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Preparation and spectroscopy study of monodispersed metal oxide nanocrystals

G. PANG*, H. JIN, Y. LI, Q. WAN, Y. SUN, S. FENG
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China
E-mail: panggs@jlu.edu.cn

A. GEDANKEN
Department of Chemistry, Bar-Ilan University, Ramat-Gan, 52900, Israel

SnO_2 nanocrystals with an average particle size of 3.5 nm are obtained by heating the mixture of hydrous SnO_2 nanoparticles and $SrCO_3$ particles. $SrCO_3$ can be removed from the product by washing with diluted HNO_3 acid. A series of SnO_2 nanocrystal samples with different particle size are prepared by heating at different temperature. All the samples obtained are characterized by XPS and Raman spectra. XPS result shows that the binding energy of $Sn3d_{5/2}$ decreases as the particle size increases. There is a surface-related Raman peak observed, which increases in intensity when the SnO_2 particles size decreases. The size-related change of the surface structure is responsible for the properties of nanocrystals.

1. Introduction

It is well known that a host of properties depend on the size of nanoparticles, including magnetic, optical, melting points, specific heats, and surface reactivity [1]. The development of reliable and reproducible methods for preparing large quantity of high crystallinity and monodispersity of inorganic nanocrystals remains an area of extensive interest. A large variety of methods have been used, such as sol-gel, precipitation, hydrothermal, sputtering, and spray pyrolysis. Each method has some advantages and also disadvantages over the others. Wet method is favorable for preparing particles with uniform size and shape in most of the cases because of the relative moderate condition. The preparation of monodispersed particles of metal oxides and hydroxide with specific shapes is as old as colloid chemistry itself. But, in some cases, the as-prepared samples obtained by wet method are amorphous or poorly crystallized and contain water. Further drying and calcination at high temperature are therefore indispensable. The calcined product is usually made up of aggregated crystalline particles. The aggregation is very difficult to be broken again after it formed.

We have developed a novel method to avoid the aggregation in preparing monodispersed particles during calcinations process. In this method, a hydrous metal oxide nanoparticles is precipitated from an inorganic salt solution. The hydrous metal oxide colloid particles are mixed with $SrCO_3$ particles before further calcination is applied. The agglomerations of metal oxide nanoparticles are inhibited during the calcinations process. We have succeeded in preparing monodispersed yttria-stabilized zirconia (YSZ) and SnO_2 nanoparticles [2, 3]. A monodispersed nanocrystalline YSZ with an average particle size of 4.7 nm is obtained by using this method. A very high surface area of 165 m^2/g and a significant band gap increase from 4.13 to 5.44 eV are observed. The average particle size of SnO_2 nanocrystals obtained by using this method is 3.5 nm, compared with 5.9 nm for the sample prepared by conventional method. The band gap of SnO_2 nanocrystals increases from 3.65 eV with a particle size 5.9 nm to 3.97 eV with a particle size 3.5 nm.

Modifying the surface structure is widely used in controlling the size and shape of inorganic nanocrystal. The growth of inorganic nanocrystal can be controlled by capping with certain surfactant [4, 5]. Zeolite is also used as the host for preparing nanocrystal [6]. Smaller nanocrystals can be stabilized at higher temperature when they adsorb on a substrate [7]. Stabilizing smaller nanocryatals on a substrate is crucial in

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*Author to whom all correspondence should be addressed.

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controlling the particle size as well as explaining some important properties that are exhibited in nanoscales. The surface structure plays a key role in its applications as catalysis, chemical gas sensing, and microelectronics. The surface structure of bulk SnO_2 has been extensively studied [8–10]. A variety of surface reconstructions are observed as a function of heating temperature and preparation conditions. The surface structure of SnO_2 nanocrystals is reported to be correlated with the amorphous tin oxide, which contains elongation of Sn–O bond in a distorted octahedral [11, 12].

