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Optical properties of amorphous organo-modified silica nanoparticles produced via co-condensation method

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Abstract

Structural defects in amorphous organo-modified silica nanoparticle have been studied via optical absorption and photoluminescence. The defect center, E′, oxygen defect center (ODCs), self-trapped exciton, OH-related surface defect, hydrogen-related species and carbon-related species were found in the amino-functionalized modified silica. These interesting emitting surface centers were observed in the range of vacuum ultraviolet (VUV), UV–vis and near-IR. Raman results were also demonstrated transverse- and longitudinal-optical pairs due to the surface defect-related optical properties.

Keywords: Amorphous silica; Nanoparticles; Co-condensation; Photoluminescence; Optical absorption

1. Introduction

Silica nanoparticles have been widely studied owing to several interesting optical phenomena caused by surface defects related to large surface/volume ratio [1]. This ratio provides the chemisorptions of OH groups on the surface of the particle and physisorption of water molecules. Removal of physisorped water (dehydration) and dehydroxylation of adjacent hydroxyl group by heat treatment activate particle surface towards structural defect. Point defects are generated from any defect in perfect SiO_4 continuous network, including oxygen and silicon vacancies. In the presence of organosilanes, silica particle may deal with a series of surface structural defects during condensation and/or cross-condensation reaction of organosilanes on the silica surface [2]. Numerous typical defects for silica nanoparticles such as surface E′ centers (paramagnetic positively charged oxygen vacancies, ≡Si•Si≡, or neutral dangling Si bonds, ≡Si•), non-bridging oxygen hole centers (NBOHCs; dangling oxygen bonds, ≡Si–O•), neutral oxygen deficient centers (ODCs; ≡Si–Si≡), twofold-coordinated silicon lone pair centers (≡Si–O–Si–O–Si≡), silanone group (O=Si=O), dioxasilyrane (=SiO_2), silylene (diamagnetic defect; =Si:) centers, peroxy linkage (PORs; ≡Si–O–O•), hydrogen-related species (≡Si–H and ≡Si–OH) and interstitial O_2 molecules [3–6]. These point defects can also be divided into two groups: paramagnetic and diamagnetic. Paramagnetic defects have optical absorption which represents half-occupied energy level in the optical band gap. Thus, hole transition or electron transition to the valence band is possible. Diamagnetic defects have absorption band associated with electron transition to the conduction band [7]. These defects and their combination are able to exhibit diversity of absorption and PL bands in broad range of wavelength, near-infrared, visible, and ultraviolet (UV). Hence, optical absorption and photoluminescence (PL) are the two useful properties for monitoring optical changes resulting from structural defect in the nanoparticle bulk and surface.

Since, silica nanoparticles have been extensively used as filler in fabrication of nanocomposites, modification of silica surface with coupling agent enhanced compatibility of filler with polymeric matrix. Co-condensation is one of the common modification techniques due to the homogeneous incorporation of organic functional group to the interior and exterior of the bulk of silica particle, compared with post-grafting method [8]. Although numerous co-condensation modification methods have been reported for porous silica, the modification of silica

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nanoparticles was less investigated. In our previous work [9], we have reported the preparation of organo-modified silica nanoparticles using APTES as modifier. Organo-functionalized silica nanoparticles were prepared by reacting tetraethyoxyhosilane (TEOS) and γ-aminopropyltriethoxysilane (APTES) in ethanol with water. In this continuation work, we focused on the evaluation of structural and optical properties of organo-modified silica nanoparticles by using XRD, PL, UV–vis and Raman techniques.

2. Experimental

2.1. Procedure

A quantity of 0.45 mol L^{-1} of TEOS (99%, Fluka) and 0.12 mol L^{-1} of APTES (99%, Aldrich) were first dissolved in 30 mL of absolute ethanol (99.5%, Systerm) simultaneously under low frequency ultrasound (Bransonic, Model 5510, 42 kHz) for 10 min. Then, 1 mL of distilled water was dropped into the reaction media with the fixed feed rate to facilitate hydrolysis of TEOS in the ultrasonic bath for 3 h. Then, the gelled samples were centrifuged and washed with ethanol and distilled water (3× 7 min, 6000 rpm). Drying was carried out using freeze drying as a non-thermal dehydration process under vacuum for overnight in a freeze dryer (Labconco, Freezon 12). The samples were heated at low temperature 220 °C for 2 h.

