



ORIGINAL ARTICLE

Preparation methods of Nanostructures synthesis with different size and shape

Elham Afzali

Department Of Chemistry, Payam-e-Noor University , Miandoab, Iran.

ABSTRACT

Several approaches have been employed to synthesize nanomaterials so we investigate some of these techniques. In this regard, Eu doped Y_2O_3 nanoparticles were synthesized via different methods include combustion, Pechini and hydrothermal. Then the resultant nanoparticles were investigated by means of scanning electron microscopy (SEM) and Transmission electron microscopy (TEM).

Keywords: Nanoparticles, Yttrium oxide, Combustion, Pechini, Hydrothermal.

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INTRODUCTION

Semiconducting nanomaterials are the most promising nanoparticles because of their applicable physical and chemical properties such as high color purity and low response time. These properties are different from bulk material due to the quantum size effect [1,2]. Moreover, the nanostructures provide opportunities to investigate the influence of spatial confinement and problems related to surfaces or interfaces that has significant role in different fields such as engineering, materials science, physics, chemistry, pharmacy, medicine, biology, and so on. Nanomaterials can be categorized as zero dimensional (nanoparticles), one dimensional (nanowires, nanorods, and nanotubes), two dimensional (nanocoatings and nanofilms), and three dimensional (nanocrystalline and nanocomposite materials). This classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm) [3-5]. In this work, we discuss recent advances in the different types of semiconducting nanomaterials synthesis. The growth of bulk or nanoscale materials includes the procedure of precipitation of a solid phase from solution. Knowing the procedures and factors controlling the precipitation helps to develop the engineering of the growth of nanostructures to the preferred scale, dimensions and form. There is a specific limit of solubility for various solutes. In this term, addition of excess substances in the solute will lead to precipitation and formation of nanostructures. Therefore, the solution must be supersaturated to take place the nucleation process for nanostructure formation. This can be occurring in two ways. (1) Directly dissolving the solute at high temperature and then cooling to low temperatures. (2) Adding the necessary reactants to produce a supersaturated solution during the reaction [6,7]. The precipitation process then basically consists of a nucleation step followed by particle growth stages [8,9]. Commonly, homogeneous nucleation, heterogeneous nucleation, and secondary nucleation are the three types of nucleation procedures. Homogeneous nucleation takes place in the absence of a solid interface by combining solute molecules to produce nuclei. The energy of supersaturated solution is not steady. So this type of nucleation occurs due to the driving force of the thermodynamics.

$$\Delta G = -\frac{4}{V}\pi r^3 k_B T \ln(S) + 4\pi r^2 \gamma$$

The overall free energy change, ΔG , is the sum of the free energy. This equation is described because of the formation of a new volume and the free energy due to the new surface formed. For spherical particles where V is the molecular volume of the precipitated species, r is the radius of the nuclei, k_B is the Boltzmann constant, S is the saturation ratio, and γ is the surface free energy per unit surface area. As shown in Fig. 1 when S is higher than 1, ΔG has a positive maximum at a critical size. This free energy in high level is the activation energy for nucleation. Particles larger than the critical size will reduce their

free energy for growth and constitute nuclei that grow to form units. The critical nuclei size r^* can be obtained from $d\Delta G/dr = 0$.

$$r^* = \frac{2V_f}{3k_B T \ln(S)}$$

According this equation and Fig. 1 particles with $r > r^*$ will grow and particles with $r < r^*$ will dissolve. Additionally, it can deduced that in the high saturation ratio (S), the smaller critical nuclei size (r^*) is shaped. When the concentration decreases under the critical level, nucleation discontinues and the particles continue to grow by molecular addition until the equilibrium concentration of the precipitated species is reached. A short nucleation period causes the homogeneity of the size distribution. The smaller particles grow faster than the larger ones because the free energy driving force for smaller particles is larger than for larger ones. At this time the quick nucleation and growth or keep the saturation condition steady during the reaction make the particles nearly monodisperse. Besides, to the growth by molecular addition, particles can grow by aggregation with other particles. This is named secondary growth. The amount of particle growth by aggregation is more than that by molecular addition. When particles grow to a specific size, they will grow by linking with smaller unspecific nuclei instead of collisions with other stable particles. At the end, these nanoparticles should be arrested during the reaction either by adding surface protecting reagents, for example organic ligands or inorganic capping materials [7] or by placing them in an inert environment such as an inorganic matrix or polymers [9]. If the interaction between the capping agents and the solvent is proper the nanostructures are stable. To help arrest these nanoparticles, different solvents are applied to change the solubility or the reaction rate [6,7,9].

EXPERIMENTAL

Combustion

$Y(NO_3)_3$ and $Eu(NO_3)_3$ were freshly prepared by reaction of Eu_2O_3 and Y_2O_3 with HNO_3 . The excess acid was eliminated by slow warming.

Aqueous solutions of europium and yttrium nitrates were mixed together to attain the desired stoichiometry. Afterward, urea as a fuel was added to the solution. The molar ratio of urea/cations ion is about 2.5, which is stoichiometric value in combustion reaction. This solution was heated in a muffle furnace until the water evaporated and combustion occurred. The combustion powder was then thermally treated at 873 K for 1 hour.

