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Synthesis of MCM-41 Mesoporous Silica by Microwave Irradiation and ZnO Nanoparticles Confined in MCM-41

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Abstract: ZnO nano clusters were confined in ordered mesoporous MCM-41 silica materials. The guest-host ZnO-MCM-41 were characterized by XRD, SEM, EDS, TEM, GA, FTIR and UV-Visible methods. By GA and EDS results, the BET surface area and pore volume of MCM-41 decreased after ZnO confined in it and the contents of the nano ZnO is about 10% in the ZnO-MCM-41 samples. By XRD, TEM and FTIR results, the hexagonal structure of MCM-41 retained after confining nano ZnO in the mesopores and normal crystalline ZnO hasn't been found. It conformed that nano ZnO were confined inside the mesopores of the MCM-41 successfully and the nano ZnO structure in MCM-41 is different from the bulk ZnO. UV-Vis studies show that the nano ZnO clusters in MCM-41 has a 50 nm blue shift of adsorption edge compared to the bulk ZnO which will increase the band gap.

Keywords: ZnO nano clusters, mesoporous MCM-41, silica, host-guest

1 Introduction

Ordered Mesoporous silica MCM-41 is promising as catalysis, adsorption, separation and host-guest compounds because of the high BET surface area (700-1200 m²/g), large pore volumes (1cm³/g), pore sizes (1.5-30 nm) and well-ordered hexagonal structures^{1,2}. In particular, the uniform, rod-like pore structure of MCM-41 as pure silica materials is ideal host material for semiconductors due to their degree of order and the large band gap of SiO₂, which serve as barrier material ³. Several

semiconductors compounds were confined in MCM-41 or SBA-15 mesoporous silica. The compounds are oxides or chalcogenides, including CdS, CdSe, ZnS, TiO₂, ZnO, Fe₂O₃ etc.⁴⁻¹². The compounds confined in the MCM-41 is nano-sized particles and showed the blue shifts of the absorption band according to the Diffuse reflectance ultraviolet-visible spectroscopic results⁴⁻⁶. However, the MCM-41 samples they used were all unmodified and as such have stability problems after several hours in boiling water or one day in some aqueous buffer solutions¹³. In this work, the MCM-41 samples were synthesized by a normal hydrothermal method and modified by post-synthesis hydrothermal treatment to improve their hydrophobicity¹³. The ZnO nanoclusters were confined in modified MCM-41 by post-synthesis hydrothermal treatment. The modified MCM-41 has a larger pore volume and pore size while the stability was improved compared to the normal MCM-41. The MCM-41 before and after confining ZnO nanoclusters were characterized by a variety of techniques including TGA, XRD, EDS, TEM, FTIR, Raman and UV-Vis.

2 Experiments

2.1 Chemiclax

Chemiclax: Sodium hydroxide (NaOH), cetyltrimethylammonium bromide (CTAB), fumed silica, Zinc acetate, ethanol were used. The NaOH was from Merck Pty Ltd, all other chemicals were from Aldrich. All chemicals were of analytical reagent grade. All water used was distilled.

2.2 Normal Synthesis

The preparation procedure was as follows^{14,15}. CTAB (16.4 g) was dissolved in 50 g distilled water. NaOH (2.54 g) and 40 g distilled water were mixed at room temperature. The CTAB solution was then added to the NaOH solution, stirring for 30 minutes. Fumed silica (15.90 g) was added to the mixed CTAB and NaOH solution. Finally, 30 g distilled water was introduced, stirring at 75°C for 1 h to obtain a gel. It was then transferred into a PTFE-coated autoclave and heated to 120°C for 2 days. The as-synthesised sample was filtered and dried prior to calcination at 550°C for 9 h in air or in nitrogen for 1 h followed by air for 8 h with a heating rate of 1°C/min.

2.3 Post Synthesis Hydrothermal Treatment

The post-synthesis hydrothermal treatment was carried out by replacing the mother liquor with distilled water after the normal synthesis^{14,16}. The as-synthesised sample (3 g) with 50 mL distilled water was put into a PTFE-coated autoclave, and kept in the oven at 135° or 150°C for 24 h. Finally, the solid product was filtered, washed, dried and calcined in air as in the normal preparation. The MCM-41 used for confining ZnO is the modified sample by post-synthesis treatment.

2.4 ZnO nano clusters confined in MCM-41

0.04 M Zn(CH₃COO)₂ solution was prepared by Zn(CH₃COO)₂ · 2H₂O and ethanol. 1g MCM-41 was put in the 50mL zinc acetate solution, stir for 2h at room temperature. Then the mixture was filtered, washed by ethanol and dry at 105°C overnight. Finally the sample was annealed at 450 °C for 2h in air.

2.5 Characterization

X-ray powder diffraction (XRD) data was obtained using a Philips X'Pert MPD PW 3050 diffractometer operated at 40kV, 40mA using a copper LFT tube and a Multi purpose sample stage.

Gas adsorption (GA) analysis measurements using nitrogen at 77 K were conducted on a Micromeritics Tristar 3000. Before analysis, the 0.1-0.3 g of each sample used was evacuated at 250°C overnight to remove water from the sample. Surface areas (S_{BET}) were calculated using the BET model¹⁷. Total pore volumes (V) were estimated based on the amount of nitrogen adsorbed at a relative pressure of about 0.99 and adsorption average pore diameters (D_{BJH}) were calculated using the BJH model for the adsorption branch of the isotherm¹⁷⁻²¹. The wall thickness (t) was estimated as the unit cell dimension minus the BJH pore diameter. Although the BJH model is known to underestimate the pore diameter of MCM-41, which will cause an overestimation of the wall thickness by this method, it is useful for comparison purposes²⁰.

