nonmagnetic matrix due to the increase of particle–particle separation. In our case, the variation of $K_{sh}$ for the NZFO NPs after coating with PANI may be ignored due to the spherical morphology of NZFO and PANI/NZFO NCs. Hence, according to Eq. (5), $K_{\text{eff}}$ may decrease due to the reduction of surface anisotropy and interparticle interactions after PANI coating. On the basis of the above discussion, the decrease in coercivity of NZFO NPs after PANI coating is expected.

**Lithium battery cathode material LiFePO$_4$ [54]**

Due to its overwhelming advantages of low toxicity, good thermal stability and relatively high theoretical capacity, olivine type LiFePO$_4$, which was first introduced as a lithium battery cathode...
material by Padhi et al. appears as a potential candidate to be used as positive electrode in next generation of Li-ion batteries. Stoichiometric amounts of LiOH·H₂O, FePO₄·4H₂O and polyethylene glycol (PEG; mean molecular weight of 10,000, 250 g PEG/mol FePO₄) powders were used as the starting materials by RPR method. As shown in the flow chart (Fig.1.35), they were mixed by grinding for 10 min, and then appropriate amount of de-ionized water was added to get a rheological body. Finally, the resulting precursor was heated in a tube furnace to get the powders of LiFePO₄-C at 700°C for 12h in Ar flow. LiFePO₄ was synthesized under the assumption that the following reaction occurred:

\[
2n\text{LiOH} \cdot \text{H}_2\text{O} + 2n\text{FePO}_4 \cdot 4\text{H}_2\text{O} + \text{HO(C}_2\text{H}_4\text{O})_n\text{H} \rightarrow 2n\text{LiFePO}_4 + 2n\text{C} + (13n+1)\text{H}_2\text{O} \quad (6)
\]

**FIGURE 1.35**
Flow chart of the RPR synthesis process

During the heating of the PEG-contained precursor, Fe³⁺ was reduced to Fe²⁺ with the help of hydrogen and carbon as the reducing agent, which are generated from the decomposition of PEG, producing a strong reductive atmosphere. The X-ray diffraction pattern of the as-prepared LiFePO₄-C composite is shown in Fig.1.36. All peaks can be indexed as pure and well-crystallized LiFePO₄ phase with an ordered olivine structure and a space group of Pnma (JCPDS card no. 83–2092). Previously, there was report that some detectable impurities such as Li₃PO₄ has been identified in LiFePO₄ prepared by conventional
solid-state reaction using the Fe(II) raw material. In contrast, we did not detect any impurities, indicating that this RPR routine using the Fe(II) raw material is a feasible method to prepare pure LiFePO₄. No evidence of diffraction peaks for crystalline carbon (graphite) appeared in the diffraction pattern, which indicates that the carbon generated from PEG is amorphous carbon and its presence does not influence the structure of LiFePO₄. Basing on Scherrer’s equation d = 0.9λ/β¹/² cosθ, one can know that with the increasing of the dimension of crystal grains (d), the full-width-at-half-maximum (FWHM) length of the diffraction peak (β¹/²) is decreasing on a 2θ scale. It is found the β¹/² (Fig. 1.36) is a little wide, which indicates that the crystal grains are small. The calculated crystal grain size is about 23 nm from the Scherrer’s equation according to D111, D121 and D131 values.

FIGURE 1.36
XRD pattern of as-prepared LiFePO₄-C composite

The result indicates the soft RPR process and the carbon reduced from the decomposition of PEG during the heating prohibited the growth of LiFePO₄ grains efficiently. The amount of carbon in the LiFePO₄-C composite is about 6.13 wt.% through the element analysis (EA), in other words, the molar ratio of C:LiFePO₄ is about 0.86. In order to examine the surface elements’ content of the LiFePO₄-C powders, XPS analysis was performed, as shown in Fig.1.37, a sharp peak at about 285.3 eV corresponding to C 1s with a high intensity is seen. The Binding Energy of Fe 2p, O 1s and P 2p are determined to be 711.4, 532.5 and 133.9 eV respectively. However, as Lee et al. reported [55], Li 1s emission peak is not seen clearly because it is superposed on the Fe 3p peak at about 56 eV, precluded accurate determination of its binding energy and estimation of the element content. According to XPS analysis, on the surface of LiFePO₄-C powders, the C:P molar ratio thus obtained is about 19:1, which indicates the surface composition should be mainly the carbon and carbon is coated on the LiFePO₄.
particles rather perfectly [56]. Moreover, the result of XPS analysis shows that the as prepared material comprised of all the constituent elements of LiFePO$_4$.

