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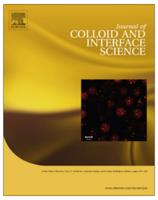

A method to form semiconductor quantum dot (QD) thin films by igniting a flame at air–liquid interface: CdS and WO_3

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ABSTRACT

We reveal an easy, inexpensive, efficient one step flame synthesis of semiconductor/metal oxide thin films at air–liquid interface, subsequently, transferred on suitable substrate. The method has been illustrated by the formation of CdS and WO_3 QDs thin films. The features of the present method are (1) Growth of thin films consisting of 0.5–2.0 nm sized Quantum Dots (QDs)/(ultra-small nanoparticles) in a short time, at the air–liquid interface which can be suitably transferred by a well-known Blodgett technique to an appropriate substrate, (2) The method is suitable to apply layer by layer (LbL) technique to increase the film thickness as well as forming various compositions as revealed by AFM measurements. The films are characterized for their structure (SAED), morphology (TEM), optical properties (UV–Vis.) and photoluminescence (PL). Possible mechanism of formation of QDs thin film and effect of capping in case of CdS QDs is discussed.

1. Introduction

The applications of quantum dots are reported in medical field as the bio-markers [1,2]. In the field of energy, QDs are shown to advance the performance of solar cells [3]. In the application of solar cells, the QD film is a component complementary to other active components of the device. This constraint imposes a practical condition to grow homogeneous QDs thin films without disturbing the properties of pre-coated layers of solar cells [4]. Thus, the method of growing QD film turns out to be a crucial factor. Similarly, there are other numerous applications of QD thin films reported in the literature, for example, Light emitting diodes (LED) [5], photodetector [6] and nanosensor [7] wherein method of preparation of QD thin film is important.

Normally, QDs of materials are formed through the bulk reactions, resulting in the end product, QDs dispersed in water/organic solvents. Subsequently, for the QD thin film applications, various techniques of thin film formation, namely, sol–gel [8], spin coating [9], Langmuir–Blodgett [10], dip coating [11], etc. are used to form devices such as LED, solar cells [12] or other optoelectronic devices [13]. Thus, low temperature depositions of QD films of desired materials is searched by the scientific community. Also, normally, capping agents/dispersing agents are used for QDs formation [14]; however, these additives may prove detrimental in final devices. Therefore, the methods to synthesize QD/QD films without using capping agents/dispersing agents are desired.

Methods such as Langmuir Blodgett (LB), spray coating, dip coating, spin coating can be suitable for semiconductor QDs film formation at low temperature [15–17]. However, LB is limited to organic amphiphiles and polymers. It is difficult to control the morphology, particle size, thickness of the film, etc. in the other methods namely, spray coating, dip coating, and spin coating respectively [18,11,9]

The formation of QDs by using capping/dispersing agent such as TOPO [19], other phosphorus containing capping agents [20] is very common. The procedures to form QDs in solutions/solvents in these methods are very critical. The parameters such as reaction temperatures, sequence/chronology of introduction of chemicals in reaction vessel become decisive to obtain the desired properties of the final product [19]. Also, the procedure consists of multiple steps along with the requirements of high energy and longer reaction time. The other methods to form semiconductor QDs in solution include precipitation [21], sol–gel, etc. [22]. For these methods, an additional step of film formation would be required during which exists a possibility of change in the properties of QDs originally formed.

Chemical vapor deposition [23] is a frequently used method for QDs film formation; but normally, high temperatures, use of special equipment are required. Other methods used for preparation

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of QDs thin films, are electrospray organometallic chemical vapor deposition (ES-MOCVD), RF magnetron sputtering, atomic layer deposition, etc. [24–26]. Most of these methods require costly equipment, special conditions like neutral atmosphere of argon gas/nitrogen gas, highly specific chemical/physical condition such as pH, long processing time, high energy inputs. Therefore, formation of QDs thin film by an easier, less time consuming method would be a welcome contribution. If such a method does not require use of costly equipment and special reaction conditions; these would be additional features. The use of chemicals which are not environment-friendly is a serious concern of present day research. In this respect also, the procedure using environment-friendly chemicals would be preferred.

Combustion synthesis [27–29] and flame synthesis [30,31] of nanomaterials are claimed as scalable processes for oxide formation; however, those are energy intensive and difficult to regulate. Therefore, these processes are not reported for QDs formation and more so for QDs thin film formation. Although, flame processes are claimed to be cost effective, the design of reactors and mechanism of nanoparticle formation suggest that only a fraction of input energy is used for the actual reaction. Also, whether it is spray pyrolysis in flame or flame spray hydrolysis, the above given limitation holds true [32,33]. For the composite formation, the optimization of reaction parameters would be critical as the precursor with different properties need to be used. Sol-flame synthesis has been reported for growing nanoparticle @ nanowires, (Co_3O_4 @ CuO) [34]. The synthesis process consists of multiple steps and is applied for a specific function by decorating nanoparticles on the surface of a nanomaterial. Also, there is no universal design of reactor for the various flame synthesis methods, mentioned above. Therefore, the design of a reactor becomes an important parameter apart from the parameters involving reaction mechanism. The generalization of the technique of "flame synthesis" is difficult.

