

Effect of Surfactants on Synthesis of SiO₂ Nanopowder Using Sol-Gel

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Abstract: In this work the silicon dioxide powder was prepared by optimized and simple sol-gel method and also provides a basic understanding of the effect of surfactants on the growth of SiO₂. The precursor solutions were made by mixing tetraethylorthosilicate (TEOS) with surfactants dimethyl-formamide or formamide and isopropanol and deionized water. The silica powder calcinated at 500°C formed in this study was found to be spherical structure. We deal with different surfactants, which are helpful for the enhancement of optical properties and surface morphologies. Optical properties of the samples were characterized by PL spectroscopy and growth rate of SiO₂ can be observed through scanning electron microscopy. SEM and PL analysis revealed that all the required morphologies and excitation and emission intensity were observed which were indicative of the successful synthesis of silica particles.

Keywords: silicon dioxide, surfactant, sol-gel process, optical properties, surface morphology, nanoparticles

I. Introduction

Metal oxides play a very important role in many areas of chemistry, physics and materials science. Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites. Silica, commonly named silicon oxide, is configured with four to six oxygen atoms and also comes in other forms. In SiO₂, the Si-O-Si bond lengths vary from 1.55 to 1.65 Å while the bond angles vary from 136° to 180° and these changes are found to correlate to changes in the band gap energy from 8.4 to 11.6eV. Therefore, amorphous silica continues as the focus of much fundamental research to understand its electronic structure, bonding characterization, defects, and optical properties. Recently the metal and oxide powder of the precursors have become useful materials in various

fields because they have new physicochemical properties which do not appear in the corresponding bulk materials [1]. Silica powder has demonstrated various properties according to its purity, shape, size and distribution and these have been investigated [2].

Various methods for the preparation of nanoparticles are employed such as plasma synthesis, chemical vapour deposition, micro emulsion processing, combustion synthesis, sol-gel processing, hydrothermal techniques etc. Recent efforts for the preparation of nanoparticles are focused to control size, morphology and surface reactivity of nanoparticles. The sol-gel process, as the name implies, involves the evolution of inorganic networks through formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The first reaction is a hydrolysis which induces the substitution of OR groups linked to silicon by silanol Si-OH groups. As previously, these chemical species may react together to form Si-O-Si (Siloxane) bonds which lead to the silica network formation. This two

phase's material consists of shaped solid exhibiting specific properties. These nanoparticles are either in colloidal form or agglomerated dry powder. The sol-gel technique has been used for reproduce new porous nanomaterials, with well-defined structures and complex shapes. Sol-gel is a very flexible route for the synthesis of inorganic, organic-inorganic networks such as glasses, ceramics [3], films or powders [4]. Basic principles of the sol-gel chemistry are therefore presented in the context of silica gel formation; sol-gel silica is an amorphous, porous material.

A great number of potential applications of these materials in the catalysis and separation area [5] and advanced materials [6], [7] have been developed in a short period of time [8]. The work of Beck, Vartuli, Kresge et al. in 1992 about the preparation of the first ordered mesoporous silica materials by templating of surfactant aggregates created an unparalleled research development toward novel porous oxidic materials [9]. Applications of mesoporous oxides are found in the fields of catalysis, chemical sensing, and separation or as "nanoreactors" [10], [11]. Porous silica sol-gel materials are of intense current interest. Mesoporous silica sol-gels have larger pores and pore/silica volume ratios, and these materials usually exist as powders [12], [13], [14]. Mesoporous silica sol-gel materials in the form of monoliths are highly desirable for a variety of applications such as optical sensing [15]. Spherical silica nanoparticles ($n - \text{SiO}_2$) with controllable size have been synthesized using tetraethoxysilane as starting material and ethanol as solvent by sol-gel method. Morphology and size of the particles was controlled through surfactants [16]. Surfactant adsorption is a process of transfer of surfactant molecules from bulk solution phase to the surface/interface; they reduce the surface tension [17]. Recent studies of silica-based meso-structures [18] and mesoporous silicas [19] showed that the size of nanometer-sized silica nanoparticles strongly affects the excitonic dynamics, also resulting in size-dependent PL properties. Accordingly, the origin of the size effect in excitonic PL from silica based mesostructures is expected to be different than that in semiconductor nanoscale materials because of the contribution of another exciton-type the small-radius exciton [20]. Many efforts have been made to control the particle size and morphology of silica nanoparticles using different type of surfactants as templates. In the preparation of silica nanoparticles, the rate and extent of the hydrolysis reaction of TEOS were found to be greatly influenced by reaction conditions, therefore, in the present study use of surfactants has been explored to control the particle size of the silica at nano level and morphological attributes were investigated through SEM and PL analysis [21].

