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Synthesis of nanocrystalline thin films at the organic/aqueous interface

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ABSTRACT

This article provides a review of wet chemical routes for the synthesis of nanocrystalline thin films at liquid/liquid interface. The properties of these films at the interfaces of two immiscible liquids have recently been studied with great interest. The recent developments in this area are highly significant and the growth of films at the liquid/liquid interface has made this technique very attractive. This report will also review the effect of concentration of precursors, the particles size, and the morphology of these films grown at interface.

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1. Introduction

The self-assembly of nanoparticles at the interface have been used in many applications including microelectronic devices (Akimov *et al*., 2010; Alkinov and Koh, 2008; Huynh *et al*., 2002; and McDonald *et al*., 2005). The driving force of the assembly at the interface is the reduction of interfacial energy between two liquids by self-assembly of nanoparticles. However, the assembly of nanoparticles can be spontaneous as they organize themselves by non-covalent interaction at the interface or by the interfacial interactions of nanoparticles dispersed in one of the liquids (water) with any stabilizer such as ligand in another liquid (oil). As the nanoparticles approach, each other in solution the attractive forces between nanoparticles will be strong, at the same time, the repulsion from steric crowding of the ligand will create an equilibrium, which helps to the assembly of nanocrystals. Ligands such as long chain thiols (Korgel *et al*., 1998) amines, (Sun *et al*., 2000) have been used as good stabilizers for bringing about assembly of nanocrystals. The interface between two immiscible liquids has not been studied sufficiently, and recently there has been growing interest in understanding the structure and properties of the liquid–liquid interface. A liquid–liquid interface is heterogeneous region that having a thickness in the range of a few nanometers up to some micrometers. The interface region between unlike liquids such as water/oil is unique environment and scaffold for deposition, nucleation and growth of metal chalcogenide-nanocrystalline thin films (Kumar *et al*., 2002; Health *et al*., 1997; Chin *et al*., .1998). It can be used in fabricating nano-materials devices which have applications in electronic, optical, magnetic, and industrial applications as well (Brus, 1991; Alivisatos, 1996; Lengl *et al*., 1996; Alivisatos *et al*., 1998; Empedocles *et al*., 1999; Volkov and Deamer, 1996). Brust and co-workers used two immiscible liquids to prepare metallic nanoparticles (Brust *et al*., 2001). This method was originally reported by Rao and his group (Rao, C.N.R *et al*., 2003) who formed thin films using water/oil interface to create thin films of metals and chalcogenides nanocrystalline.

The growth process at the interface was effected by different factors such as time, temperature, as well as concentration of the precursor. The growth of thin films at liquid/liquid interface is a cheap method and the films grown by self-assembly of nano-crystalline material have relatively less defects and are stable. These films can then be easily separated from the interface to a solid substrate. When two unlike liquids meet an interface results between two liquids, the particles of each liquid will disperse with each other in the regions of this interface, forming thin films of nanocrystalline. The main problem that has been studied at two immiscible liquids is dynamics and charge transfer reaction (Agrawal Ved., *et al*., 2005).

2. Assembly of nanocrystals at the interfacial region between organic/aqueous

Water-oil interface has been considered as unique environment for assembly of nanocrystals into thin films and has received great attention (Rao, C.N.R and Kalyanikutty, 2008; Vanmaekelbergh *et al*., 2004; Wange *et al*., 2010). Noble metal nanocrystals have been successfully assembled at the water–oil interface (Wang *et al*., 2005) by using 2,2-dithiobis[1 - 2(bromo -2- methylpropionyloxy)ethane] with 2-bromo-2-methyl-propionate, which was suitable due to a suitable contact angle ranging between 80°–110° was obtained. This new strategy play an important role for the assembly of hydrophilic nanostructures into thin film, like this assembly has been developed as a novel and facile strategy to create thin film of nanocrystals based devices, such as photodetectors (Fang *et al*., 2010). The basis of progress in the electronic devices is the emergence of the assembly of nanocrystals to create stable adherent molecular films on glass substrates.

The small spherical particles can attach to interfacial region between two liquids (Fig. 1) because of the energy to separate it is high, and it depends on the interfacial tension at the interfacial region, the size and shape of particles and the contact angles among the particles, water and oil layer.