2.2. Characterization

Photoluminescence (PL) and Raman measurements were performed using Jobin Yvon HR 800 UV spectrophotometer equipped with HeCd ultraviolet laser (KIMMON IK320 IR-F, λ = 325 nm, 20 mW) source for PL and Argon ion laser (Spectra physics 183-D42, λ = 524 nm, 20 mW) source for Raman at room temperature, respectively. Solid state UV–vis absorption spectra were collected using PerkinElmer Lamda 45 spectrophotometer. X-ray diffraction patterns were recorded using SIEMENS D5000 X-ray diffractometer.

3. Results and discussion

Organo-modified silica nanoparticles have been prepared through co-condensation method by using γ-aminopropyltriethoxysilane (APTES). Fig. 1 shows TEM of the powders. For comparison, a pure silica powder with particle size ∼10 nm was synthesized by using TEOS [10].

The organo-modified powder consists of nearly spherical with average particle size of ∼60 nm and low aggregation (Fig. 1(a)). This may be due to the presence of organic groups on the silica during surface modification. Under the base-catalyzed condition, the gel network is predominantly formed from $Si(OEt)_4$ because it reacts faster than $RSi(OEt)_3$ and then condenses to form incomplete three-dimensional gel network that might prevent from the formation of curvature of spherical particles. The particle size of modified silica is sixfold higher than that of the pure silica may be due to the increase in the concentration of $–NH_2$ group that leads to the enhancement in the rate of hydrolysis and condensation reaction, which consequently, induces the growth of the larger particles.

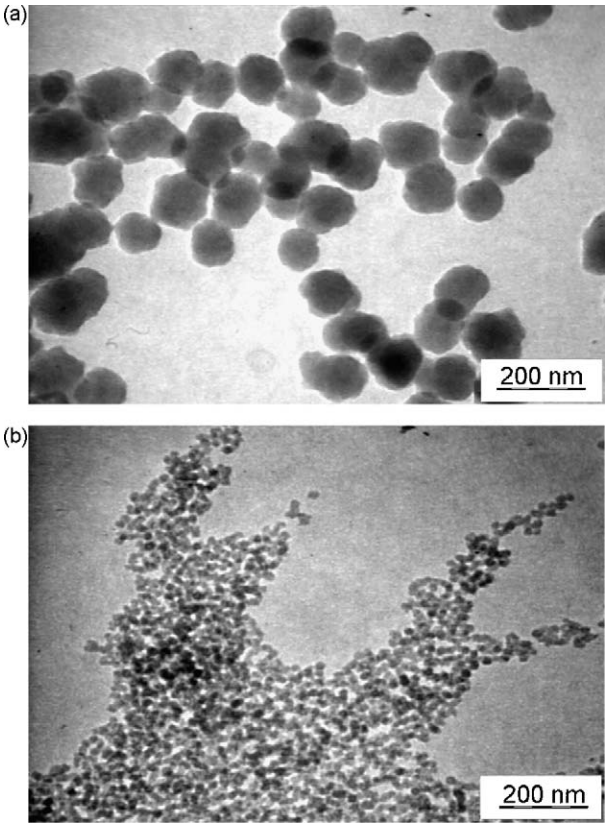

Fig. 1. TEM images of (a) modified silica, and (b) pure silica.

Fig. 2 shows the XRD patterns of an amorphous state of organic-modified and pure nanosilica produced using APTES and TEOS, respectively. The broad XRD reflection peaks may be due to the small size effect and incomplete inner structure of the particles [11]. The structural stability of silica does not change with the incorporation of organic group into silica.

Fig. 3 shows the PL spectra of organo-modified and pure silica at room temperature. Several emission bands were observed for organo-modified silica nanoparticles in the UV, blue, green, and IR spectral regions. The main emission band at ∼414 nm (blue band, ∼2.99 eV) is attributed to the neutral oxygen vacancies (ODCs; ≡Si–Si≡) and intrinsic diamagnetic defect center (two trapped center; ≡Si–O–Si–O–Si≡), self-trapped exciton (photoexcited electron–hole pairs; STE) that spatially confined with SiO_4 tetrahedron [12–14] and carbon-related species (resulting from organo-group in APTES) [15]. The blue light emitting center is corresponding to the defect resulting from the dehydroxylation reaction of a pair of geminal silanol group on the surface of silica by heat treatment. Thus, the intensity of blue light emission can be enhanced by increasing the concentration of silanol groups that may generate some defect points, such as silanone and silylene from dehydroxylation process in appropriate heat treatment. In addition, some disorderly and defect center can be expected by introducing an organosilane derivative to nanometer-size amorphous silica particles through a linkage between two