The morphology for LiFePO$_4$-C powders was observed on SEM, as shown in Fig. 1.38. We can see that lots of independent particles pack closely between the porous structure of carbon and the average particle size is around 0.8µm (Fig.1.38a). The image of one particle selected randomly from Fig.1.38a is shown in Fig. 1.38b, which can be seen clearly that the particle is a kind of secondary particle composed of small size particles (around 200 nm). To further understand this investigation, we ran particles size distribution analysis on the sample, as shown in Fig.1.39. The value at 50% cumulative population ($d_{50\%}$) represents the average particle size. The average particle size was 216 nm for the as-prepared LiFePO$_4$-C powder. The result is consistent with the result of SEM morphology. However, the particle distribution has two regions, the peak around smaller particle size should be due to LiFePO$_4$-C powders, and the other peak at larger particle size region can ascribe to agglomerated large particles that were not dispersed perfectly. Note that the average particle size of the synthesized LiFePO$_4$ is larger than its crystal grain size that calculated from XRD patterns, implying that the particles are formed from the agglomeration of several grains, which is confirmed by the TEM images, as shown in Fig.1.40. From the TEM images, it can be seen clearly that uniform fine LiFePO$_4$ crystal grains (<50 nm) disperse in the carbon webs, most of the grains are wrapped and connected with carbon. The observation of SEM and TEM images accords with the results of XRD and XPS analysis. Based on the above analysis, the formation of the LiFePO$_4$-C powders during the heating process was proposed as follows. First, a large number of very small nanometer LiFePO$_4$ crystal grains grow in the carbon network, then the grains aggregate together and form the nanometer LiFePO$_4$ particles, and finally, the secondary LiFePO$_4$ particles are formed by the agglomeration of several nanometer LiFePO$_4$ particles, which was closely connected by the carbon. The conductivity of LiFePO$_4$-C compound would be
enhanced due to existence of the formed carbon between the crystal grains, the LiFePO$_4$ particles and the close connection of the secondary particles by the carbon network.

**FIGURE 1.38**
SEM images of as-prepared sample. (a) Overall morphology for LiFePO$_4$-C; (b) one particle in the image (a). Inset: magnification of the selected area.
FIGURE 1.39
Particle size distribution of as-prepared LiFePO₄-C sample

FIGURE 1.40
TEM images of as-prepared LiFePO₄-C sample
Matters needing attention in using rheological phase reaction method

The reaction design with rheological phase reaction method is very important, such as in what reactant substances, the ratio of reactants, choice of solvent and the amount of reaction by-products has been separated, full analysis and calculated should be carried out in advance. With a flow of preparation of nano materials disguise process, the convection disguised system factors such as the modulation process: mixing method, mixing time, mixing speed, flow disguise the system will directly determine the quality of the finished product; washing in the washing process of ways and means, directly affects the amount of washing liquid nano wrapping material properties, particle size; dry conditions, such as: drying temperature and time control of its stability nanomaterials, activity, solubility have a greater impact.

In the existing literature, for some more concerned about heating the reaction. For the rheological phase reaction diffusion dissolve in part, is less concerned with the reports, while the mechanical grinding process provided by convection phase reaction which can influence not been reported. Existing research results indicate rheological phase reaction method in synthetic chemistry, especially in compounds with novel structural and functional materials. The synthesis will play a more important role, so further study of the chemical state of flow in disguise reaction principle and the reaction stage reaction characteristics and influencing factors for synthetic chemistry and materials science development will have great scientific significance.

It believe that with convection phase reaction method further studies, more and more researchers are constantly prepared using rheological phase reaction of a variety of new materials, the rheological phase method will be increasingly sophisticated and mature, its application will be more widely.

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