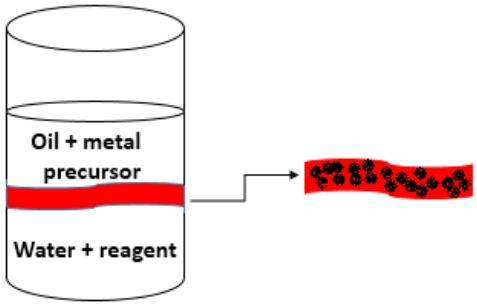

Fig. 1. Schematic diagram showing nanocrystalline thin film formed at the organic (oil)/water (Aqueous) interface

It is estimated that large particles for the contact angles measured through the water in the range 10°-170° and interfacial tensions higher than ~20 mN/M, the desorption energy is larger than thermal energy. Therefore, particles are trapped at the interface between organic (oil) and aqueous (water). Their movement depends on interactions through the aqueous and oil phases. The strategy of assembly of thin film nanocrystals at interface and the route of forming and trapping nanocrystals thin film is easier than any other chemical deposition. By the use of an organic solvent that held in contact with aqueous solution and at low temperature, suitable precursor thin film should be formed. To order nano-crystals and attach at interface the contact angle must be 90°. If the contact angle is larger than 90°, the particles will adhere at the oil phase while below this angle will prefer the water phase.

3. Size dependent influences of nanocrystals

From the theory of energy levels in solid-state physics, the electronic properties of a bulk semiconductor are calculated by the energy band gap (Eg) between valence band (V_B) and conduction band (C_B):

Energy band gap = conduction band – valence band

The smaller particles size, their electronic structure changes, and the charge of the carriers yields discrete energy states in the valence and conduction bands because of size confinement there is no enough space for electron and hole pairs to form. The electronic and optical properties of small particles are similar compared to those of a molecule of extended solid. Size dependent properties occur once the particle size becomes smaller than the Bohr radius. The Bohr radius is defined as,

$$\gamma_B = \frac{\varepsilon_0 \varepsilon_r}{\pi e^2 m * m_0}$$

where h is the Plank constant, ε_0 is dielectric constants of the vacuum and ε_r is dielectric constants of the semiconducting material, e, m^* and m_0 are the permittivity charge. The effective mass of the charge carriers and the electron mass, respectively. Generally, if dimensions of semiconductor nanoparticles smaller than Bohr radius, in this case called quantum dots. In quantum dots, the energy of band gap becomes size-dependent (Brus, 1984).

$$\mathrm{Eg} * = \mathrm{Eg}(bulk) + \frac{\hbar^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 r} - \frac{0.124e^4}{\hbar^2(4\pi\varepsilon\varepsilon_0)^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)^{-1}$$

where Eg* band gap of nanoparticles, Eg band gap energy of the bulk, h = Planck's Constant, r = particle radius , m^*_e = 0.19 m_e (effective mass of a conduction band electron), m^*_h = 0.80 m_e (effective mass of a valence band hole), ε_0 =8.854X10^{-12} $C^2N^{-1}m^{-2}$ (permittivity of free vacuum), ε = 5.7 (relative permittivity of semiconductor), e = elementary charge = 1.602X10^{-19} C.

4. Thin films deposition

The ways of thin film deposition are very important for development of material structures forming semiconductor devices. The development of techniques for the deposition of wide variety of thin films of high quality and of different phases is highly important. The investigations into the different liquid/liquid phases and their relationship with the quality of the films grown at these phases has supported the rapid growth of technology in this field.

5. Chemical deposition method

Chemists have tried to synthesize nanocrystalline thin films using a 'bottom-up' approach, which is arranging smaller components into more complex assemblies. The most promising route of creating nanocrystalline thin films of different types of materials was chemical method. These methods have made significant progress in terms of the variety and quality of thin films. Recently, one and two-dimensional materials in the form of nanostructures have been synthesized using these methods. Noble metal nanocrystals have been formed in alcohol (Bradley *et al.*, 1991) and Citrate (Hauser *et al.*, 1940) by reducing corresponding metal salt.

Thermolysis methods involve the heating of precursors in a liquid with a high boiling point. This liquid can act as a thermolysis medium as well as the capping agent for the production of nanocrystalline material. The nanoparticles produced are in the form of a colloidal solution, which can be deposited on a solid substrate by spreading a colloid in an organic solvent, usually hexane. The thermolysis temperature, the time of growth, the concentration of precursors as well as the type of capping agent effect the size and shape of nanocrystalline material. The other common technique used for the deposition of thin films is called Chemical Vapor Deposition (CVD). The CVD can either be Low Pressure (LPCVD) or Aerosol Assisted (AACVD). The AACVD have the advantage that it does not require a volatile precursor; the precursor should simply be soluble in any organic solvent whereas LPCVD requires a volatile precursors. Thermal decomposition helps to control the size nanoparticles and increase the size to obtain larger quantities of product. Other methods for the synthesis of nanoparticles include Photochemical (Marandi *et al.*, 2005), electrochemical reactions (Okitsu *et al.*, 2002), or other methods involving molecular precursors .The main factor for the quality of synthesis method is the monodispersity of nanocrystals formed. It is significant to form nanoparticles with the same size for their assembly and consistent properties.

