

Effects of temperature and pH value on the formation of In_2O_3 nanoparticles by solution growth method

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Abstract: Indium oxide nanoparticles were produced by solution growth method and effect of temperature and pH value was discussed. It was seen that for fix concentration of solution and constant value of pH, density of nanoparticles decreases as temperature increases. It can be related with super saturation of solution, which decreases with temperature. SEM micrographs at same (concentration and temperature) with different pH values point out that with increasing pH value, the length of the gaps forms the enhanced sphere and consequently the space between the gaps.

Keywords: Indium oxide nanoparticles, Solution process method, Super saturation.

1. Introduction

Indium is a Block P, Period 5 element, while oxygen is a Block P, Period 2 element. Indium oxide (In_2O_3) is an n-type transparent semiconductor with a wide band gap (~ 3.0 eV). In_2O_3 exhibits a number of interesting attributes and has been studied extensively. In_2O_3 films are also used as heat mirrors for solar energy applications [1]. It can be used as CO sensor [2]. The highly conductive and porous 3D graphene structure of Indium Oxide greatly enhances the performance of lithium-ion batteries by protecting the nanoparticles from the electrolyte, stabilizing the nanoparticles during cycles and buffering the volume expansion upon lithium insertion [3]. The crystalline form exist in two phases, the cubic (bixbyite type) and rhombohedral (corundum type) [4]. These interesting attributes make In_2O_3 an important material for a different of practical functions [5-7]. The thermally radiated treated In_2O_3 nanoparticle sample showed improvement in crystallinity while maintaining a large surface area of nanostructure morphology. The direct transition optical absorption at higher photon energy and the electrical conductivity of the In_2O_3 nanoparticles were significantly enhanced by the treatment [8]. A number of different fabrication techniques have also been reported, such as thermal oxidation [9], dispersion method [10], electrochemical deposition method [11] etc. Thin films of indium oxide can be prepared by sputtering of indium target in argon/oxygen atmosphere [12]. Mono crystalline nanowires were synthesized from indium oxide by

laser ablation, allowing precise diameter control down to 10 nm. Field effect transistors were fabricated from those [13]. Indium oxide nanowires can serve as sensitive and specific redox protein sensors [14]. Exploitation of green chemistry approach for the synthesis of Indium oxide nanoparticles using green synthesis has received a great attention in the field of nanotechnology. A biogenic method that involves the Katira gum (*Astragalus gummifer*) leading to the formation of different morphological In_2O_3 using the precursor Indium (III) Acetylacetonate and TG-DTA is characterised for calcination temperature and it is found to be above 500°C [15]. E. Nirmala et al. studied the annealing temperature effect on Indium oxide (In_2O_3) nano spherical crystalline particles prepared by hydrothermal technique at 350°C , 400°C and 450°C [16]. Crystallizing substance from liquid solutions are of interest because they are safe and atmospherically friendly, and may be performed at relatively low temperatures ($< 250^\circ\text{C}$). Still, there are some issues on In_2O_3 nanoparticles, which are not understood completely. So lots of effort needs to be done in order to understand its fundamental attributes and enhance its performance in functions. The electrical and optical characteristics of oxide nanowires can be controlled by the amount of oxygen during growth [17].

Anil U. Mane et al. investigated the atomic layer deposition (ALD) of indium oxide (In_2O_3) thin films using alternating exposures of trimethylindium (TMIn) and a variety of oxygen sources: ozone (O_3), O_2 , deionized H_2O , and hydrogen peroxide (H_2O_2). The ALD In_2O_3 films showed resistivities as low as $3.2 \times 10^{-3} \Omega \text{ cm}$, and carrier concentrations as large as $7.0 \times 10^{19} \text{ cm}^{-3}$. This

TMIn/O₃ process for In₂O₃ ALD should be suitable for eventual scale-up in photovoltaics [18]. The high transmittance ($\approx 89\%$) in the visible spectral range was obtained in the ion assisted films with the large oxygen content and the small surface roughness [19]. Indium oxide is an amorphous transparent conducting oxide (TCO). In general, amorphous materials are deposited at lower temperatures [20, 21] which tend to simplify the deposition process and expand the number of substrates the material can be deposited on, such as plastics. Amorphous materials are isotropic with lack grain boundaries. Hence they tend to etch more uniformly with lower surface roughness and can be deposited uniformly over large areas [22 - 26]. Some amorphous materials can also be less prone to fracture, hence being more pliable, lending themselves to the possibility of flexible electronics [22, 27].

