Sol-gel preparation and spectroscopic study of the pyrophanite MnTiO$_3$ nanoparticles

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Abstract The nanosized xerogel of titanium dioxide (TiO$_2$) and manganese oxides (MnO$_2$, Mn$_2$O$_3$, Mn$_3$O$_4$) was prepared by the sol-gel method using manganese chloride (MnCl$_2$·4H$_2$O) and titanium isopropoxide (Ti(O-iPr)$_4$) as precursors in cetyltrimethylammonium bromide (CTAB)/ethanol/H$_2$O/HCl micelle solutions, following the calcinations of the produced powders at different temperatures. The nanostructure and phase composition of these nanoparticles were characterized with X-ray powder diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). The spectroscopic characterizations of these nanoparticles were also done with UV-Vis spectroscopy and laser Raman spectroscopy (LRS). The XRD patterns show that the pyrophanite MnTiO$_3$ phase was formed at the calcinations temperature of 900°C. The TEM images show that the nanoparticles are almost spherical or slight ellipsoidal and the sizes are 50 nm on average. The UV-Vis spectra show that the nanosized MnTiO$_3$ have significant absorption bands in the visible region. There are new absorption peaks of MnTiO$_3$ nanoparticles in LRS compared with the pure TiO$_2$ powder.

Keywords: pyrophanite MnTiO$_3$, nanoparticles, spectroscopy, CTAB micelle, sol-gel.

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Titanium dioxide (TiO$_2$) is one of the green catalysts, which has attracted much attention due to its promising applications in the purification of air, the bactericidal action of water, and environmental photocatalytic degradation of organic pollutant compounds in waste water$^{[1,2]}$. TiO$_2$ includes three phases: brookite, anatase and rutile. The effective photoexcitation of TiO$_2$ semiconductor particles requires the application of light with energy higher than the titania band gap energy ($E_{bg}$). The band gap energy of TiO$_2$ is about 3.2 eV for anatase and 3.02 eV for rutile, therefore the absorption thresholds correspond to 380 and 410 nm for the two titania forms, respectively. Thus, if natural sunlight should be used for the photoexcitation of this material, only the ultraviolet fraction (about 5%) of the solar irradiation has sufficient energy for this process. It is believed that the extension of light absorption can improve photocatalytic activity of semiconductor. A possibility to overcome this obstacle is doping numerous ions like noble metals, transition metals into the titanium dioxide to change the absorption band to a visible range. The effect of doping is to change the equilibrium concentration of electrons or holes, and the light absorption band of metal-TiO$_2$ can...
be shifted into the visible region\[3\]. In transition metal, manganese acts as efficient catalyst in many industrially important oxidation processes, due to its variable oxidation states (+2, +3, +4 and +7).

In recent years, Ding\[4\] and Gallardo-Amores\[5\] reported the synthesis and photocatalystic properties of TiO\(_2\)-MnO, TiO\(_2\)-MnO\(_2\) composite nanomaterials. We have prepared the MnTiO\(_3\) nanoparticles using commercial TiO\(_2\) and MnCl\(_2\)-4H\(_2\)O as base materials\[6\]. The objective of this paper is to investigate the synthesis of pyrophanite MnTiO\(_3\) nanoparticles. It was produced by calcinations of xerogel of TiO\(_2\) and manganese oxide (MnO\(_2\), Mn\(_3\)O\(_4\), Mn\(_2\)O\(_3\)), which was prepared by the sol-gel method using manganese chloride (MnCl\(_2\)-4H\(_2\)O) and titanium isopropoxide (Ti(O-iPr)\(_4\)) as base material in CTAB/ethanol/H\(_2\)O/HCl micelle solutions. The structure and spectroscopic properties of nanoparticles were investigated.

1 Experimental

1.1 Materials

Cetyltrimethylammonium bromide (CTAB), titanium isopropoxide (Ti(O-iPr)\(_4\)) and manganese chloride tetrahydrate (MnCl\(_2\)-4H\(_2\)O) were purchased from Aldrich Chemical Co. and were used as received. Titanium dioxide powder P-25, which is predominantly anatase (70% anatase, 30% rutile), was purchased from Degussa Co. (Germany) and was used without any further treatment. The other materials were of analytical grade and used as produced without further purification. Distilled water was used throughout this study.

1.2 Preparation of MnTiO\(_3\) nanoparticles

A typical synthesis procedure is as follows: first, the mixture of distilled water with ethanol, HCl and MnCl\(_2\)-4H\(_2\)O, was put in reflux at 70°C and stirred constantly for 30 min; second, the mixed solution of CTAB and ethanol was added; third, Ti(O-iPr)\(_4\) was added drop by drop to the above mixture while refluxing, and then the solution was further refluxed for 12 h at 70°C; finally, the resulting solution was left to an open container at 70°C until the xerogel was formed upon solvent evaporation. This method gives a MnCl\(_2\)/Ti(O-iPr)\(_4\) molar ratio of 1.00, CTAB/Ti(O-iPr)\(_4\) molar ratio of 0.20, water/Ti(O-iPr)\(_4\) molar ratio of 17.00, hydrochloric acid/Ti(O-iPr)\(_4\) molar ratio of 1.40, ethanol/Ti(O-iPr)\(_4\) molar ratio of 20.00. The xerogel was dried in air at 100°C for 12 h, ground to fine powder and calcined in air at 600, 700, 800, 900°C for 6 h, respectively.

1.3 Characterization techniques

To investigate the phase composition and the crystallite size distribution of the nanoparticles after the calcinations, X-ray powder diffraction (XRD) measurement was performed. XRD patterns were recorded on a Philips X’pert-MPD diffractometer, using Cu K\(_\alpha\) radiation. The crystallite sizes were calculated from the peak widths using the Scherrer equation. The transmission electron microscopy (TEM) studies were carried out with a JEOL JEM2010 transmission electron microscope. Semiquantitative analyses were carried out on an energy-dispersive X-ray (EDX) spectroscopy spectrometer connected to a Hitachi S-2400 Scanning Electron Microscope. X-ray photoelectron spectroscopy (XPS) studies were performed with a Vacuum Generators photoelectron spectrometer (VG-Scientific ESCALAB 250 spectrometer) with monocratomized Al K\(_\alpha\) X-ray source. The C1s signal (285 eV) was taken as an internal standard to calculate the binding energies (\(E_b\)). The UV-Vis absorption spectra were obtained with a Varian Cary 1C UV-Visible spectrophotometer. The samples were ultrasonically dispersed in distilled water at 10\(^{-4}\) mol·L\(^{-1}\) for 30 min. Raman spectra were recorded with a BRUKER (Germany) FRA-106/S spectrometer, using the 1064 nm excitation line of Nd-YAG Laser. The data were collected by keeping the power at 50 mW, 100 scans and 4 cm\(^{-1}\) resolution.

2 Results and discussion

2.1 Preparation of MnTiO\(_3\) nanoparticles

The oil-in-water (O/W) micelle could be formed by CTAB cationic surfactant in water, ethanol, HCl mix solutions\[7\]. Micelle formation is greatly affected by