

Integrating nano and microparticles

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Received 25 May 2005; accepted 7 December 2005

A variety of nanomaterials have been developed in last few years with interesting physico-chemical properties. Most of the attempts so far have been to gain understanding of this new class of materials and look for potential applications. This has lead to the formulation of some scaling laws to explain, reasonably well, the properties of nanomaterials. It is realized, however, that the nanomaterials are often too difficult to handle due to their chemical, thermal etc instabilities as well as smallness. There is now a growing interest to integrate nanoparticles with microparticles to get advantages of both the nano and micro world of materials. The synthesis and characterization of ZnO, CdSe, TiO₂ and SiO₂ nano to micro particles and about core-shell particles have been studied.

Keywords: Microparticles, Nanoparticles

IPC Code: B82B

1 Introduction

During the last two to three decades, our ability to investigate 'small materials' has increased tremendously. It is possible to image the solids in sub-micrometer range to sub-nanometer size using electron and scanning probe microscopes. This is accompanied by attempts to synthesize materials with controlled size and shape. A large variety of physical, chemical, biological and hybrid techniques¹⁻⁶ have been employed to synthesize materials with just a few to hundreds of atoms per particle. With reduction in the number of atoms per particle, dramatic changes start occurring⁷. After intense research, it is well documented now that mechanical, optical, thermal, magnetic etc properties indeed depend upon the number of atoms and the way they are organized^{7,8}. In other words, the size as well as shape of the particles indeed is extremely important. This is quite understandable because starting with a single atom if we bring more and more atoms together we pass through tremendous changes in the electronic structure which affects the properties of materials. Thus, for the same material, we have a possibility of tailoring the properties from transparent to opaque or magnetic to non-magnetic or hard to soft etc. How the properties of materials change at small scale becomes interesting, as a basic curiosity as well as due to tremendous possibility of their industrial applications.

Size dependent changes occur on one hand due to reduced number of atoms and due to changed dimensionality on the other hand. Change of dimension may be such that the material reduces in all the three directions making a quantum dot or a zero dimensional (0-D) material or the material reduces in just two directions making a quantum wire (1-D) or the material reduces in just one direction making a thin film (2-D) material. It has been observed that for dots, wires or thin films below about 100 nm the properties are size dependent. These materials are therefore termed as nano materials.

Being too small to be imaged by optical or scanning electron microscope nanomaterials had to wait until powerful microscopes such as scanning probe microscopes like Scanning Tunneling Microscope (STM), Atomic Force Microscope (AFM), Scanning Near Field Optical Microscope (SNOM), Transmission Electron Microscope (TEM) etc became available to a large community of scientists.

Another aspect of nanomaterials is their large surface to bulk atoms ratio which also makes them highly reactive. In some applications like gas sensors this is quite useful. However, this makes nano materials highly unstable due to their tendency to aggregate in order to minimize the surface free energy. Often the nanomaterials have to be surface passivated to make them stable. This is done by using

appropriate coating or surface capping with suitable inert molecules or surfactants so that the particle size does not change during the course of time. Another method of retaining the particle size is by arresting the particles in some inert matrix like glass, zeolite or polymer.

Further, it is often found that nanomaterials are too small for some applications like detection of large ($\sim$ few hundreds of nanometers or larger size) bio-molecules. If nanomaterials are coated as a thin shell on larger (few hundreds of nanometer size) 'cores' forming 'core-shell' particles then they can be used as templates and also have novel properties similar to that in composite materials.

We have synthesized by some chemical method nanoparticles including spherical and rod particles (< 10 nm) of ZnO and CdSe. We have also seen photo-crystallization as an interesting process to convert TiO_2 nanoparticles from amorphous to crystalline state. Using chemical method larger (> 50 nm to few micrometer size) spherical particles of silica and titania have been synthesized. These act as 'cores' for semiconductor nanoparticles forming 'shell' around the particles. Alternatively shells of silica can be grown around nanoparticles.