Pechini

In this term the nitrate solution was prepared via the mentioned procedure. Then citric acid and ethylene glycol was added into distilled water. The molar ratio of citric acid/ cations was 2.5 and this value for ethylene glycol/cations was 1. This solution were mixed together and stirred for one day at 353 K. The polyesterification occurred and citric acid acts as a chelator to form polychelate. The solution was dried and the powder was heat treated for 1 hour at 873 K. In this technique, nanopowders are confined in polychelate and their growth was limited and therefore the nano scale product can be prepared.

Hydrothermal

Hydrothermal synthesis is a general technique to synthesize zeolite/molecular sieve crystals. This method exploits the solubility of nearly all inorganic materials in water at high temperatures and pressures and subsequent crystallization of the dissolved material from the fluid. Water at elevated temperatures plays a critical role in the precursor material revolution because the vapor pressure is much higher and the structure of water at elevated temperatures is different from that at room temperature. The properties of the reactants such as solubility and reactivity alter at high temperatures. The changes mentioned above provide more characteristics to create various nanoparticles and nanotubes. It may not possible at low temperatures. Throughout the synthesis of nanostructures, different parameters such as temperature, reaction time, water pressure can be adjusted to maintain a high nucleation rate and proper size distribution. Various nanoparticles such as TiO_2 , $LaCrO_3$, ZrO_2 , $BaTiO_3$, $SrTiO_3$, $Y_2Si_2O_7$, Sb_2S_3 , CrN , $\beta-SnS_2$, PbS , Ni_2P , SnS_2 , Bi_2S_3 , and SiC nanostructures have been successfully synthesized in this way [10-24].

In our study of synthesis of Y_2O_3 nanoparticles, before heat treatment of nanoparticles that synthesis in the combustion method the sample was dispersed in distilled water. Then Stoichiometric amount of the hexamethylenetetramine was added. The solutions were moved into a stainless steel autoclave. It was sealed and kept in an oven at 423 K for 16 hours. Then, the solution was cooled to room temperature and in order to remove unreacted organic and inorganic compounds the resulting white solid product was filtered and washed with distilled water and ethanol for 3 times. The wet powder dried at 353 K and then was heat treated at 873 K for 1 hour in air atmosphere.

RESULTS AND DISCUSSION

The nanoparticles were characterized scanning electron microscopy and transmission electron microscopy. SEM investigations were conducted by a Leica Cambridge electron microscope, Streoscan 360 with an accelerating voltage of 20 kV. TEM investigation was carried out using a Philips CM-200 FEG instrument. Fig. 2 shows the TEM micrographs of Y_2O_3 nanoparticles synthesised by combustion and Pechini methods. According to these images it can be seen that the combustion samples are agglomerated and the particles are hardly distinguished. But the synthesized nanoparticles with Pechini method are well distinguished, which show lower agglomeration of these nanoparticles. SEM analysis of samples was performed to survey the morphology of nanoparticles (Fig. 3). From this micrograph it can be established that the nanoparticles synthesized by combustion method are agglomerated while the agglomeration of nanoparticles synthesized by Pechini method are weak with the particle size of about 7 nm. On the other hand, SEM micrograph of nanoparticles in hydrothermal way shows that the morphology of these nanoparticles is so different from the others.

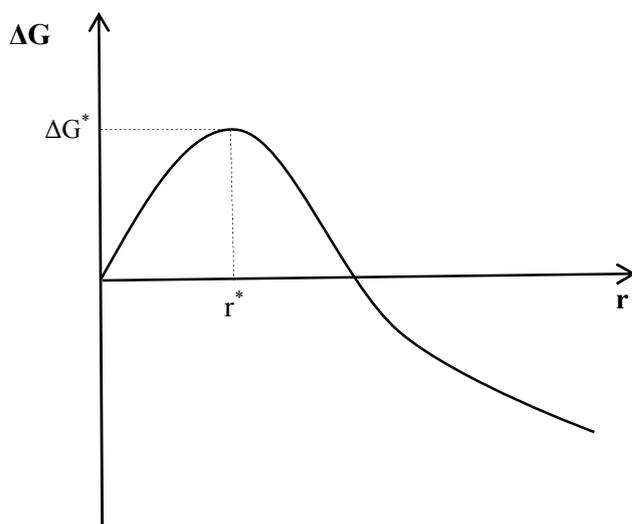


Fig. 1: diagram of free energy (ΔG) as a function of the growth particle size (r)

