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Adsorption study of Pb^{2+} ions on nanosized SnO_2, synthesized by self-propagating combustion reaction

ARUNKUMAR LAGASHETTY* and A VENKATARAMAN†

Appa Institute of Engineering & Technology, Gulbarga 585 101, India
†Department of Materials Science and Chemistry, Gulbarga University, Gulbarga 585 106, India

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Abstract. Novel combustion synthetic route for the synthesis of nanosized SnO_2 is reported. X-ray, tap and powder densities of SnO_2 are calculated. Adsorption of Pb^{2+} ions on combustion derived nanosized SnO_2 is studied. The as synthesized SnO_2 and lead ions adsorbed SnO_2 are characterized by X-ray diffraction (XRD), scanning electron micrograph (SEM), and infrared spectroscopic (IR) techniques. The eluent is characterized by atomic absorption spectroscopy (AAS) and solution conductivity (SC) to know the reduction in the concentration and increase in conductance of lead solution after adsorption on the SnO_2 surface. The potential use of solid adsorbents for the adsorption of heavy metal pollutants is envisaged in the present work.

Keywords. SnO_2; nanosized; Pb^{2+}; adsorption; eluent; pollutant; adsorbent.

1. Introduction

The development of new route for the synthesis of any solid is an integral aspect of material chemistry (Rao 1994). Some of the reasons are the continuing need for fast and energy efficient technique, the necessity to avoid compacting reactions in known process, and the challenge implied in the synthesis of metastable phases by passing through thermodynamically reversible routes (Mallikarjuna *et al* 2003). In this context, the work done by Rao *et al* on the synthesis of materials employing new routes is of particular interest (Figlarz 1989; Gopalakrishnan 1995; Rao *et al* 2003).

In recent developments, techniques such as sol–gel and other soft chemical (Chimie douce) (Brinker and Scherer 1989; Helen and Kamath 2000) methods have led to the preparation of engineered and advanced meterials.

Use of microwave for the synthesis of inorganic compounds has gained great importance in recent years (Rao and Ramesh 1995; Wang *et al* 2003). The method offers several advantages over the conventional routes, the most important of them being the very short time and energy economy. Several microwave reactions are now known to occur at lower temperature than in conventional methods. The rapidity of the reactions offers excellent conditions for retention of metastable phases. This novel method has been found to result in better reaction yields and better structural uniformity of products than conventional ceramic methods.

Metal oxide materials prepared by sol–gel chemistry are high surface area and high porosity materials attractive in applications such as insulators and catalytic supports. The versatility of sol–gel chemistry provides a means of controlling the shape, morphology and textural properties of the final materials (Rao *et al* 1999; Lagashetty 2003). Sol–gel chemistry also provides a means of preparing mixed oxide phases and can be controlled on both the molecular and nanoscales (Panneerselvam *et al* 2001).

Synthesis of nanosized material is done through a self-propagation route employing a carboxylate precursor. This synthetic route can be considered interesting for its simplicity, reproducibility and easy scale up. It produces a homogeneous precursor with a controlled stoichiometry and also does not require expensive chemicals. It is a low-energy reaction and can be carried out in a china dish in an open atmosphere. In this self-propagation combustion reaction, a suitable fuel for our study was found to be poly (ethylene glycol).

The decrease in particle size up to nanoscale increases the surface area and hence increases the number of adsorption sites (Mallikarjuna and Venkataraman 2003). Synthetic g-$A1_2O_3$ and g-Fe_2O_3 show excellent adsorption behaviour (Berger *et al* 1997; Lagashetty *et al* 2003). These vacant sites in the structure are mainly responsible for the adsorption of heavier ions. A critical review on understanding the adsorption behaviour of nanoscale materials and nanocomposites are reported (Tesfai *et al* 1998).

In the present investigation, we report the self-propagating combustion synthetic route using a new precursor (tin oxalate) for the synthesis of nanosized SnO_2. Poly

*Author for correspondence

(ethylene glycol) is used as a fuel in this reaction. Various methods are adopted to calculate density of SnO_2. The adsorption behaviour of lead ions on the surface of as synthesized SnO_2 is studied.

2. Experimental

2.1 *Materials and methods*

All the chemicals used were of AR grade. Poly (ethylene glycol) of molecular weight, 4000, was obtained commercially. Cold oxygen free distilled water was used in the present work.

Self-propagating combustion synthetic route was adopted for the synthesis of SnO_2 particles. The polyethylene glycol was used as a fuel for the combustion reaction. Adsorption study of lead ions on as synthesized SnO_2 was carried out by dynamic method at room temperature.