2. Experimental details

The reactants used for the preparation of SnO_2 are $SnCl_4{\cdot}5H_2O$, $Sr(NO_3)_2$, NH_4OH, and NH_4HCO_3. A hydrous SnO_2 precipitation is obtained by dropping ammonium hydroxide into $SnCl_4$ solution. The precipitation is centrifuged and washed with deionized water, then dispersed in water under sonication and formed a suspension. $SrCO_3$ nanoparticles are prepared by dropping NH_4HCO_3 solution into 0.05 M $Sr(NO_3)_2$ solution under sonication. The $SrCO_3$ nanoparticles are washed with deionized water, then dispersed in water and formed a suspension. The $SrCO_3$ nanoparticles suspension is added into the hydrous SnO_2 suspension under stirring. The proportions of hydrous SnO_2 and $SrCO_3$ are 1 : 2.5 in weight. The mixture is centrifuged, dried at 120°C, and calcined at 600°C for 2 h. $SrCO_3$ is washed out by dissolving it in 10% HNO_3 solution under sonication. The solid product is washed with deionized water for several times and dried in vacuum at room temperature. At this stage, the product is referred to as SRT. The samples are further heated at different temperature, 200, 400, 600, 800, and 1000°C, for 2 h and referred to as S_{200}, S_{400}, S_{600}, S_{800}, and S_{1000}, respectively. The particle size is calculated from the X-Ray line broadening, using the Debye-Scherrer equation. HRTEM was observed on Microscope Philips CM 30. XPS was measured on an ESCA-LAB MKII X-ray photoelectron spectrometer with Al Kα radiation, the C1s signal was used to correct the charge effects. All the samples are treated in vacuum (0.1 torr) at 120°C for 5 h before the XPS measurement. Raman spectra were recorded on a Bruker RFS 100 Raman spectrometer at room temperature with 2 cm^{-1} resolution.

3. Results and discussion

The average particle sizes estimated from the broadening of the XRD are 3.5, 3.6, 4.0, 5.9, 8.8, and 17.9 nm for the samples S_{RT}, S_{200}, S_{400}, S_{600}, S_{800}, and S_{1000}, respectively. Fig. 1 shows the HRTEM micrograph of sample S_{RT}. The particle sizes observed from the HRTEM micrograph is ca. 3.0 to 4.0 nm, which is consistent with the XRD result. Fig. 2 shows the XPS results. The observed binding energy is different for the SnO_2 nanocrystal samples with different particle size (Table I). S_{RT} has the largest

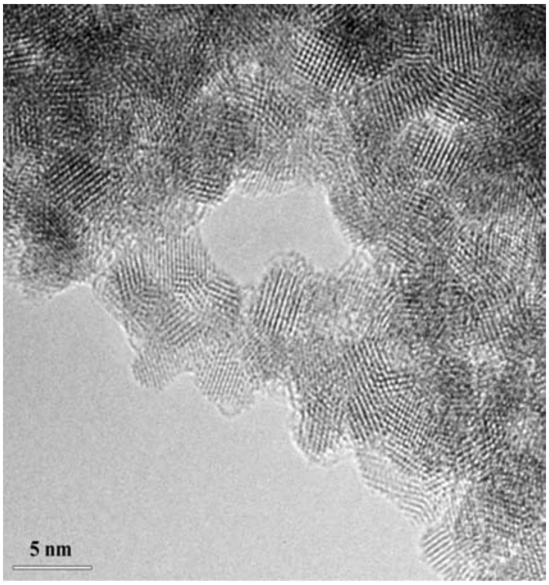

Figure 1 HRTEM micrograph of sample S_{RT}.

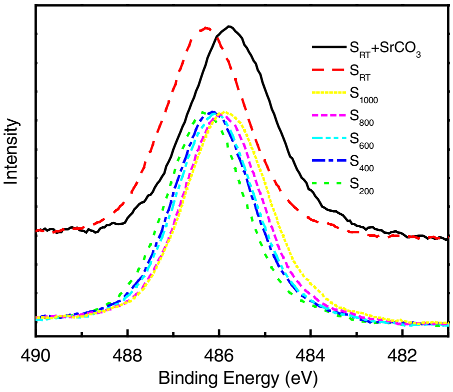

Figure 2 XPS spectra of Sn $3d_{5/2}$ for the sample S_{RT} supported on $SrCO_3$, S_{RT}, S_{200}, S_{400}, S_{600}, S_{800}, and S_{1000}. All the samples are treated in vacuum (0.1 torr) at 120°C for 5 h before the XPS measurement.