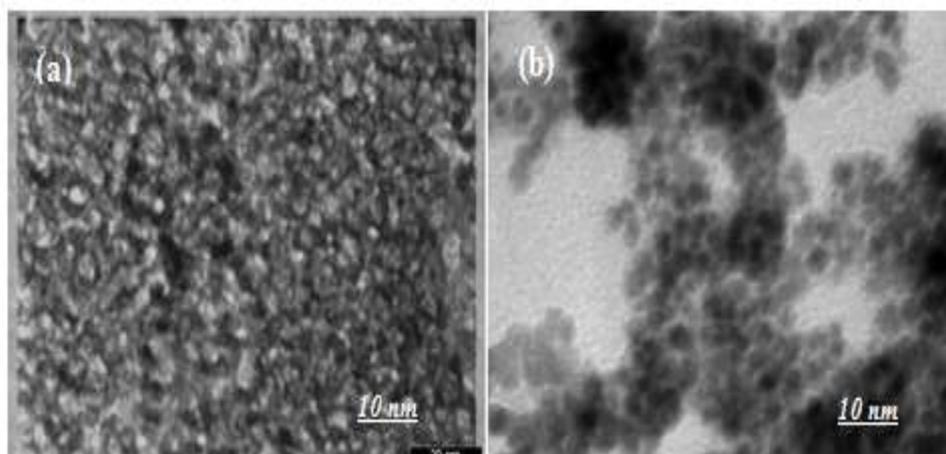


Fig. 2: Transmission electron micrographs of Y_2O_3 nanoparticles, (a) combustion and (b) Pechini sample.

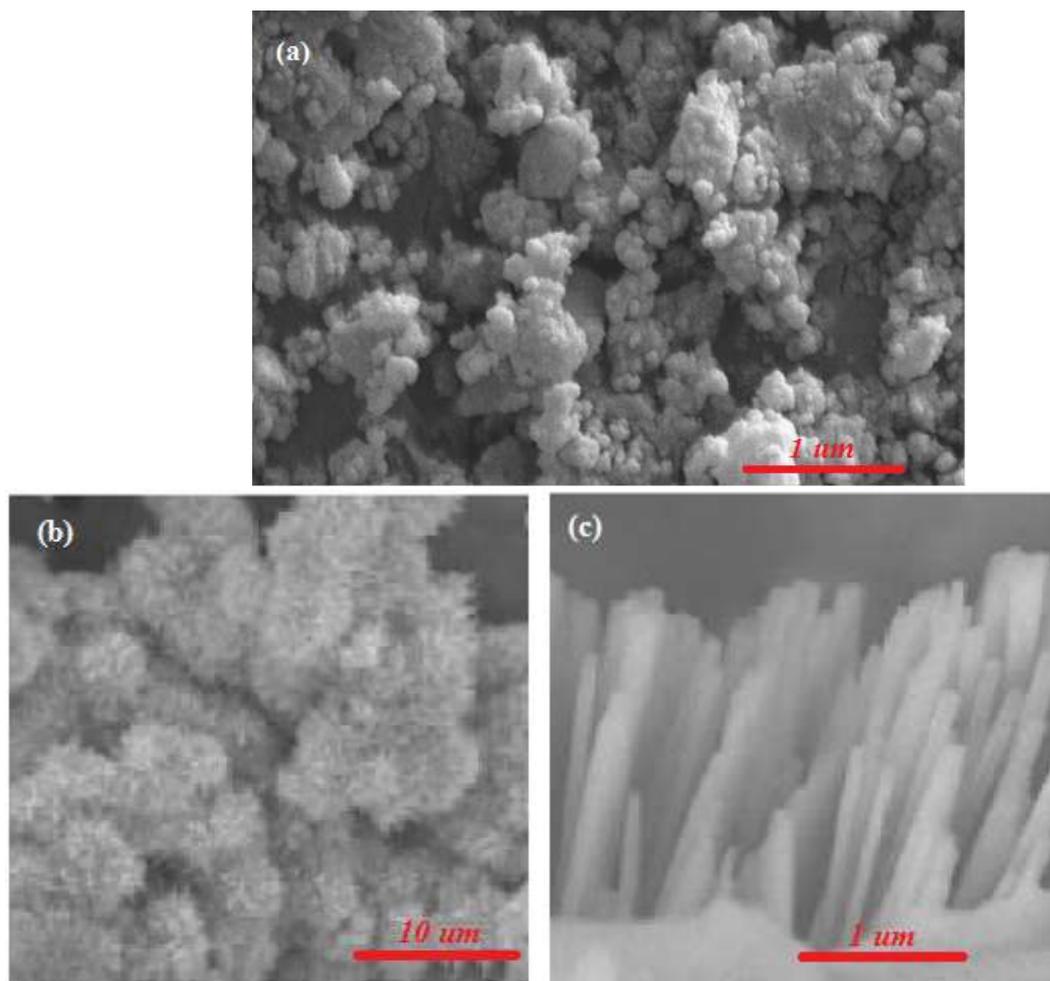


Fig. 3: SEM micrograph of synthesized nanoparticles with (a) combustion, (b) Pechini, and (c) hydrothermal technique.

CONCLUSION

In this work, we discuss the synthesis and properties of nanoparticles. We start with a discussion of the different methods of the synthesis of the nanoparticles. Techniques using different mechanism to make nanostructures are briefly discussed. Y_2O_3 nanoparticles were synthesized by combustion, hydrothermal and Pechini methods. In comparison of these nanoparticles, Pechini sample has smaller particles and crystallites with lower agglomeration.

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