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A sonochemical-assisted synthesis of spherical silica nanostructures by using a new capping agent

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Abstract

Spherical silica nanostructures have been prepared using the sonochemical method. The silica nanoparticles were obtained by hydrolysis of tetraethyl orthosilicate (TEOS) in an alcohol solution. The influence of different surfactants i.e. cationic, anionic, polymeric and a new Schiff base on the morphology of the synthesized silica has been investigated. Our results show that using acetyl acetanato ethylene diimine as a new capping agent leads to produce nanostructures with suitable size distribution. The effect of different parameters such as concentration, ultrasonic wave power and reaction time on the morphology and size of the products was examined. Nanoparticles were characterized by XRD, SEM, FT-IR and EDS techniques.

Keywords: Silica; Sonochemical; Nanostructures

1. Introduction

Nanomaterials exhibit a wide range of practical applications in devices such as photocatalytic, supercapacitors, nanoelectronics and nano-optoelectronics. Nanostructures have gained much attention among materials, because the nanocrystal properties not only depend on their composition but also depend on their size, shape, and size distribution. The reactivity of nanoparticles can be adjusted by controlling the morphology because the exposed surfaces of the particles have distinct crystallographic planes depending on the shape. Silica is synthesized in different shapes, i.e. cubic, spherical and mesoporous [1–4]. Silica nanostructures exhibit new physicochemical properties which do not appear in their bulk material.

In the recent years, silica is increasingly used as ceramics, chromatography devices, electronic components, photo electricity devices, catalysis [5], stabilizers [6], pigments [7], pharmaceutical [8] and chemi-mechanical polishing tools [9]. Various methods such as: micro emulsions, Stöber and sonochemical methods are currently used for synthesizing of spherical SiO_2 nanoparticles [10–17], among them, sonochemical method is one of the best because of its capability to be a facile route operating under ambient conditions. Ultrasonic irradiation causes cavitation in a liquid medium where the formation, growth and implosive collapse of bubbles occurs. The collapse of bubbles with short lifetimes produces intense local heating and high pressure. These localized hot spots can generate a temperature of around 5000 °C and a pressure of over 1800 kPa that these spots are appropriate for many chemical reactions [18–21]. The following reactions take place in a typical sonochemical method:

(i) Silanol groups are first formed by hydrolysis.
(ii) Siloxane bridges are then formed by a condensation polymerization reaction.
(i) Hydrolysis: $Si\ (OR)_4 + H_2O \leftrightarrow Si\text{–}(OH)_4 + 4ROH$
(ii) Condensation: $2Si\text{–}(OH)_4 \rightarrow 2(Si\text{–}O\text{–}Si) + 4H_2O$

By utilizing ultrasound irradiation the formed bubbles collapse, resulting the generation of high speed microjets which can generate nanoparticles.

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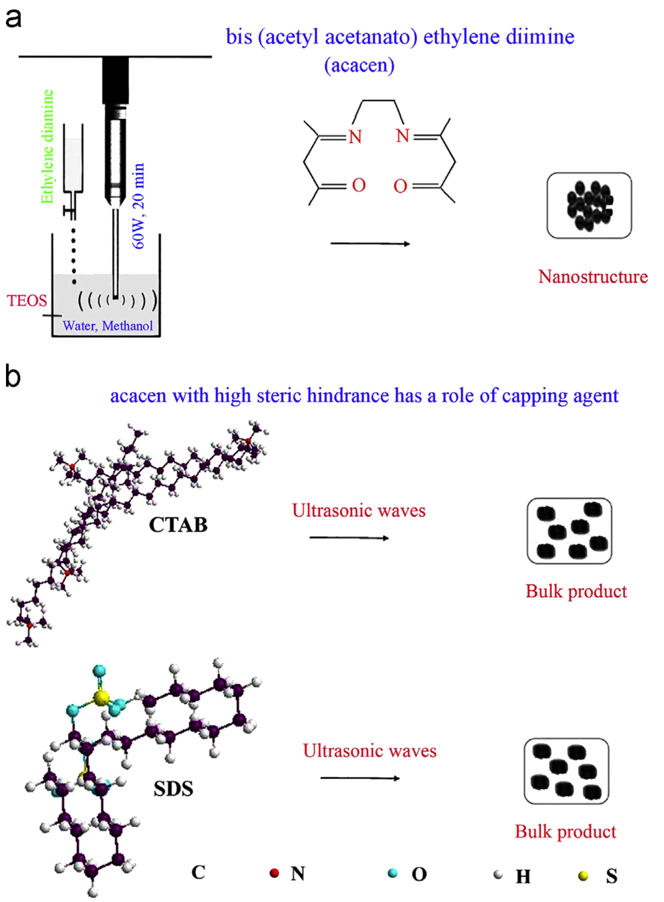

Fig. 1. Schematic diagram of (a) formation of nanostructures and (b) effect of CTAB and SDS on the particle sizes.