2. Experimental procedures

In the present work, In₂O₃ nanoparticles were fabricated by solution processed fabrication. Fabrication has taken place inside an isothermal oven, and glass containers, dishes or vials, which were used as containers for the samples and reactant solutions. The chemicals used in this operate include Indium (III) nitrate hydrate (In(NO₃)₃·xH₂O, 99.999% purity) and hexamethylenetetramine (C₆H₁₂N₄, 99% purity) obtained from Aldrich, and In₂O₃ nanoparticles (size in the range of 50-60 nm) used for making In₂O₃ seed layers obtained from nano and amorphous materials. In₂O₃ nanoparticles may be fabricated on different samples, such as silicon, glass and indium tin oxide (ITO). We synthesize In₂O₃ nanoparticles from 4mM concentration solution. Equimolar solution of Indium (III) nitrate hydrate and hexamethylenetetramine with concentration of 4 mM was prepared. The prepared solution was transferred into a vial and samples (Si or ITO/glass) were placed at the bottom of the vial. The vial was then heated at 90 - 120 °C for 3 h. After the reaction, the samples were dried in an oven at 100 °C. Before fabrication, the sample was seeded with In₂O₃ nanoparticles. The seeding was performed by dispersing the nanoparticles in deionized water in ultrasonic bath for 1-2 h, putting a decrease of the dispersion on the sample and drying the sample in an oven at 150 °C for 2 h. Then, the sample was sonicated for several seconds to remove the excess nanoparticles on the surface, and finally dried at 100 °C. In order to investigate the influence of the temperature on the shape of obtained In₂O₃ nanoparticles, different reaction temperatures were tested. The setup of the grown materials was investigated by scanning electron microscopy (SEM) using Cambridge 440 SEM and Leo 1530 FESEM.

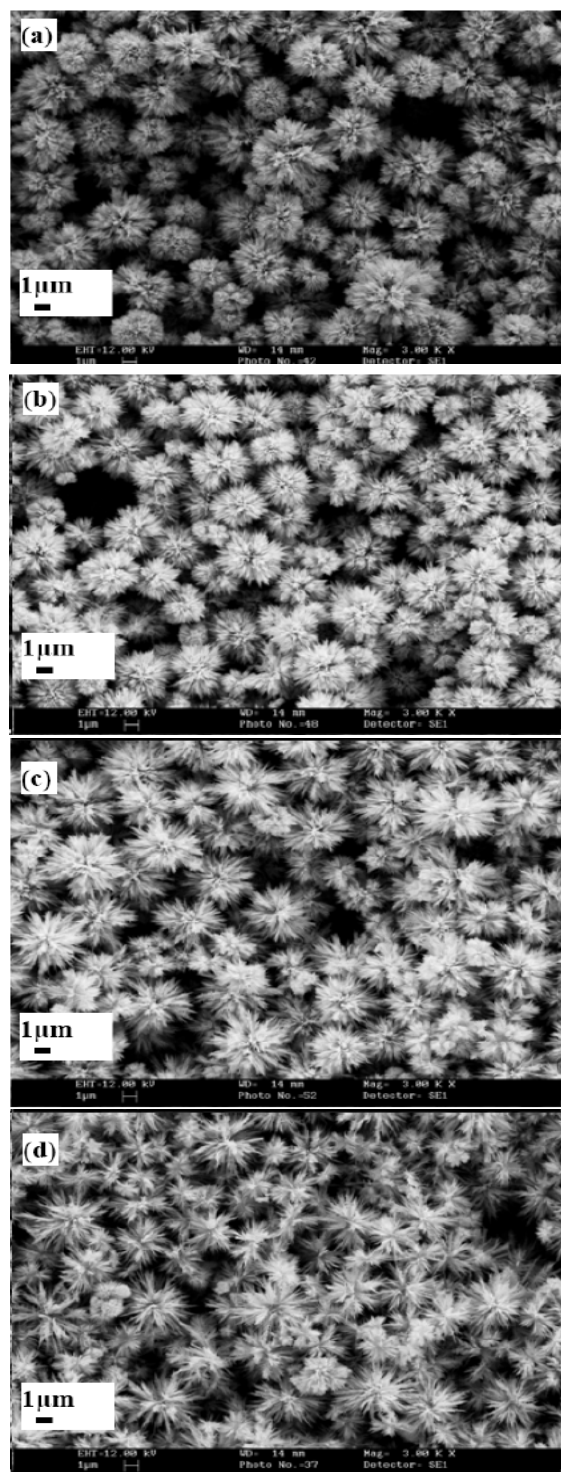


Figure 1: SEM images of In₂O₃ nanoparticles obtained from solution concentration 4 mM with pH = 6 at temperature 90 °C (a), 100 °C (b), 110 °C (c) and 120 °C (d).

