Preparation of nanocomposite CNTs/PbO and CNTs/CuO via microemulsion process

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Abstract. The nanocomposite CNTs/PbO and CNTs/CuO were prepared via W/O microemulsion process. The properties of the microemulsion system for preparing the nanocomposite were studied by drawing ternary phase diagrams of microemulsion. The effects of the ratio of surfactant/cosurfactant, temperature, and salt concentration on the phase region of W/O microemulsion were investigated. A suitable microemulsion system is composed that the ratio of CTAB/cosurfactant was 4:6, the ratio of surfactant/cosurfactant was 2:3, and the reaction temperature was 25°C. The microscopic morphology of the nanocomposite CNTs/PbO and CNTs/CuO was characterized by transmission electron microscopy TEM. The specific surface area decreased obviously after nanocomposite PbO/CNTs and CuO/CNTs mixed in a 1:1 ratio by grinding.

1. Introduction

Solid propellant is the power source material of solid rocket motor, and plays an important role in the development of missile and space technology. Solid propellants often use the “lead-copper-carbon” ternary catalyst which is constituted of lead oxide, copper oxide and carbon black. Carbon plays a particular role in the double-base propellant. Powling etc first came up with the theory of lead-carbon catalysis[1]. It is proved that carbon accelerates the reduction of NO, and the existence of lead salt catalyst activates carbon. The study of Lengelle [2] and Denisyuk [3-4] found that the small amount change of carbon black concentration can cause a great change of PbO catalysis. The discovery of carbon nanotubes can further improve the performance of solid propellants. Ramaswamy [5] prepared carbon nanotubes and organics composites as the propellant Matrix, which was significantly enhanced in the ignition, total energy, safety and mechanical properties of the propellant. Therefore, the preparation of nanocomposites with the carbon nanotubes as the carrier has become a research hotspot.

The common synthesis methods of nanocomposites are: sol-gel method, precipitation method, microemulsion method and so on. The sol-gel method has the disadvantages of high cost and long synthesis period. In addition, some metals such as alkali metals that are not easily polymerized by hydrolysis are more difficult to bind firmly into the gel network, which makes the type of Nano oxide obtained by this method limited. The reaction process of precipitation method is simple, but the size of the resulting material is not easy to control, and the size of the particles is not uniform. The microemulsion method is a thermodynamically stable isotropic, transparent, or translucent dispersion system formed by two insoluble liquids [6-8]. It usually consists of active emulsifiers, auxiliary emulsifiers, oil phases, and water phases. Nanoparticles prepared with microemulsion have the
advantages of small particle size, good dispersion, and no impurities, and the equipment and process of this method are simple. In recent years, more and more attention has been paid to it.

At present, there is relatively little literature on the preparation of carbon nanotubes loaded with metal oxides by microemulsion method. Our group [9] prepared PbO/CuO/CNTs nanoparticles by microemulsion method, and the morphology of the samples was characterized by SEM, TEM, XRD, etc. The nanoparticles prepared greatly improved the activity and selectivity of the catalyst. However, the ratio of PbO and CuO in the prepared PbO/CuO/CNTs nanocomposite could not be controlled. Therefore, in this paper, the carbon nanotubes are individually loaded with PbO and CuO, and the CuO/CNTs and PbO/CNTs are fully mixed in a 1:1 ratio by grinding. It is hoped to get the nanocomposite particles with a good load and controllable ratio.

2. Experiment

2.1 Materials
CNTs and CTAB were obtained from Sigma-Aldrich Chemical Co., analysis of pure; Cyclohexane, Cu (NO$_3$)$_2$ and Pb (NO$_3$)$_2$ were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2 Synthesis
Composite of carbon nanotubes and metal oxidizer was synthesized with microemulsion method. The procedures of were CuO/CNTs as follows: First added hexadecyl trimethyl ammonium bromide (CTAB) and n-pentanol into hexahydrobenzene at room temperature, stirred for 30 min, and dropped water slowly by microburet until the solution became transparent and W/O (water-in-oil) microemulsion is got. Added ammonia water, copper nitrate into the solution and stirred for 1 h. At the same time, added purified carbon nanotubes to react for about 24 h. After that centrifuged the mixture, cleaned it by mixture of water and alcohol 5 times, filtered and heated the product in a muffle at 300℃ and got the CuO/CNTs sample. In the same way, the PbO/CNTs sample was obtained. Then mixed CuO/CNTs and PbO/CNTs at a mass ratio of 1:1 together and got the final product after grinding.