Our efforts are to prepare uniform size, dry powder of silica nanoparticles and to study their beneficial role in photo-active materials. In this study, silica nanopowder prepared with surfactants which show the better result. The aim of the present paper is to investigate the influence of modifiers of organic and inorganic nature on the optical properties of SiO_2 nanopowder obtained by the sol-gel method from TEOS with the use of different surfactant. In the present work, several samples of SiO_2 were prepared by sol-gel techniques. We used SEM to study the morphology of the samples prepared by using different surfactant. We further measured the optical properties of each samples of silica oxide materials. The results suggest that the enhancement factor depends upon the size of nanoparticles and the spectral shape as well as dynamic behavior of the emission intensity.

II. Experimental

II.1. Materials

All reagents used were of analytical grade purity and were procured from Merck Chemical Reagent Co. Ltd. India. In this synthesis procedure, we use TEOS (tetra orthosilicate) as a precursor material with addition of surfactant dimethyl formamide (DMF) and formamide, acetic-acid used as catalysts and solvents as isopropanol.

II.2. Synthesis of Silica Nanoparticles

In the synthesis of SiO_2 particles, tetra orthosilicate (2mole) was mixed with isopropanol (20ml) used as solvent and surfactant (1mole) either dimethyl-formamide as denote mechanism 1 and formamide as denote mechanism 2, mixture was stirred, after 10 min added catalyst acetic acid (1mole) to the above mixture. The mixture was stirred magnetically 20 min at room temperature and become a homogeneous solution. The suspensions obtained were dried in an oven for 3 hours at 300°C , dried SiO_2 particles were obtained. The obtained powder samples were calcined in furnace for 1 hour at temperature 500°C for further material characterization. For convenience, the abbreviation $S_{\text{mechanism1}}$, $S_{\text{mechanism2}}$ and S_{control} denote SiO_2 prepared with dimethyl-formamide, with formamide and without surfactant.

III. Characterization

The prepared silica nanoparticles were characterized for surface morphology was studied by using SEM

(JEOL- JSM-6390) and for optical properties was studied by using PL Hitachi F-7000 Fluorescence Spectroscopy.

IV. Result and Discussion

IV.1. Scanning Electron Microscopy

We used SEM to study the morphology of the samples prepared by using different surfactants. The sample is highly homogeneous, although some of the nanoparticles feature smaller sizes. SEM images of samples reveal that without surfactant and variable water: isopropanol ratio, the SiO_2 crystallites agglomerate and the boundaries diffuse to form discrete structures as shown in Fig. 1 (a) S_{control} . This shows that the material is amorphous in nature in powder form. Fig. 1(b) (c) $S_{\text{mechanism1}}$ as shows that the sample of silica with dmf at 300°C shows small spherical structure as compared to dmf at 500°C . And, from Fig. 1 (d) (e) $S_{\text{mechanism2}}$ shows that the SiO_2 with formamide at 300°C shows as also same spherical shape as compared to formamide at 500°C . SEM observation of surfactants at dried temperature, dmf shows that the obtained product exclusively consisted of porous spherical nanoparticles as compared to formamide. But silica powder with formamide calcined at 500°C for 3 hours are shown spherical shape of diameter 1.53 micron which is smaller than dmf. It was possible to achieve such a high degree of well defined porosity due to optimization of the synthesis conditions and using formamide. Surfactants also prevented the nanoparticles to grow bigger.