These particles have large potential applications as follows: ZnO is an important material mainly used in photocatalysis, gas sensor, varistors, flat panel displays, field emission displays, cosmetics etc^{9,10}. Recently, doped ZnO has been identified¹¹⁻¹³ as a material for spintronics applications. CdSe nanoparticles are useful in applications like biological labeling¹⁴, chemical libraries¹⁵, gas sensors¹⁶, light emitting diodes¹⁷ etc. TiO_2 nanoparticles find applications as pigment, catalyst support, gas and humidity sensor, solar cell, optical coating material^{18,19}. Core-shell particles have been used for variety of applications as fluorescent diagnostics¹⁴, enhancing luminescence²⁰, chemical and colloidal stability²¹, drug delivery²², preparation of bio conjugates etc²³. In view of large number of applications of ZnO, CdSe, TiO_2 and core-shell particles, synthesis and characterization of such nano and microparticle integration are presented in the paper.

2 Experimental Details

2.1 Synthesis

ZnO nanoparticles (method 1, size < 5 nm)—Nanoparticles of zinc oxide have been prepared using following route. The reaction was carried out at room temperature. 0.1 M zinc acetate was dissolved

in 20 ml di-methyl sulphoxide and allowed to stir for few hours. To this stirring solution, 0.1 M NaOH in 20 ml methanol was added dropwise. After complete addition, white precipitate was formed. Thioglycerol (0.1 M) was added to this and the resultant solution was allowed to stir for 2 hr. Finally, precipitate was washed with methanol several times and allowed to dry to get ZnO nanoparticles in powder form.

ZnO particles (method 2, diameter ~ 500 nm and length $\sim 6 \mu\text{m}$)—The aqueous solution of 0.03 M zinc acetate (for 50 ml) was stirred for 30 min at room temperature. 0.2 M HMT (hexa methylene tetra amine) was added dropwise to above solution at room temperature. The clear solution was allowed to reflux at 90°C for 40 min and then cooled down to room temperature. After refluxing, precipitate was formed. The resulting precipitate was centrifuged and washed with double-distilled water for five times and redispersed in double-distilled water. Water was allowed to evaporate at room temperature to obtain ZnO microparticles in powder form.

CdSe nanoparticles (diameter < 10 nm)—CdSe nanoparticles were prepared using a chemical route as described below. Solution of cadmium acetate $((\text{CH}_3\text{COO})_2\text{Cd} \cdot 2\text{H}_2\text{O})$ was prepared by dissolving 0.002 M of cadmium acetate dihydrate in 50 ml dimethyl formamide (DMF) and stirred in ambient atmosphere. Mercaptoethanol solution, 0.01 M was mixed with constant stirring and then 0.002 M $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ (sodium selenite pentahydrate) was added to above solution. The resulting solution was stirred for few minutes and further refluxed for 2 hr at $\sim 80^\circ\text{C}$ without stirring.

Size selective precipitation was carried out using acetone as a non-solvent. The resulting precipitate thus obtained was washed 5 times in methanol and then dried in vacuum to obtain CdSe nanoparticles in powder form. The size of the particles could be varied by changing the concentration of capping agent.

TiO_2 nanoparticles (< 10 nm)—Titanium ethoxide (0.65 ml) was dissolved in 30 ml ethanol and stirred for one hr at room temperature. 0.01 g of NH_4F was dissolved in 1 ml double distilled water and added to above solution while stirring was continued for 30 min. Finally, the precipitate was washed and dried at room temperature. Part of the dried powder was exposed to UV radiation for 3 and 6 hr. A UV lamp giving a wide band from ~ 200 -400 nm and 15 W power was used.

Silica particles ($< 0.5 \mu\text{M}$)—Nearly monodisperse silica particles ($< 5\%$) were synthesized by a

procedure originally suggested by Stöber *et al.*²⁴. A solution of ethyl alcohol (15 ml), water (3 ml) and ammonium hydroxide (0.75 ml) was stirred vigorously at room temperature for 30 min. To this solution, TEOS (tetraethyl orthosilicate) (1.2 ml) was added dropwise and total solution was stirred for 3 hr. Ammonium hydroxide stock solution was prepared using ammonia (25%) and water in equimolar (1:1) proportion. Finally, the dispersion was centrifuged and precipitate was washed with ethanol. The particles obtained by this procedure are very stable. They can be stored as dry powder and dispersed in ethanol at a later time without any degradation.