2.3 Method
The steps of drawing the ternary phase diagram of microemulsion were as follows: Surfactant CTAB and cosurfactant n-amyl alcohol as a point in the triangulation (As), the mass ratio of the two is 1:2, 2:3, 3:4. The mixture of surfactant and cyclohexane with a mass ratio of 0:10, 1:9, 2:8, ..., 8:2, 9:1, 10:0 is the second point. Distilled water is the third point of the phase diagram. Put them into glass test tubes separately, then put glass test tubes into ultrasonic cleaners, and slowly drip distilled water at a certain temperature. The amount of distilled water is adjusted by the conductivity which determined by the conductivity meter. The maximum area of microemulsion is found out from the ternary phase diagram to determine the best ratio. Change the temperature, the salt concentration of Cu(NO$_3$)$_2$ or Pb(NO$_3$)$_2$, repeat the above experiment, and draw a new ternary phase diagram.

3. Results and discussion

3.1 Microemulsion system
During the process of synthesis, the size and shape of the nano-oxides depend on the structure of water nuclei in W/O microemulsion to a great extent. Hence the research on constitution and boundary of phase, which balanced coexistence in the microemulsion, is very important. In present work, ternary diagram was adopted to analyze the essential factor, which affects microemulsion, including temperature, surfactant or cosurfactant and concentration of solution, in order to find the best microemulsion system and thus to control the core formation and growth of oxides on the nanotemplate. Fig. 1 shows the ternary phase diagram of microemulsion.

Figure 1(a) reveals that dimension of W/O microemulsion will be the largest if the proportion of CTAB and n-pentanol is 3:4, that is to say the Hydrophile-Lipophile Balance (HLB) is 10.5. The
reason is that as the HLB of the composite surfactant increases, the hydrophilic property of the two molecules goes up, the force of solubilization of polar molecules is reinforced, the content of solubilize water rises and dimension of the microemulsion increases.

It is essential to select the appropriate temperature of preparation with microemulsion. As can be seen from Figure 1(b), the structure of microemulsion changes little with temperature, and after repeating the experiment we confirm that 25°C is the optimum temperature.

Figure 1(c) and Figure 1(d) shows the effects of the salt concentration of Cu(NO₃)₂ and Pb(NO₃)₂ on microemulsion. Ions of water nuclei in high concentration could reduce its solubilization and affect the deposit capacity. Ions reacted with polar molecules in surfactant so as to decrease the repulsion between molecules in surfactant, strengthen the side attractive force and increase the rigidity of the water nuclei film. The results show that the appropriate concentration of Cu(NO₃)₂ and Pb(NO₃)₂ are 0.48 and 0.6 mol/L, respectively.
3.2 Microstructure of nanocomposite
The microstructure of nanocomposite PbO/CNTs and CuO/CNTs was characterized by transmission electron microscopy (TEM type: JEM-2011). As shown in the figure 2, many particles are deposited on the surface of carbon nanotubes. The sizes of particles are between 20 nm and 50 nm and evenly deposit in spite of agglomeration of oxide particles in parts. It is clear from the right figure, which demonstrates the amplifying nanotubes that oxide particles firmly combine with the surface of carbon nanotubes and evenly loaded on carbon nanotubes.

3.3 Specific surface area of nanocomposite
The specific surface area of nanocomposite PbO/CNTs and CuO/CNTs was measured by specific surface area meter (SSAM type: SA3100) with BET method.
From Figure 3, we can find the specific surface area of different samples: $D_{\text{CNTs}} = 43.5 \, \text{m}^2/\text{g}$, $D_{\text{CuO}} = 35.0 \, \text{m}^2/\text{g}$, $D_{\text{PbO}} = 18.0 \, \text{m}^2/\text{g}$, $D_{\text{PbO/CuO}} = 25.0 \, \text{m}^2/\text{g}$. From these data, it can be seen that the specific surface area of CNTs loaded with CuO and PbO respectively decreases compared to the specific surface area of purified CNTs, and the specific surface area of CNTs loaded with PbO decreases more. After mixing both, the surface area is reduced, indicating that the load effect is good, which is consistent with the TEM observation.

4. Conclusion
Microemulsion method was adopted to synthesize nano-metal oxide deposited on carbon nanotubes. Ternary diagram was used to study influencing factors of W/O microemulsion system. The optimum technical parameters of the process are the proportion of surfactant and cosurfactant (3:4), temperature $25^\circ \text{C}$, and concentrations of Cu(NO$_3$)$_2$ and Pb(NO$_3$)$_2$ (0.48 and 0.6 mol/L, respectively). Transmission electron microscopy (TEM) was applied to test the microstructure of the product. The specific surface area decreased obviously after nanocomposite PbO/CNTs and CuO/CNTs mixed in a 1:1 ratio by grinding indicating that the load effect is good.

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