2.2 *Preparation of tin oxalate precursor*

This precursor was prepared by dissolving equimolar quantities of tin chloride and oxalic acid and stirred well. The precipitate of tin oxalate obtained was filtered through sintered glass crucible and was washed with oxygen-free distilled water till free from chloride ions and oxalic acid, finally with dry acetone and was then dried under vacuum.

2.3 *Synthesis of nanosized SnO_2*

The tin oxalate was mixed with poly (ethylene glycol) in the weight ratio 1 : 5 and ground well in a pestle and mortar. Resultant solid was placed in a crucible and heated in air. It was observed that initially poly (ethylene glycol) melted, then frothed and finally ignited to form SnO_2. On cooling to room temperature no trace of carbon impurities was observed in the final residue of SnO_2.

2.4 *Density measurement*

2.4a *Density evaluation from X-ray data*: The X-ray densities of the samples were computed from the values of lattice parameters using the formula (Smith *et al* 1959)

$$d = 8\frac{M}{Na^3},$$

where 8 represents the number of molecules in a unit cell of a spinal lattice, M the molecular weight of the sample, N the Avogadro's number and a the lattice parameter of the sample.

The lattice constant for the cubic was calculated using the equation

$$d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}.$$

2.4b *Tap density*: The as prepared SnO_2 was crushed in agate mortar using a pestle and mortar. A known amount of this powder was filled into a graduated cylinder of 25 ml capacity. The cylinder was tapped until the powder level remained unchanged. The volume occupied by the powder was noted. The ratio between the weight of the substance and the volume gave tap density (Kinsman 1978).

2.4c *Powder density*: The powder densities were measured using Archimedes principle (Hiremath 2001) with a pycnometer and xylene as a liquid medium. The pycnometer of volume 25 ml was used. The following weights were taken and used in the density calculation.

Weight of the bottle = W_{1g}, weight of the bottle + substance = W_{2g}, weight of the bottle + substance + xylene = W_{3g}, weight of the bottle + xylene = W_{4g}, density of xylene = r_{sol}, density of sample = r_{sample}.

$$r_{sample} = \frac{(w_2 - w_1)\, r_{sol}}{(w_4 - w_3) + (w_2 - w_1)}.$$

2.5 *Adsorption study*

One gram of as synthesized tin dioxide was taken in a 250 ml conical flask and 50 ml of known concentration of lead acetate solution was added in the conical flask. This flask was placed on a mechanical shaker at 150 rpm rate for adsorption of lead ions on SnO_2 particles. After 12 h the solution was eluted and preserved for atomic absorption spectroscopic study, meanwhile solution conductivity of eluent was noted. The solid product i.e. adsorbent, was washed with water and air-dried. The solid was characterized by employing XRD, SEM and IR techniques.

2.6 *Characterization*

The X-ray diffraction patterns were obtained employing a Jeol JDX-8p spectrometer using Cu$K\alpha$ radiation. The X-ray generator was operated at 30 kV and 20 mA. The scanning range, $2\theta/\theta$ was selected. The scanning speed = $1° \text{ min}^{-1}$ were employed for determination of precise lattice parameter. High purity silicon powder was used as an internal standard.

The shape, size and distribution of the powder, as prepared tin oxide sample and microstructure of the sample were examined using a Leica-440 Cambridge Stereoscan, scanning electron microscope image. The SEM was operated at 20 kV. The samples were made conducting by sputtering of gold using a Polaron d.c. "sputtering unit" operated at 1·4 kV and 18–20 mA.

The infrared spectra of tin dioxide were recorded on a Perkin–Elmer FTIR spectrophotometer [Model 1000] in the range 300–4000 cm^{-1}.

The solution conductivity gives information about conducting nature of the solution. The conductance of eluent solution before and after adsorption of lead was taken by employing Elico 8 2T conductivity bridge.

The concentration of lead solution before and after adsorption of lead on the synthesized tin dioxide were understood by atomic absorption spectroscopy (AAS). The AAS of lead solution were recorded on a Smith-Hieftji,1000 automated AA/AE spectrometer.

3. Results and discussion

3.1 *X-ray diffraction study*

Figure 1a presents XRD pattern of as synthesized SnO_2 nanoparticles. The sample peaks (indexed in the pattern) are well in agreement with JCPDS 41-1445. It reveals a good crystalline tetragonal (*p*42 *mnm*) structure.

Figure 1b presents XRD pattern of Pb^{2+} adsorbed on SnO_2 nanoparticles. This pattern shows some additional reflections corresponding to lead adsorption on the SnO_2. The lead peaks (JCPDS-44-0872) are indexed in the pattern. Presence of lead peaks is clearly visible along with other less intensity peaks in the adsorbed pattern. This shows Pb^{2+} ions adsorbed on the SnO_2 material, which again is in conformation with IR studies, where additional frequencies are observed.