Titania coated silica particles—Silica particles synthesized by above procedure could be coated with TiO₂. Coating procedure consists of controlled hydrolysis of titanium butoxide in presence of silica particles. For this purpose, a 0.1 gm of silica particles were ultrasonically dispersed in 30 ml of ethyl alcohol. Titanium butoxide (0.2 ml) and water (0.48 ml) was dissolved in 50 ml ethyl alcohol in a separate flask. This solution was vigorously stirred at room temperature for 15 min. To this solution, the dispersion of silica particles was added rapidly and the total mixture was stirred vigorously at room temperature for another 15 min. Finally, the mixture was refluxed at 80 °C for 90 min and allowed to age for 60 min. The dispersion was centrifuged and a white precipitate was obtained. The precipitate was washed with ethyl alcohol and dried.

2.2 Characterization Techniques

The characterization of above samples has been carried out using UV-Vis absorption, X-ray Diffraction, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). These are briefly discussed below.

Optical absorption—Shimadzu 300 double beam spectrometer was used for UV-Vis absorption measurements. Samples were prepared for measurements by dispersing in ethanol in case of ZnS, CdS and methanol in case of ZnO. Pure ethanol and methanol were used as reference for ZnS, CdS and ZnO respectively. Spectra were recorded from 200 to 600 nm.

X-ray diffraction—X-ray diffraction analysis of powder samples was carried out on Philips PW1840 powder diffractometer. Copper radiation (CuK_α 1.54 Å) was used in the analysis with nickel filter.

Transmission Electron Microscopy—Philips CM 200 FEG microscope equipped with a field emission

gun was used for TEM analysis of the samples. EDAX analysis could also be carried out using this microscope. For the analysis, powder samples were dispersed in ethanol and a drop of solution was placed on ~ 5 nm thick carbon film on copper grid. After air drying, the grid was inserted in the microscope and using 200 KeV energy images were acquired.

Scanning Electron Microscopy—JEOL, JSN 6360 scanning electron microscope was used for SEM analysis. The samples in the form of films were prepared by putting a drop of the sample on glass substrate and drying it in air. A thin layer of platinum (~ 10 to 20 nm) was coated on the sample to ensure that no surface charging occurred. Energy dispersive analysis of X-rays (EDAX) analysis was also carried out using the same instrument.

3 Results and Discussion

The nanoparticles and core shell particles in different shapes and sizes of variety of materials have been synthesized. The results on technologically important materials like ZnO, TiO₂, SiO₂ and CdSe have been presented. Zinc oxide is a wide band gap (3.3 eV) material. Due to its recent application in spintronics, large number of groups have taken up the work on ZnO. Some papers^{25,26} have also appeared especially on ZnO nanomaterials. In many cases, the chemical vapour deposition (CVD) has been used to obtain ZnO nanostructures. The ZnO particles with narrow size distribution are shown in Fig. 1. The particle size is ~ 3.3 nm as estimated from effective mass approximation²⁷ and ~ 4.5 nm using X-ray diffraction analysis (not shown here). The particles are crystalline having Wurtzite structure as is evident from the diffraction pattern.

The method 1 used to synthesize ZnO nanoparticles was not suitable for growing ZnO rods. However, we could grow ZnO in the shape of rod with method 2. It can be seen from SEM image in Fig. 2 (a) that very large rods (~ 3 μm) and diameter (~ 500 nm) have been obtained. It may be mentioned that as no TEM was done on these samples, it is not possible to say if these are tubes and we tentatively refer to them as rods. The rods are of nearly uniform size and possibly some or all are hexagonal in shape. This is clear from a magnified image in Fig. 2(b). Although not shown here, we could see many other shapes like stars, flowers, tetrapods etc. by the same chemical method with some alterations in synthesis parameters.