Thermogravimetric analysis (TGA) were studied on TGA Q 500/thermal Star mass spectrometer analysis system.

Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectrometry (EDS) analysis for the micrograph and the composition were carried out on a FEI Quanta 200 ESEM. The samples were coated by carbon before analysis.

The Transmission Electron Microscopy (TEM) analysis was performed on Philips (CRYO) CM200 microscopes TEM/STEM systems. The samples were suspension in ethanol for the TEM tests.

FT Infrared spectra were recorded on a Nexus 870 FT-IR Spectrometer in the range 200-4000 cm^{-1} by CsI method. The number of scans is 64, and the resolution is 2 cm^{-1} . The FT Raman was run on a Perkin Elmer 2000 in the range of 3800-200 cm^{-1} with 400mW of Laser Power. The photo adsorption spectra were recorded on a Varian Cary 100 UV-visible spectrophotometer in the range of 600-200 nm.

3 Results and discussion

3.1 Thermogravimetric analysis (TGA)

The dried as-synthesized ZnO-MCM-41 was run on a TGA system for knowing the calcining temperature of the as-Syn. Sample. By TGA results of the as-synthesized ZnO-MCM-41, the decomposition temperature of the Zinc acetate is about 400°C (shown in Figure 1). So the calcination was run at 450°C for 2h in air. And according to the TGA results, it is confirmed that zinc acetate can be found in the MCM-41 sample and MCM-41 can adsorb zinc acetate in ethanol.

3.2 X-Ray powder diffraction

From the powder X-ray diffraction pattern of the calcined MCM-41 silica before and after confining nano ZnO clusters, the hexagonal structure was retained (Figure 2). After the formation of ZnO clusters in the pores, the XRD peaks of the MCM-41 are reduced in intensity and slightly shifted to smaller d spacings. The loss in intensity is due to the fact that the introduction of scattering material into pores leads to an increased phase cancellation between scattering from walls and the pore regions^{3,22}. The contraction of mesoporous structures on calcination or thermal treatment is due to the influence of the impregnation treatment. It probably increases the connectivity within the silica walls and results in a small contraction of the structure^{3,22}. No reflections of the bulk ZnO compound are present even if the sample

was calcined at 550°C for 2 h that is consistent with the results shown by Lu et al. and Dapurkar et al.⁴.

3.3 Nitrogen physisorption

The BET surface area and pore volume decreased 30% after confining ZnO nano particles in MCM-41 with respect to the initial MCM-41. And the pore diameter of the ZnO-MCM-41 decreased as well. It means that the ZnO nanoclusters were confined inside the pores of the MCM-41 successfully. Both isotherms are of type IV, typical for mesoporous material (Figure 3). The position of the step evoked by capillary condensation is shifted to lower relative pressure due to the decrease in pore size. The BJH adsorption pore diameter of the MCM-41 is 3.3 nm.

3.4 Scanning Electron Microscopy and Energy-dispersive X-ray spectrometry

The SEM micrograph showed that hexagonal particles of MCM-41 clearly. By EDS results, It confirmed the presence of the ZnO in the MCM-41 and the contents of ZnO nano in MCM-41 is about 10 wt%. The EDS spectrum was seen in Figure 4.

3.5 Transmission electron microscopy

The hexagonal arrangement of the pores can be still observed over a long range after the impregnation of ZnO according to the TEM image (Figure 5). Furthermore no ZnO bulk particles were found on the outer surface of the MCM-41. This coincide with the results of XRD and GA adsorption that semiconductor particles were confined inside the mesopores.

3.6 FT Infrared and Raman spectroscopy

FT infrared and Raman spectra of initial MCM-41 were recorded in the range 200-4000 cm^{-1} wave number, uncalcined guest-host sample($\text{Zn}(\text{CH}_3\text{COO})_2$ -MCM-41) and calcined ZnO-MCM-41 were shown in figures 6-8. The adsorption band of zinc acetate was found before calcination according to the FTIR results. The FTIR and Raman spectra of ZnO-MCM-41 and initial MCM-41 are similar because of the nano ZnO is unnormal crystalline that consistent with the XRD results.

3.7 UV-Visible diffuse reflectance spectra

The UV-Visible diffuse reflectance spectra of the ZnO-MCM-41 are shown in Figure 9. The pure siliceous MCM-41 gives very little absorption in this range. The onsets of

absorption of the ZnO-MCM-41 is about 390 nm and the adsorption of nano ZnO in MCM-41 showed a blue shift 50nm compared to the bulk ZnO. The blue shift indicated that the band gap of the nano ZnO in the MCM-41 increased and the size quantization effect exists. The particle size of the ZnO is not more than 3.3nm which is the BJH pore size of the MCM-41.

According to the results of XRD, EDS, TEM, FTIR, Raman, UV-Vis and nitrogen adsorption-desorption, it is confirmed that the nano ZnO was confined inside the mesopores of the modified MCM-41.

4 Conclusions

By XRD, SEM, EDS, GA, TEM, FTIR, UV-Vis techniques, it is confirmed that nanostructured ZnO semiconductor particles were formed inside mesopores of the modified MCM-41. The UV-Vis result showed that the nano ZnO has quantum effect, while the adsorption of nano ZnO has 50 nm blue shift compared to the bulk ZnO which leads to increase the band gap. As a new displaying material, nanoclusters ZnO confined in pure silica MCM-41 is promising because of the uniform nano particle size and the large band gap of silica.

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