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Review

Shape and size controlled growth of SnO_2 nano-particles by efficient approach

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ABSTRACT

Three-dimensional crystalline tin dioxide (SnO_2) nanostructures have been synthesized herein using a cost-efficient hydrothermal method. Synthesis parameters have been optimized in order to obtain desired morphologies (spherical nanoparticles (NPs) or elongated prismatic nanorods (NRs)). Materials were characterized by X-ray diffraction, electron microscopy techniques, Raman spectroscopy and thermogravimetric techniques to determine the growing mechanism of the nanoparticles. Prismatic SnO_2 nanorods were found to present arrangement of flower-like ensembles. The SnO_2 final morphology (NPs or NRs) slightly influences band gap values and photo emission wavelengths.

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1. Introduction

Tin dioxide is an n-type semiconductor used for different technologies with a direct band gap (Eg = 3.6 eV at 300 K) [1] and a rutile structure. Its potential applications are photocatalysis [2,3], devices such as transistors [4], field emitters [5], electrodes for lithium ion batteries [6–9] and for the detection of pollutants like naphthol by electrochemical methods [10]. Moreover, since its conductivity presents significant variations depending on the gaseous environment, SnO_2 is also used as a sensor for detection of toxic gases [11,12]. Nanoparticles (NPs), with size close to the exciton Bohr radius [13] and a quantum confinement with light emission at 375 nm, exhibit strong red shifts of the light emission when dopants are present [14,15]. It is also well known that chemical and physical properties of SnO_2 are closely related to the particle size, geometric shape and exposed crystallographic facets for each specific application. In this respect, the unique atomic arrangement form into elongated nanorods (NRs) with prismatic facets can make SnO_2 an interesting material for specific applications such as photocatalysis, electrochemical reactions or gas sensors.

In the last years, there have been many efforts to synthesize SnO_2 particles with specific nanometric and micrometric sizes [16,17]. Different synthesis methodologies were applied such as thermal evaporation, laser ablation [18], hydrothermal [19,20] and sol gel [21] among others.

The hydrothermal process is a cost-efficient methodology for the synthesis of SnO_2 particles whose morphology [22] depends on the precursor solution features. The hydrothermal method consists in transferring thermal energy to a precursor solution subjected to high auto-pressurizing conditions to grow particles with specific shape and size. In this respect, the choice of adequate parameter values is always critical to control morphology while reaching micro or nanometer size range. For the hydrothermal method, many parameters can influence the final characteristics of NPs explaining why a large variety of SnO_2 particles have been reported in the literature. However, the mechanisms responsible for controlling the particle formation and growth by hydrothermal treatment are still not completely understood [23]. Therefore, to obtain nanoparticles with tailor-made characteristics, it is necessary to study in an exhaustive way experimental parameters in order to understand the processes involved in the methodology applied. One of the main purposes when optimizing parameters is also to be able to obtain reproducible morphology without requiring the use of surfactants as template which can leave contaminants on the final nanomaterial.

This article reports the synthesis and characterization of SnO_2 particles in order to control size and morphologies through variation of heat treatment time and of the amount of reagents such as ethanol, sodium hydroxide and tin tetrachloride pentahydrate. Based on these parameters values, a mechanism explaining the particles growth is herein proposed.

2. Experimental

2.1. Reagents and synthesis procedure

All used chemical reagents such as ethanol (C_2H_5OH), sodium hydroxide (NaOH) and tin tetrachloride pentahydrate ($SnCl_4.5H_2O$) were of analytical grade. In a typical synthesis, 15 mL of tri-distilled water was added to a mixture of both $SnCl_4.5H_2O$ and NaOH. The resulting solution was kept under constant stirring until obtaining a clear stable solution. Parameters and quantities used are indicated in Table 1. Then 15 mL of ethanol were added drop wise while maintaining constant stirring. Next the resulting solution was transferred to a Teflon vial with 40 mL volume capacity before being placed inside a stainless steel autoclave maintained at 200 °C for different periods of time (Table 1). After the hydrothermal treatment, the resulting solid was cooled down to room temperature. Weak blue dispersed particles are observed. The particles were collected and washed with tri-distilled water three times by centrifugation. Finally, the powder was dried at 80 °C for 12 h.

Table 1
Synthesis parameters description, variation and optimized values. The temperature was 200 °C and 15 ml of tri-distiller water for every cases.

Parameters	Changing values	Optimized value
NaOH (g)	0.18, 0.36, 0.54, 0.72 and 0.9	0.54
Ethanol (ml)	5, 9, 10 and 15	15
$SnCl_4$ (g)	0.25, 0.5, 0.75 and 1	0.5
Heat Treatment time (h)	6, 12, 24, 36, 48, 60 and 72	48
Resets (Refill New precursor solution)	1, 2, 3, 4 (reloads) each one after 48 h of heat treatment	