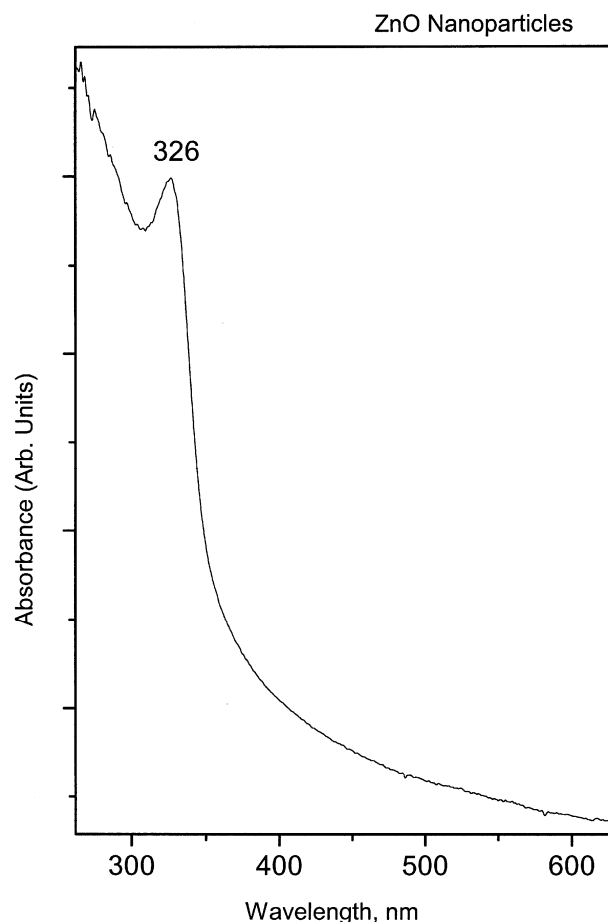


Fig. 1—UV-Vis absorption spectrum of zinc oxide nanoparticles.

CdSe also belongs to same group of ZnO viz. II-VI semiconductors, with direct band gap. It has been synthesized by various routes, with best particles being obtained by a method² involving organometallic compounds and reaction carried out at 350°C. Surface passivated nanoparticles with very narrow size distribution and intense photoluminescence are achieved. However, the synthesis involves very expensive and toxic precursors. The synthesis procedure discussed in the experimental section also produces nanoparticles giving fluorescence from blue to red. The luminescence obtained is quite intense. In Fig. 3, TEM of CdSe particles with particle size ~ 3.0 nm is shown. The particles have a hexagonal structure.

Further, we have synthesized TiO_2 nanoparticles ~ 6 nm in size. However, the particles were amorphous as shown in Fig. 4. When dry powder was irradiated with UV radiation, photocrystallization took place and TiO_2 turned into anatase phase. The photocrystallization of nanoparticles as well as