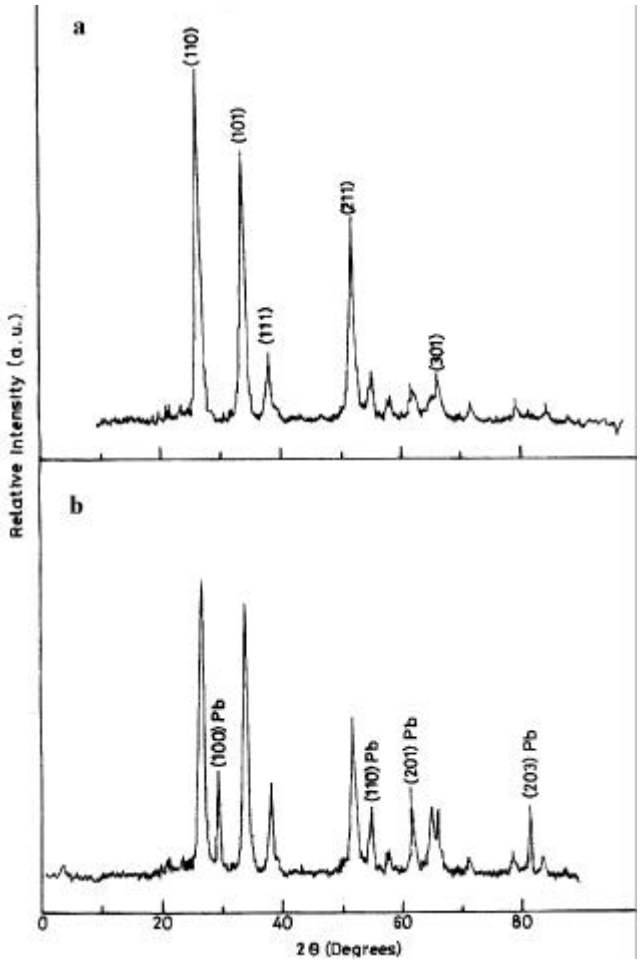

Figure 1. XRD patterns of **a**. SnO_2 particles and **b**. Pb^{2+} adsorbed SnO_2 particles.

3.2 *SEM study*

The surface morphology of the as synthesized tin dioxide is studied by scanning electron micrograph. Figure 2 shows SEM image of as synthesized tin dioxide. This image shows the interconnected ultrafine SnO_2 particles with nanosized dimensions forming agglomerates. All the particles are irregular and some are spherical in nature.

Figures 3a–b show SEM of lead adsorbed tin dioxide at low and high magnifications. In lower magnification we see beautiful surface adsorbed needle shaped lead particles on spherical agglomerates of SnO_2. However, on higher magnification (figure 3b), we observe highly intense needle shaped lead particles on the surface of as synthesized SnO_2. By observing the morphology of these two samples, we confirm the adsorption of lead ions on SnO_2 surface.

3.3 *IR studies*

The vibrational frequencies of pure SnO_2 and that of lead adsorbed SnO_2 are given in table 1. The IR spectrum of pure SnO_2 shows the characteristic lines at 445 and 550 cm^{-1} i.e. below 1000 cm^{-1}, which shows the metal–oxygen vibrational frequency range (Rao 1963). The IR bands at around 1558 cm^{-1}, 1400 cm^{-1} and 1365 cm^{-1} are characteristic of the acetate groups. Band at 1012 cm^{-1} is assigned to in plane bending of CH_3 group. The other three bands at around 1160 cm^{-1}, 1158 cm^{-1} and 1090 cm^{-1}

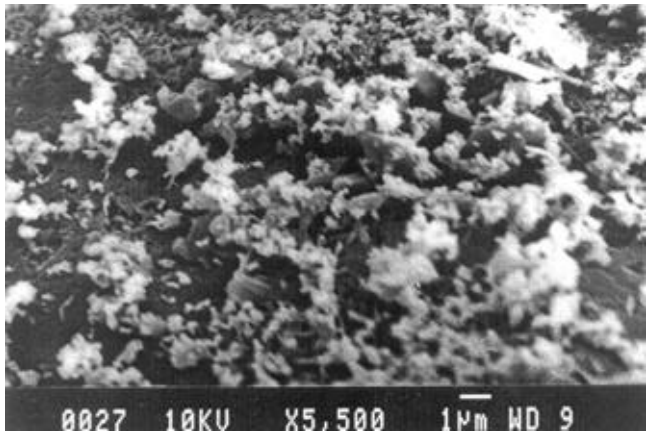

Figure 2. SEM of SnO_2 particles.