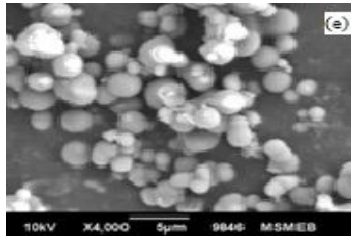
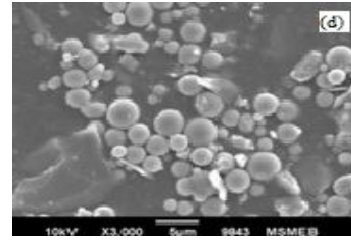
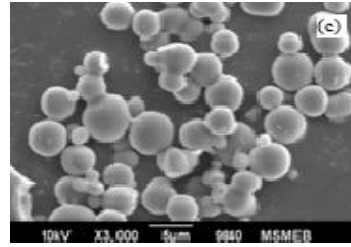
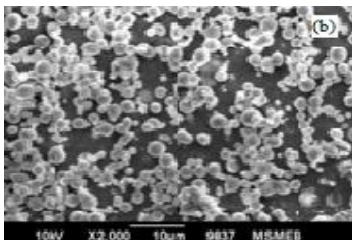
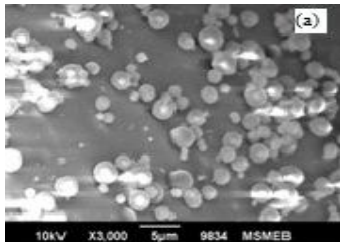


Fig. 1. SEM photographs of the studied samples; (a) without surfactant S_{control} , (b) $S_{\text{mechanism1}}$ at 300°C , (c) $S_{\text{mechanism1}}$ at 500°C , (d) $S_{\text{mechanism2}}$ at 300°C , (e) $S_{\text{mechanism2}}$ at 500°C

IV.2. PL Spectroscopy study of SiO_2 structures

Fig. 2 (a) (b) shows the fluorescence spectra of the SiO_2 for without surfactants and different surfactants dimethyl-formamide and formamide. From the Fig. 2 (a), it could be observed that there is a narrow peak appearing at around 381 nm and the structures of the emission spectra do not change. In the synthesis of silica nanoparticle dried at 300°C , which shows dmf having high intensity as compared to without surfactant and formamide for given wavelength at around 381nm. And, from the Fig. 2 (b) shows that SiO_2 nanoparticles with dmf and formamide calcined at 500°C , it could be observed that there is a narrow peak appearing at around 381nm. The result shows that formamide having high intensity than dmf.

PL is done to observe whether material is excited or not at wavelength showing maximum intensity. By this emission of spectrum range (310 nm to 500 nm) excited by particular wavelength gives broad peaks of maximum emission. The resultant graphs are analysed in intensity vs. wavelength. Graphs show drastically variations in peak values at same excitation wavelength when we change the surfactants. Fig. 2 (c) (d) shows

the PL spectra, in EM mode, of SiO_2 for without surfactants, dmf and formamide. Fig. 2 (c) shows that formamide having high emission intensity than dmf and without surfactants. And, from the Fig. 2 (d) which shows that formamide having high emission intensity as compared to dmf. The samples obtained without surfactants, more internal silanol groups are retained in the silica network and hence due to this silanols more stresses developed which causes irregularities on the silica layer which can be observed, and to overcome this destructive phenomena consists of the use of drying control chemical additives (DCCA) i.e. DMF and Formamide. For samples obtained with DCCA, water is removed more easily and less internal silanols remain in the samples and a better result observed.