6. Formation of nanocrystalline thin films at the organic/ aqueous interface

To generate nanocrystalline thin films, suppose that the system comprises of an organic liquid (toluene or hexane or petroleum ether) containing a metal precursor acting as a metal source held in contact with an aqueous layer containing a suitable reagent for reduction or sulfidation (Na_2S or K_2S...etc). With the appropriate selection of temperature, concentrations of precursor and time, the reaction will take place at the interface and thin films of nanocrystals can be formed at the interfacial region. The density of two phases will change during diffusion, which will allow the mixing of the ions in two phases (Fig. 2).

The reaction takes place at the interface forming nanocrystalline thin film of the corresponding material at the interfacial region. The deposition of this film depends on different parameters such as temperature, time, and the concentration. The reaction will proceed at the interface of two immiscible liquids generating nanocrystals as well as an ordered arrangement of nanoparticles in the form of a thin film. An emulsion formed by different phases, associated with interfacial turbulence and spontaneous agitation of the interface

between two un-equilibrated liquids. On the other hand, the diffusion at the interface between two immiscible liquids takes place in stagnant layers, which will be formed between the water/oil emulsion layers because of the changes in the concentration of the precursor and reagent (Benjamin, 1996).

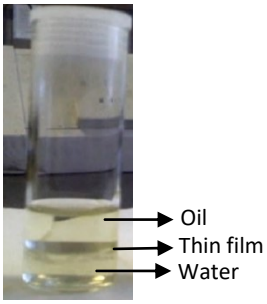

Fig. 2. Photograph shows deposited of thin film at organic/ aqueous.

7. Interfacial adsorption of nanocrystalline thin films at the interface of organic/aqueous

Liquid–liquid interfaces is main scaffold for the arrangement of nanometer-sized thin films. For instance, interfacial ordering features (Davies and Wiggill, 1960) can be used for the self-assembly of nanoparticles. The main, phenomenon is the assembly of nanocrystals at water-oil decreasing free energy, therefore, the assembly of nanoparticles at interfacial region requires decreasing interfacial tension (Huan *et al*., 2004; Lin *et al*., 2003; Reincke *et al*., 2004). The moving of nanoparticles to the interface between two immiscible liquids will decrease the entropy of the region and the internal energy at the interface must be decreased for reducing free energy at the interface. The change in internal energy is expressed as changes of energies between water-oil, particles–water, and particles–oil interfaces. The change in internal energy can be calculated from the attachment of nanoparticles at the interface according to the equation (Lin *et al*., 2003; Pieranski, 1980).

$$\Delta E = -\frac{\pi R^2}{\gamma_{w/o}\left(\gamma_{w/o} - \gamma_{p/w} + \gamma_{p/o}\right)^2}$$

From the equation above, the change in internal energy depends on radius of nanoparticles (R) whereas smaller nanoparticles adsorb faster than bigger ones. Consequently, the internal energy in the interface is suitable to make displacement of the particles from the interface. The small energy contributes in the assembly of the nanoparticles at the interface leads to overcome an energy barrier at the interfacial region. The time of nanoparticles to adhere at the interface increases as the particle size becomes large, as soon the assembly of nanoparticles at the interface. The interfacial energy will decline and nanoparticles at this region will undergo too many forces from the two immiscible liquids, which determine if nanoparticles assemble at the interfacial region or desorb at it. The energy required for nanoparticles particle to desorb at the interface depends on the interfacial energy of the interface between two liquids, size of nanoparticle as well as the contact angle among particles, water, and oil.

The free energy of particles at liquid -liquid interface calculated by the following equation (Binks and Clint, 2002; Binks and Horozoy, 2006)

$$\Delta G = -\frac{\pi d}{2^2 \gamma_{L/L}(1 \pm cos\theta)^2}$$

where d is the particle diameter, Θ is the contact angle, and $\gamma_{L/L}$ indicates the surface tension at the water/oil interface. However, particles at liquid/liquid interface interact by forces exist between particle -particle and by the forces exerted on the particles from the surrounding and interact by capillary forces caused by buoyancy and gravity (Kralchevsky and Denkov, 2001) as well as van der waals interactions when the distance between particles is very small.

8. Summary

Interfacial deposition has been successful in assembling and growing nanostructured thin films of metals and metal chalcogenides. This method is simple, cheap and environmentally friendly as in most cases the waste can be recirculated. Forces unique to the interface cause the deposits to adopt nanostructured forms. Parameters that can control the structural properties of the deposits such as grain size and morphology have been identified. It is hoped that the growing volume of interfacial deposition reactions would lead to further improve this technique so that it can be used at industrial level for the production of important semiconductor materials for applications in solar energy and electronic or opto-electric fields.

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