Using cationic (CTAB) and anionic surfactants (SDS) lead to synthesize of bulk products. Therefore we used a new Schiff base for obtaining nanostructures. Acacen acts as a surfactant and it was used as an additive to control the shape, uniformity and size of nanoparticles. Tetraethyl orthosilicate and ethylene diamine were respectively used as starting precursor and base catalyst. The effects of different parameters such as reaction time, ultrasonic wave power and concentration on the product morphology were also investigated.

2. Experimental

2.1. Materials and physical measurements

Tetraethyl orthosilicate (TEOS), ethylenediamine (en), methanol, cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS), poly vinyl pyrrolidone (PVP) and poly ethylene glycol (PEG) were purchased from Merck Company. All of the chemicals were used without further purifications. A multiwave ultrasonic generator (Sonicator 3000; Bandeline, MS 72, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 100 W, was used for ultrasonic irradiation. The ultrasonic generator automatically adjusts the power level. The wave amplitude in each experiment was adjusted as it is required. XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered Cu Kα radiation. SEM images were obtained using a LEO instrument. Prior to taking images, the samples were coated by a very thin layer of Pt to make the sample surface conducting and prevent charge accumulation, and therefore obtaining a better contrast. FT-IR spectra were recorded on Galaxy series FTIR5000 spectrophotometer.

2.2. Synthesis of bis (acetyl acetanato) ethylene diimine Schiff bases

Synthesis of Schiff base was based on acetyl acetone (acac) and ethylenediamine (en) at a mole ratio of 2:1. Acac and en was diluted in methanol and ethylenediamine was added slowly under stirring at room temperature. The solvent was removed and the resulting solid was crystallized from methanol.

2.3. Synthesis of spherical SiO_2 nanoparticles

25 ml of methanol and 10 ml of distilled water were sonicated. 4.5 mmol of TEOS and 0.22 mmol of Schiff bases dissolved in 5 ml of methanol were added under stirring. 0.1 ml of ethylenediamine was then added into the mixture as precipitating agent, under ultrasonic. After 30 min the precipitate was isolated by centrifuging and washed with methanol and water several times. The as-obtained products were dried at 80 °C under vacuum for 2 h, then calcinated at 650 °C for another 2 h.

3. Results and discussion

Schematic diagram of formation of nanostructures is depicted in Fig. 1a. SEM images of synthesized product using different surfactants such as anionic (SDS), cationic (CTAB), polymeric (PVP and PEG) are illustrated in Fig. 2a–d, respectively. These results show that using SDS and CTAB lead to synthesis of bulk products. However, by using PVP and PEG surfactants, nanostructure products are obtained. In fact employing of a new Schiff-base as the capping agent for synthesizing of silica nanostructures can be regarded as the novelty of this work. Acacen with high steric hindrance is a suitable capping agent for preparation of nanostructures. Schiff base group causes formation of nucleation rather than the particle growth (Fig. 1b).

In this work, synthesis of SiO_2 by applying ultrasonic waves with a power of 60 W for 20 min has been chosen as a basic reaction and the effect of different parameters on the morphology of the products has been investigated and compared.

SEM images of SiO_2 obtained at different mole ratios of acacen: Schiff base 1:20, 1:10, 1:2, 1:1 are illustrated in Fig. 3a-d respectively. At mole ratio of TEOS/acacen as 1:20, nanoparticles are synthesized. With increasing the mole ratio to 1:10 spherical nanostructures with smaller size are achieved. However at mole ratio of 1:2, the nanoparticle sizes are even smaller and size decrease is noticeable. Ultrasonic irradiation creates bubbles which produces high temperature and energy after decomposition. This process provides a sufficient amount of energy for formation of nanoparticles. The results confirm that in four