The use of flame synthesis for organic nanomaterial formation would be unacceptable due to their low stability at medium or higher temperature and this becomes a major drawback in the view of more and more applications of organic nanoparticles in organic light emitting diodes (OLED) [35].

We have considered all the pros and cons of various reported processes and consequently conceived a process wherein the advantages of flame synthesis are exploited and limitations are minimized.

We visualized a method wherein flame synthesis could be incorporated in the method of Liquid–Liquid Interface Reaction Technique (LLIRT) reported earlier by the authors [36–38]. The features of LLIRT are room temperature thin film formation, small particle size of the film product, low cost, control over thickness of film, etc. The prominent limitation of this process was the formation of thin films of materials requiring medium temperatures. Regarding these aspects, the present communication takes a step forward and maneuvers the conditions in such a way that the desired high temperature can be achieved in a limited zone of equipment while the overall temperature is low.

Thus, herein we report low cost combustion/flame process by incorporating a novel way in the procedure of earlier reported LLIRT, facilitating to achieve semiconductor QDs films. As a proof of the concept, we apply the technique to form QDs thin films of CdS and WO_3 on suitable substrate.

The choice of semiconductor CdS was made as it is perhaps, the most studied semiconductor, next to silicon and also has been one of the most comprehensively studied semiconductors [39]. CdS is a group II–VI, n-type semiconducting material, with a direct band gap 2.4 eV. Recently, CdS QDs exhibited important applications in various fields, especially in the field of optoelectronics (e.g. LED), solar cells, cell labeling, gas sensors, electroluminescent devices, infrared windows, photo detectors and as a photo catalyst for the degradation of organic pollutants because of its unique photochemical and photo physical properties [40–42].

"Oxide semiconductors" is an important and large assemblage of semiconductors. Any development of general procedure would be comprehensive only when its application to the above class is revealed. Therefore, we have chosen a representative of this class, WO_3 to form its QDs films by the present method. This choice is made by considering the recent applications of WO_3 films in the field of catalysis, gas sensing, solar energy, etc. [43–45].

2. Experimental methods

2.1. Materials

Cadmium Acetate dihydrate ($Cd(CH_3COO)_2{\cdot}2H_2O$), Thiourea ($SC(NH_2)_2$), Polyvinylpyrrolidone (PVP) (Mw = 40,000), petrol, were purchased from Sigma Aldrich. Phosphotungstic acid ($H_3PW_{12}O_{40}$) was purchased from Johnson and Sons, UK. For the synthesis of QD films, all the chemicals were used as received, without further purification. Throughout all the experiments double-distilled, deionized water was used. The substrates used are glass slides, quartz plates and silicon wafers. Glass and quartz substrates were cleaned by pre-treating them with freshly prepared piranha solution ($H_2SO_4/H_2O_2 = 70{:}30$, v/v) at 70 °C for 15 min, thoroughly rinsed with deionized water, and dried in nitrogen flow.

2.2. Synthesis of CdS nanoparticles thin films

CdS thin films were synthesized by maneuvering decomposition of Cd-thiourea complex at air–liquid interface. Cd-thiourea complex is an intermediate precursor to CdS. Petrol (sulfur free)/gasoline was used as a fuel to achieve the temperature of the decomposition of the complex. Although, conventional fuels such as urea and glycine are suitable for achieving reaction temperature, petrol was chosen in the present research considering its calorific value (44.4 MJ/kg) which is higher than that of other common solvents. Also, petrol forms a sustainable short lived flame at air–water interface for the desired reaction time of 3–5 s. In fact, we have tried acetone, diethyl ether and some other organic compound as a fuel before choosing petrol.

The overall procedure of film formation is similar to the method of the thin film formation by LLIRT reported earlier [37]. In a typical procedure, a solution of Cd-thiourea complex is formed by dissolving 10^{-4} M Cadmium acetate dihydrate and appropriate amount of thiourea in water. The solution is placed in a Teflon tray (15 × 15 × 2 cm) so that a meniscus is formed above the edges of the tray. To avoid dust contamination, the surface of the solution was cleaned by sweeping the Teflon barrier. Surface of subphase is divided into two compartments by fixing a Teflon thread barrier on the edges of the tray. With the help of micro-syringe, petrol was allowed to spread on the subphase in one of the compartments which formed a liquid (petrol) layer at the surface. In this process, the thread barrier gets stretched. The layer of petrol is then, immediately set on fire. During this process, Cd-thiourea complex at water–petrol interface experiences high temperature which is enough to decompose complex leading to the formation of CdS nanoparticles at the interface. The product was then compressed laterally via a Teflon thread barrier by spreading a drop of oleic acid on the surface of the subphase in the other compartment. The as-formed compressed film on the surface is transferred on to suitable substrate by immersing the substrate vertically in the solution at a constant rate of 0.5 cm/min and lifting it vertically at the same rate (Blodgett technique). The operation is repeated many times to get desired film thickness. The film thickness was