TABLE I The particle size, Binding Energy of $Sn3d_{5/2}$, FWHM of $Sn3d_{5/2}$, and the surface-related Raman shift for the sample S_{RT} supported on $SrCO_3$, S_{RT}, S_{200}, S_{400}, S_{600}, S_{800}, and S_{1000}. The subscript indicates heating temperature

	Average particle size D_{110} (nm)	Binding energy of $Sn3d_{5/2}$ (eV)	FWHM of $Sn3d_{5/2}$ (eV)	Raman shift (cm^{-1})
S_{RT}	3.5	486.29	2.02	577.7
S_{RT}+$SrCO_3$	–	485.74	2.14	–
S_{200}	3.6	486.30	1.99	574.3
S_{400}	4.0	486.15	2.01	572.5
S_{600}	5.9	486.09	1.99	571.1
S_{800}	8.8	485.94	2.01	570.4
S_{1000}	17.9	485.80	2.13	567.7

binding energy of 486.30eV. And the binding energy decreases as the particle size increases. S_{1000} has a binding energy of 485.80eV. While S_{RT} adsorbs onto the substrate of $SrCO_3$, the binding energy is 485.74 eV. The binding energy of 486.30 eV is correspondent with the value of Sn^{4+}; whereas 485.80 eV is correspondent with the value of Sn^{2+} [9]. Heating in vacuum results a reduced surface because of the removal of surface oxygen [8]. It worth noting that a broadening of the $Sn3d_{5/2}$ peak in the XPS is observed for only the S_{1000} sample, and the S_{RT} on the substrate $SrCO_3$ (Table I). The FWHM of XPS peaks increase ca. 0.13 eV for both samples when compared with all the other smaller isolated nanocrystals. The broadening of $Sn3d_{5/2}$ spectrum is related to the changes of the oxidation state [13]. The XPS results imply that the SnO_2 nanocrystals with different size present different surface structure.

Raman spectroscopy is an effective method for studying the changes of the local structure of material. There have been several reports on the relationship between the particle size and the spectral changes in SnO_2 nanocrystals [14, 15]. Fig. 3 shows the Raman results. The Raman spectrum of S_{1000} (17.9 nm) exhibits Raman shifts at 475, 633, and 775 cm^{-1}, which are similar to that of single crystal of SnO_2. The small hump at ca. 572 cm^{-1}, which is attributed to the surface phonon mode of the sample, is related to the phonon mode at 633 cm^{-1} observed for the bulk SnO_2 [14]. The disordered surface structure has a larger Sn–O bond length and wider atomic spacing distribution [16]. When the particle size decreases, the intensity of the Raman peak at ca. 572 cm^{-1} increases. There is also a slight shift of this surface-related Raman peak observed from 577.7 cm^{-1} for S_{RT} to 567.7 cm^{-1} for S_{1000} (Table I). The relationship between the change of the Raman spectra of SnO_2 and its crystal size has been explained by the local lattice disorders at the surface and interface component of SnO_2 nanostructure [17].

4. Conclusions

In summary, SnO_2 nanocrystals with an average particle size of 3.5 nm are obtained by heating the mixture of hydrous SnO_2 nanoparticles and $SrCO_3$ particles. $SrCO_3$ can be removed from the product by washing with diluted HNO_3 acid. A series of SnO_2 nanocrystal samples with different particle size are prepared by heating at different temperature. All the samples are characterized by XPS and Raman spectra. The changes of the surface structure of the nanocrystals with different particle sizes (3.5–17.9 nm) are observed. The size-related change of the surface structure is responsible for the properties of nanocrystals.

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