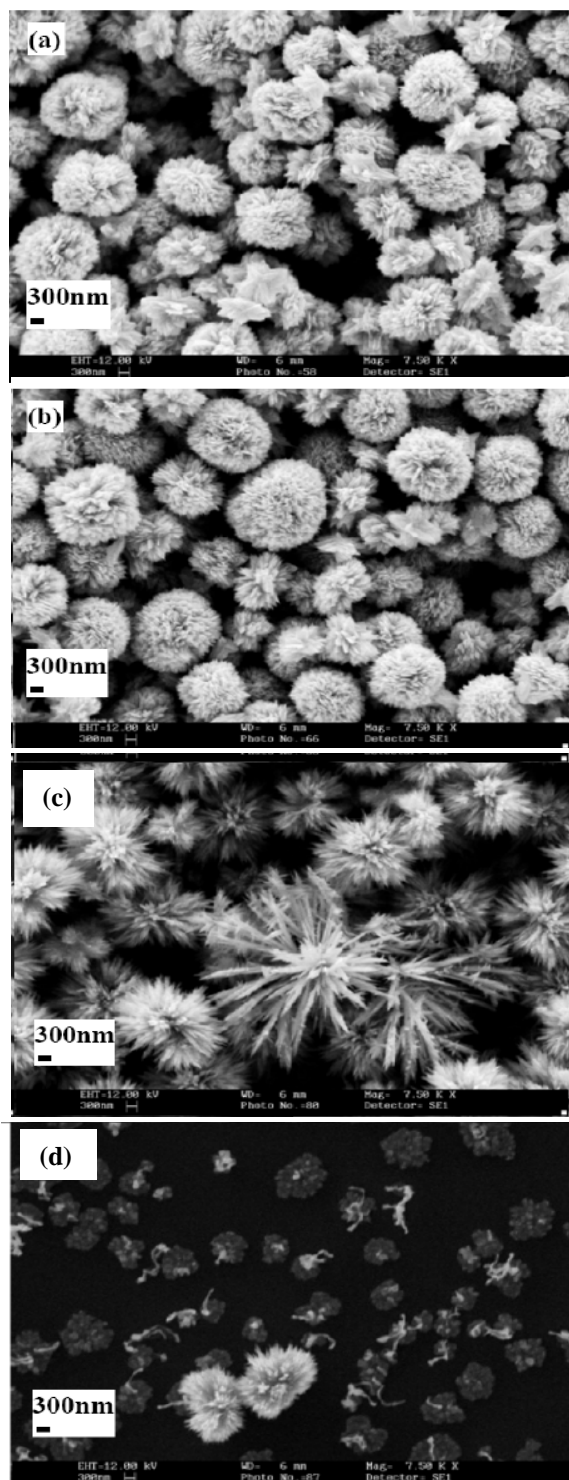


Figure 2: SEM images of In_2O_3 nanoparticles obtained from solution concentration 4 mM at 120 °C with pH value 3 (a), 4 (b), 6 (c) and 7 (d).

The surface of ITO, indium oxide, titania and yttria nanoparticles by solution-phase growth strongly depends on the pH value of the solution. So the influence of pH value on the surface of In_2O_3 nanoparticles has also been investigated. The pH value of the solution may be changed by the addition of hydrochloric acid (HCl) or Potassium hydroxide (KOH). At fabrication concentration 4 mM and temperature 120 °C, different In_2O_3 nanoparticles were fabricated from solutions with different pH values varying from 3 to 7.

3. Results and discussion

The reaction temperature will also influence the surface of obtained In_2O_3 nanoparticles. For fabrication concentration 4 mM and pH = 6, different In_2O_3 nanoparticles were fabricated at different temperatures varying from 90 °C to 120 °C. Figure 1(a) to 1 (d) show the representative SEM images of In_2O_3 nanoparticles obtained at different temperatures.

It may be observed that the length of the rods enhanced and the packing density decreases with increasing temperature. The temperature dependence of the obtained surfaces is likely due to the temperature dependence of the relative super saturation for the same concentration. Relative super saturation for the same concentration is expected to decrease as the temperature enhanced [26].

Figure 2(a) to 2(d) shows the representative SEM images of In_2O_3 nanoparticles obtained from different pH values.

With increasing pH value, the length of the gaps forms the enhanced sphere and thus the space between the gaps [25, 26]. Finally, when the pH value reaches pH = 7, only very few spherical assemblies are found. And sample is sparsely covered by rods attached to round cores.

4. Conclusions

The In_2O_3 nanoparticles have been prepared by solution growth method. SEM micrographs of same (concentration and pH value) at different temperatures show that the length of the rods enhanced and the packing density decreases with increasing temperature. SEM micrographs at same (concentration and temperature) with different pH values indicate that with increasing pH value, the length of the gaps forms the enhanced sphere and consequently the space between the gaps. At pH = 7, the sample is sparsely covered by rods attached to round cores.

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