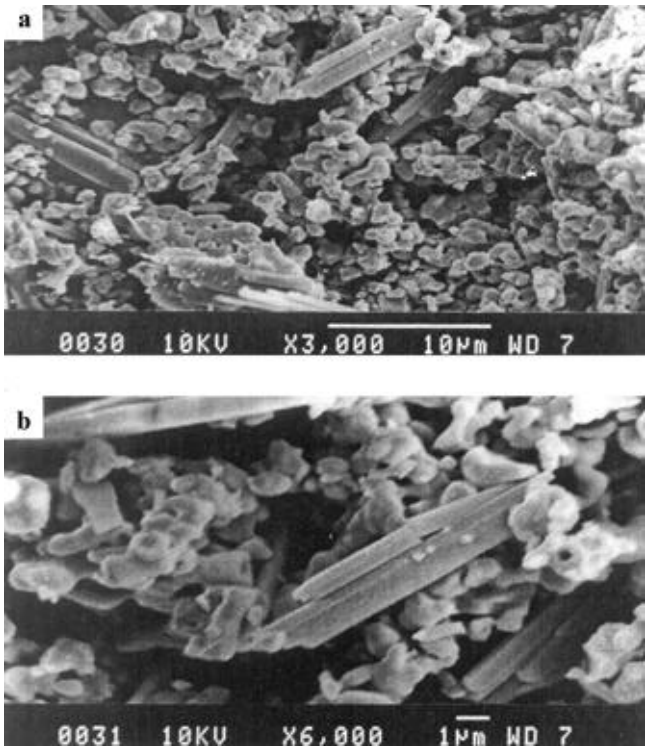

Figure 3. a–b. SEM images of lead adsorbed SnO_2 particles at low and high magnifications.

are overtones arising out of pure SnO_2. A careful examination of the IR spectra of pure SnO_2 with lead adsorbed SnO_2 shows that the new bands are weak in nature in the latter case, which indicates a weak interaction of the adsorbed Pb^{2+} ions on the SnO_2. The weak interactions are possibly due to the less amount of Pb^{2+} ions adsorbed.

3.4 *Density measurements*

Density evaluation from X-ray data, tap density and powder density are calculated and are given in table 2. The density values evaluated from different methods are approximately the same.

3.5 *Atomic absorption spectroscopy*

An atomic absorption spectroscopic characterization was carried out for the blank lead solution and the eluent lead solution (solution after adsorption). Table 3 gives the atomic absorption spectroscopy results of blank and eluent lead solutions. The initial concentration of lead acetate solution is 285 ppm, whereas after adsorption the concentration of lead solution decreases to 180 ppm. This decrease indicates the absence of some lead ions in the eluent lead solution and confirms the adsorption of lead ions on the SnO_2 surface.

Table 1. Various vibrational bands observed in IR spectra.

Sl. no.	Pure SnO_2	Lead adsorbed SnO_2
1	445	540
2	550	455
3	–	1090
4	–	1158
5	–	1160
6	–	1012
7	–	1365
8	–	1400
9	–	1558

All the values are in cm^{-1}.

Table 2. Density of SnO_2 from different methods.

Sample	Density from XRD	Tap density	Power density
SnO_2	4930	4990	3630

All the values are in kg/m^3.

Table 3. AAS and solution conductivity results of pure and eluent lead acetate solution.

Property	Pure lead acetate solution	Eluted lead acetate solution
Conductance (mho^{-1})	3×10^{-5}	$5{\cdot}8 \times 10^{-5}$
Atomic absorption spectroscopy (ppm)	285	180

3.6 *Solution conductivity*

Solution conductance gives information about the conducting nature of pure lead acetate as well as eluent lead acetate solutions. As the concentration goes on decreasing the conductance increases because of rapid movement of the metal ions. Table 3 gives the conductivity results of pure lead and eluent solutions. The conductance of pure lead acetate solution is 3×10^{-5} mho^{-1} and that of eluent solution is $5{\cdot}8 \times 10^{-5}$ mho^{-1}. This increase in conductance indicates the absence of some lead ions in the eluent lead solution and confirms the adsorption of lead ions on the SnO_2 surface.

4. Conclusions

Following are the conclusions made from the above study:

(I) The SnO_2 adsorbent shows some adsorption of lead ions on it.
(II) From XRD, SEM, IR, AAS and SC studies, it is envisaged that SnO_2 can act as a valuable adsorbent for controlling environmental pollution viz. lead and other heavy metal ions.

(III) A detailed understanding about the quantitative aspects and the structural transformations is the future direction of our work.

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