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LETTERS TO THE EDITOR

Effect of the Annealing Temperature and Time of the Particle Size of Tin Dioxide

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Over the past few years tin dioxide nanoparticles have attracted much interest owing to their diverse practical applications. This material is widely used as an oxidation catalyst and a component of transparent conductive films for touch screen displays [1, 2]. It also holds promise for application as sensing units in gas sensors and as anodes in lithium ion batteries and solar cells [1–3]. Tin dioxide doped with paramagnetic ions can exhibit ferromagnetic properties, which is of great interest for spintronics applications [4]. Furthermore, it can serve as a nucleus-forming agent in the synthesis of chromium dioxide nanoparticles which are used in hard disks [5].

The properties of a material are known to be much dependent on its particle size [6], and, therefore, much effort has been devoted to the synthesis of controlled-size tin dioxide nanoparticles [7–9]. However, by varying synthesis conditions one can hardly prepare nanoparticles larger than 10 nm in diameter. One of the simplest and easily accomplishable ways to solve this problem consists in annealing the presynthesized SnO_2 powder at different temperatures. The problem here is to find annealing temperatures and times, which would ensure uniform growth of particles but prevent their intergrowth and subsequent aggregation, resulting in nonuniform particle size distribution and, as a consequence, altered physical and physicochemical properties of the material. In this connection, in the present work we set ourselves the aim to determine optimal time and temperature range for annealing the synthesized SnO_2 particles to obtain monodisperse powders with different particle sizes.

Among the wide range of technologies used for SnO_2 synthesis, the most common is the sol–gel technology. In the present work in choosing conditions for the synthesis of nanoparticles we focused on the necessity to minimize possible particle interactions to ensure that annealing resulted in particle enlargement due to recrystallization rather due to intergrowth. The synthesis was performed at pH 3, which is close to the zero-point of charge for tin dioxide. The starting materials were anhydrous tin tetrachloride and aqueous ammonia, the temperature of the reaction mixture was 60°C. The resulting solution was washed with distilled water and left to age for 24 h. The precipitate was separated by centrifugation. To prevent the undesirable crystal intergrowth, the samples were first dried in an oven at 80°C and then annealed in a muffle furnace at 200–800°C (step 200°C) in air. The annealing time was 0.5–5 h (step 1 h).

The crystalline structure of the nanoparticles was characterized by X-ray diffraction (XRD, Bruker "D2 Phaser") using CuK_α radiation at the Resource Centre for X-ray Diffraction Studies, St. Petersburg State University. The crystallite size was calculated by the Scherrer equation using the integral peak intensity. The size and shape of nanoparticles were determined by transmission electron microscopy (TEM) on a JEOLS JEM-107 microscope. The specific surface areas were measured at the Resource Centre for Innovative Technologies of Composite Nanomaterials, St. Petersburg State University, on a Micromeritics ASAP 2020MP system. The cycle of adsorption at the liquid nitrogen temperature–desorption at room temperature

was preceded by thermal training at 120°C for 12 h. The specific surface area (SSA) values were used to calculate the particle diameter [according to the model of spherical particles, $d = 6/(\rho S_{sp})$; $\rho = 6.95$ g/cm^3]. Thermogravimetric and differential thermal analyses were performed on a Setaram SETSYS Evolution 16 instrument in the temperature range 20–1200°C under argon flow, heating rate 5 deg/min.

According to the TEM data, the synthesized nanoparticles were spherical in shape and less than 5 nm in diameter. Their specific surface area was 215 m^2/g (on a dry weight basis). The particle diameter calculated from the SSA value is 4 nm, which well agrees with the TEM data. The crystallite size determined from the XRD data was about 2 nm.

To determine the annealing temperature of the synthesized nanoparticles, we performed thermal analysis in the range 20–1200°C. Until 200°C the data showed loss of physically adsorbed water, and just this point was chosen as the minimum annealing temperature. For the maximum temperature we chose 800°C, because after this point no essential changes were observed. To find out whether the particle size can be controlled by annealing at constant temperature, the annealing time was varied from 0.5 to 5 h.

As would be expected, the dimensional characteristics of nanoparticles after annealing, obtained by three independent methods, provide unequivocal evidence showing that particle size increases with increasing temperature and annealing time. According to the XRD data, the phase composition of all samples was fully consistent with that known for tin dioxide (ICDD PDF 01-077-0447).

As mentioned above, the main goal of the present work to find optimal conditions for annealing SnO_2 nanoparticles, ensuring that the latter preserved their individual behavior and the particle size distribution in the resulting powder was as narrow as possible.

Thermal treatment of the nanoparticles leads to their aggregation, both with crystallite size enlargement and without it. With further increase of temperature, further particle aggregation may occur to result in nonuniform recrystallization and a wide particle size distribution in the final product. Therewith, some functional characteristics depend not only on particle diameter but also, and first of all, on crystallite size. Therefore, the annealing conditions should ensure that both dimensional characteristics increase simultaneously.

To assess changes with nanoparticles and determine time and temperature ranges where these changes take place, we performed mathematical analysis of the particle diameters and crystallite sizes, obtained by the BET and Scherrer methods, respectively. The temporal and temperature dependences of these parameters are exponential. Using Origin 9.0 software we performed least-squares fitting of the obtained dependences and calculated curve parameters (intercept, exponential and pre-exponential factors). Then the parameters for particle diameter and crystallite size were compared. If in the recrystallization area these parameters are close, then the particle diameter and crystallite size increase with the same proportionality factors, indicating the formation of individual particles. The process of uncontrolled particle intergrowth, and, as a result, formation of various-size aggregates reveals itself that crystallites grow faster than particle diameter.

At 200°C no appreciable changes in nanoparticle characteristics occur over the entire time range. As the temperature is elevated at 400°C and the annealing time is prolonged, both the crystallite size and particle diameter increase at virtually the same rates. Thus, the temperature range, when annealing SnO_2 nanoparticles is not accompanied by crystallite growth, is 200–400°C.

Our analysis also shows that the recrystallization of nanoparticles without intergrowth, i.e. with preservation of their individual behavior, takes place on annealing at 400–600°C for less than 5 h. Note also that if the temperature and time of the process are increased within the specified limits, the unit cell parameter *a* decrease by no more than 0.5%, whereas with the *c* parameter no clear tendency is observed. As known [6], such tendency, decrease in parameters with increase in size, is characteristic of discrete nanoparticles. At 800°C and any annealing time, as well as at the annealing time of 5 h and any temperature, nanoparticle intergrowth and aggregation are observed. These conclusions are completely confirmed by the TEM images. At high temperatures and long annealing times, various-size aggregates are seen in the images, whereas at optimal annealing temperature and times, nanoparticles with diameters corresponding to those calculated from specific surface areas.

Thus, we found the optimal time and temperature ranges in which SnO_2 nanoparticles can be annealed without losing their individual behavior.

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