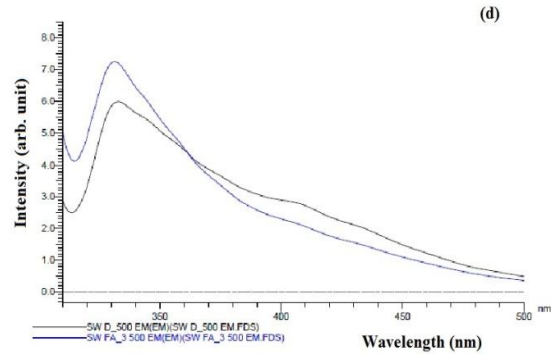
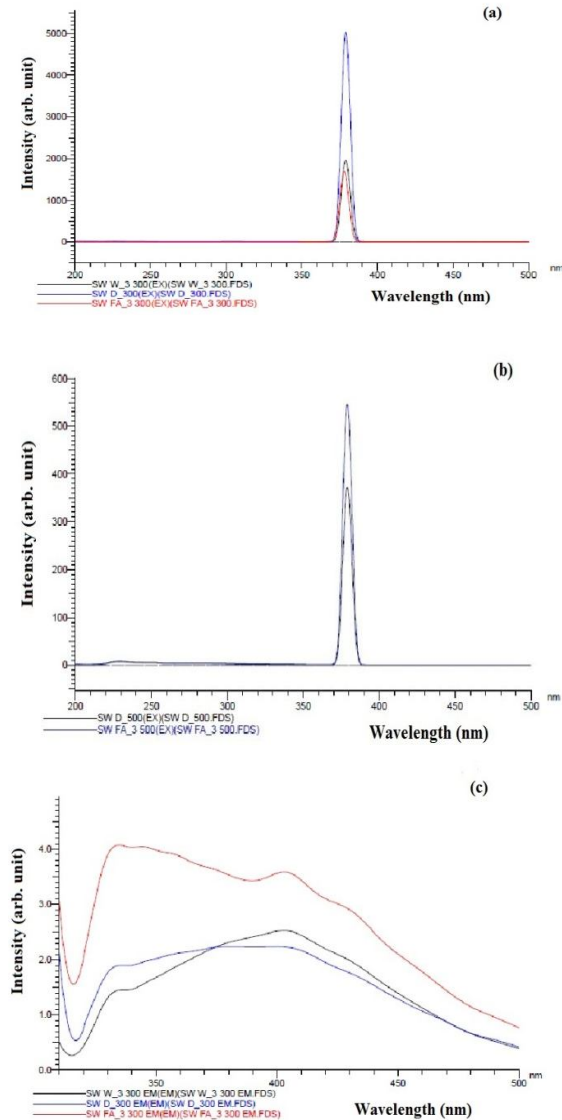


Fig. 2. PL analysis of SiO_2 nanoparticles (a) Fluorescence spectra of SiO_2 nanopowder without surfactant, dimethyl-formamide and formamide dried at 300°C. (b) Calcined at 500°C. (c) Photo-Luminescence spectra of SiO_2 nanopowder with dimethyl-formamide and formamide dried at 300°C. (d) Calcined at 500°C with surfactants.

From the PL spectra of formamide samples, it is clear that there is a blue shift in the emission spectrum with increase emission intensity having high photoactive properties. It shows a maximum peak having high intensities due to immediately formation in crystalline form. The blue band gradually disappears with decreasing laser light intensity despite the fact that green and red bands remain strong, indicating a decrease in the efficiency of the STE barrier penetration. The spectra presented in Fig. 3 (a) (b) were measured with the appropriate gate-delay/gate-width parameters, at which the blue PL band appears with maximal intensity. The blue shift was reported to originate from electron-hole recombination of the self-trapped exciton (STE) in smaller sized silica nanoparticle. The violet and green bands in the PL spectra were attributed to the electron-hole recombination and hydrogen - related species in the silica nanoparticles, respectively. The change is believed due to the different interactions between different sizes of silica nanoparticles. However, a clear understanding on the relationship between the particle size and particle-particle interactions is not elaborated. The increase in intensity of the UV band with the decrease in the particle size could be due to higher concentration of defect sites (STE and ODC) at smaller particle sizes.

V. Conclusion

We have synthesized ultrafine SiO_2 nanoparticles via sol-gel route. The different surfactants to be used has played significant role in the dimensional as well as optical properties of material. SEM studies confirm

that material SiO₂ so formed is porous spherical shape with surfactants, which could be converted into crystalline material under appropriate temperature and suitable chemical environment, and present smaller values of shrinkage and higher value of monolithicity than without surfactants. Hence the powder structure with formamide represents a porous spherical structure with strongly interconnected bond between the molecules, and enhancement in their optical characteristics. Secondly, optical behavior studied by the photoluminescence spectra represents the highly intensive form or very high peak at the same excitation of the wavelength when the silica with surfactant as formamide. PL spectra reveal that SiO₂ nanoparticles show absorbance in UV region of spectrum. For the surfactants the peak shift on blue side indicates that with decrease in water content in the gel, the material formed has smaller size and having high emission intensity with formamide surfactant than using dmf. The emission in green-blue region as revealed from PL study indicates that due to the presence of siloxane components. These studies show that silica nanoparticles with surfactants could be used in optical sensing devices and shows high photo-activity.

Acknowledgements

One of the authors (Ruchi Nandanwar) would like to thank the senior research scholars of Department of Physics, MANIT, Bhopal (M.P) for helpful discussions.

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Author's Profile

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