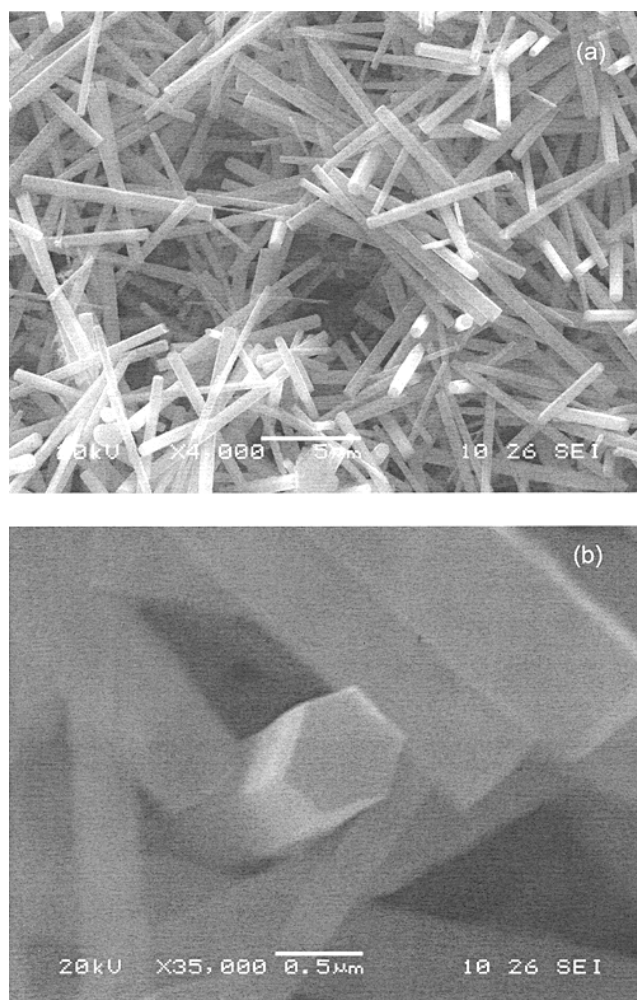


Fig. 2—Scanning electron micrograph of ZnO rods (a) and magnified view showing hexagonal (0001) plane (b)

fragmentation of nanoparticles have been recently an interesting new development^{28,29}. Our preliminary report on TiO_2 photocrystallization is therefore quite significant.

We have also coated TiO_2 on silica particles which are quite robust and can be grown as very uniform size particles at room temperature. TiO_2 on the other hand, is very difficult to obtain in desired shape and size as it is quite fragile in general. We, therefore develop the procedure to obtain TiO_2 as a coating on silica particles. As shown in Fig. 5(a), silica particles of size ~ 213 nm have been obtained. Titania coated particles are shown in Fig. 5(b). Thus, a coating of 39 nm forming a nanoshell is obtained. The ED analysis (not shown here) shows that SiO_2 particles are amorphous whereas, core-shell particles are crystalline having anatase phase of TiO_2 . The properties of core-shell particles can be different as

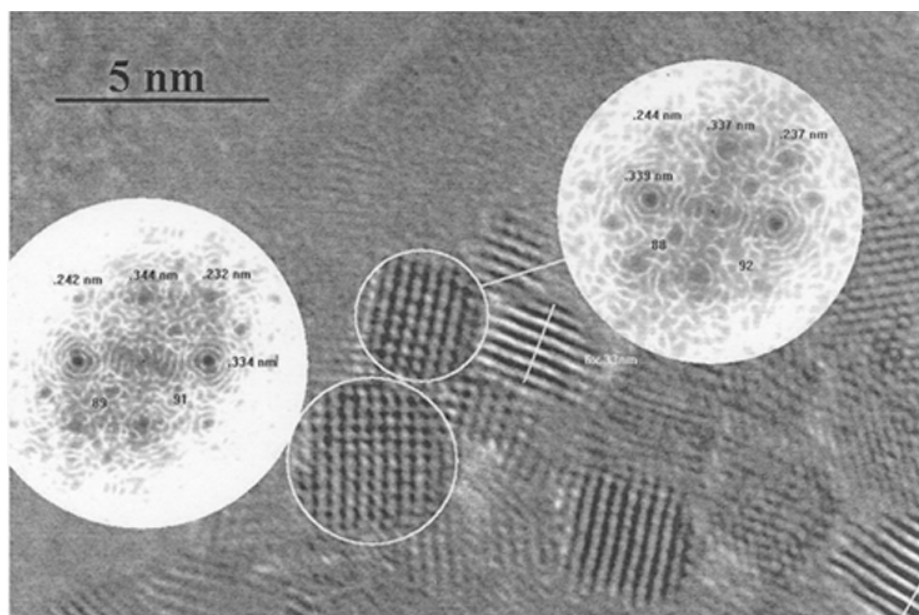
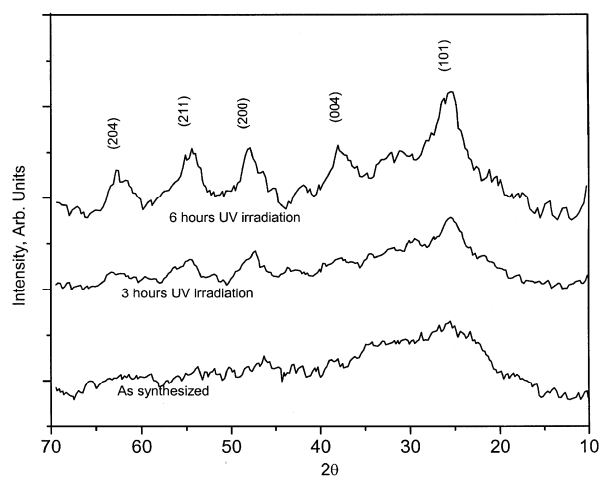


Fig. 3—HRTEM image of CdSe nanoparticles

Fig. 4—X-ray diffraction spectra of TiO₂ nanoparticles

compared to either core or shell³⁰. Further, work on SiO₂-TiO₂ particles is in progress.

We are also able to grow many other II-VI semiconductor particles and dope them³¹⁻³⁵. Various metal and metal oxide nanoparticles have also been synthesized in our laboratory and different metal-silica, semiconductor-silica core shell particles investigated^{20,36,37}.

4 Conclusions

There are various methods to synthesize nanoparticles. It is shown that chemical synthesis of nanoparticles is a very attractive method to synthesize variety of nanoparticles. The core-shell particles with

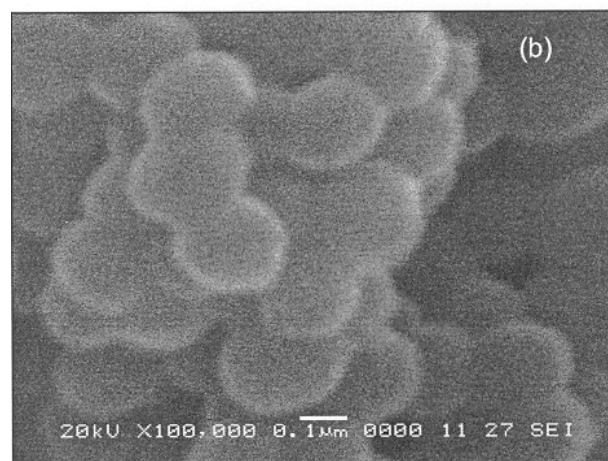
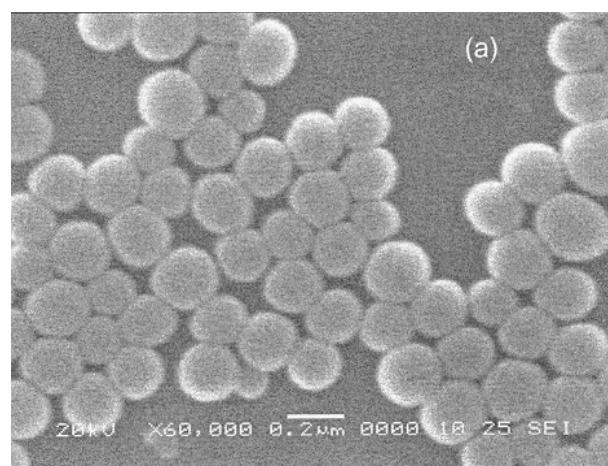


Fig. 5—Scanning electron micrograph of (A) uncoated silica particles and (B) titania coated silica particles (thick coating)

silica core can be grown so as to form nanoshells which may have additional advantages.

Acknowledgement

SKK would like to thank University Grants Commission, New Delhi, for financial support. SSA thanks ISRO-DRDO, India. ACD thanks DST, India. SKM thanks ISRO-DRDO, India. SAK thanks R&DE, for financial support. MAA thanks Iranian Embassy in India for financial support. This work is supported by DST, India and Volkswagenstiftung, Germany.

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