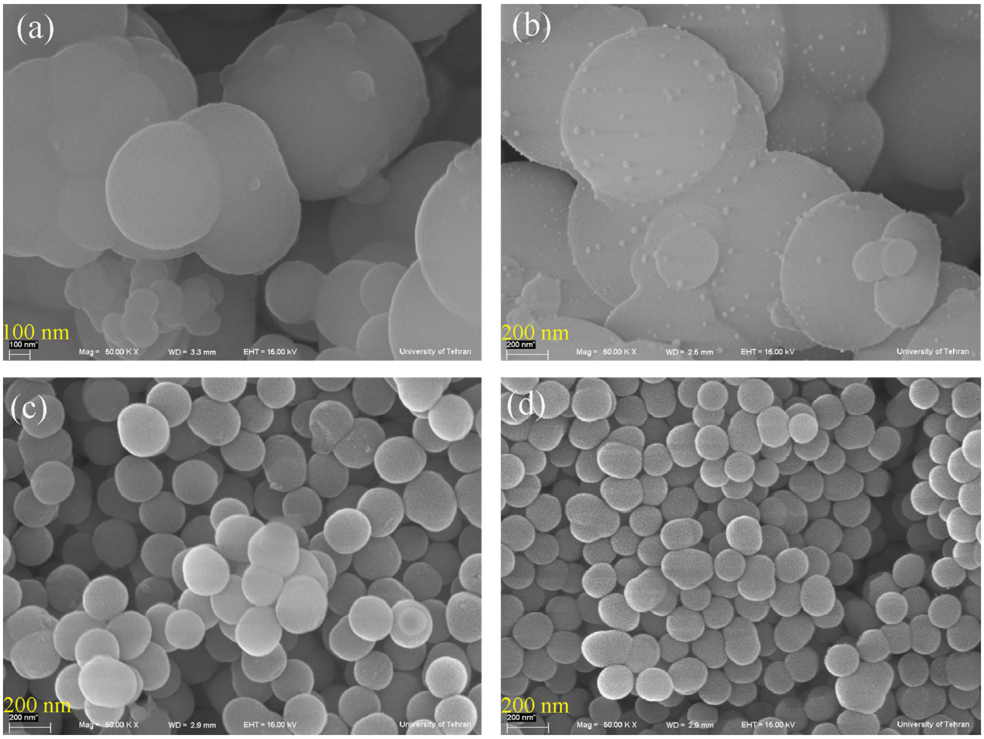

Fig. 2. SEM images of the SiO_2 nanostructure synthesized with (a) SDS, (b) CTAB, (c) PVP and (d) PEG.

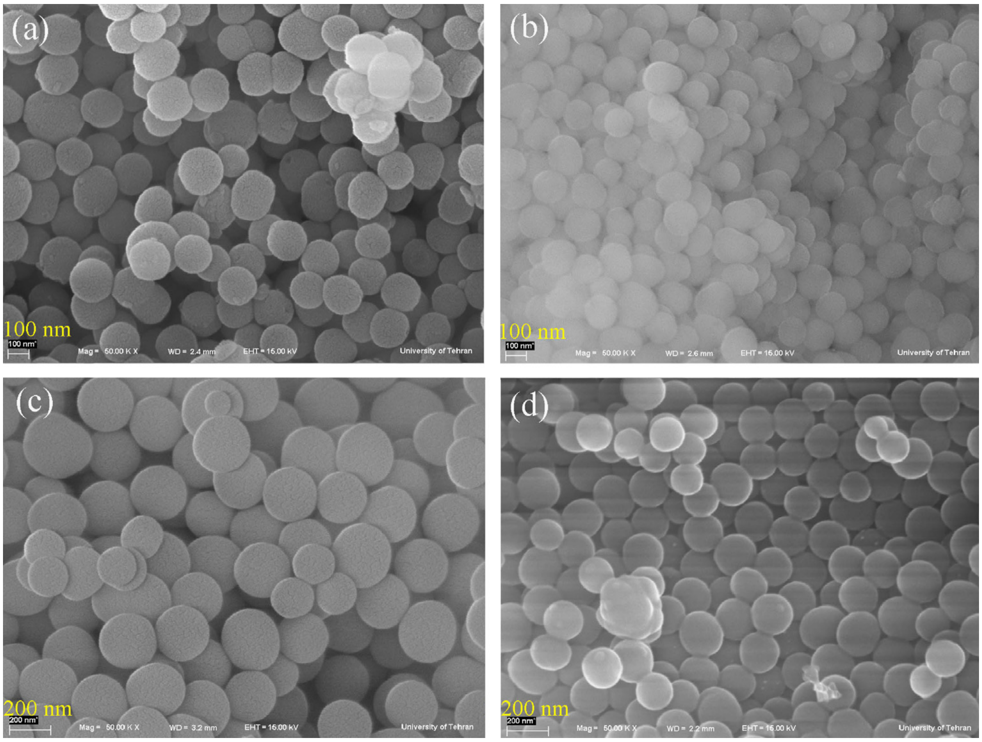

Fig. 3. SEM images of the SiO_2 nanostructure obtained with different mole ratios of acacen:TEOS as (a) 1:20, (b) 1:10, (c) 1:2 and (d) 1:1.

different synthesis conditions, nanostructures with average size of less than 100 nm can be obtained.

In order to investigate the effect of sonication time on the morphology of the products, the reaction carried out in different time of 20, 40 and 60 min. As Fig. 3a shows, at mole ratio of TEOS/acacen as 1:20 spherical nanoparticles were achieved. By increasing the sonication time from 20 to 40 min (Fig. 4a, b), nanostructures were synthesized. Further increase of the sonication time to 60 min, causes more uniform nanostructure size distribution. (Fig. 4c, d). The effect of sonication power on the

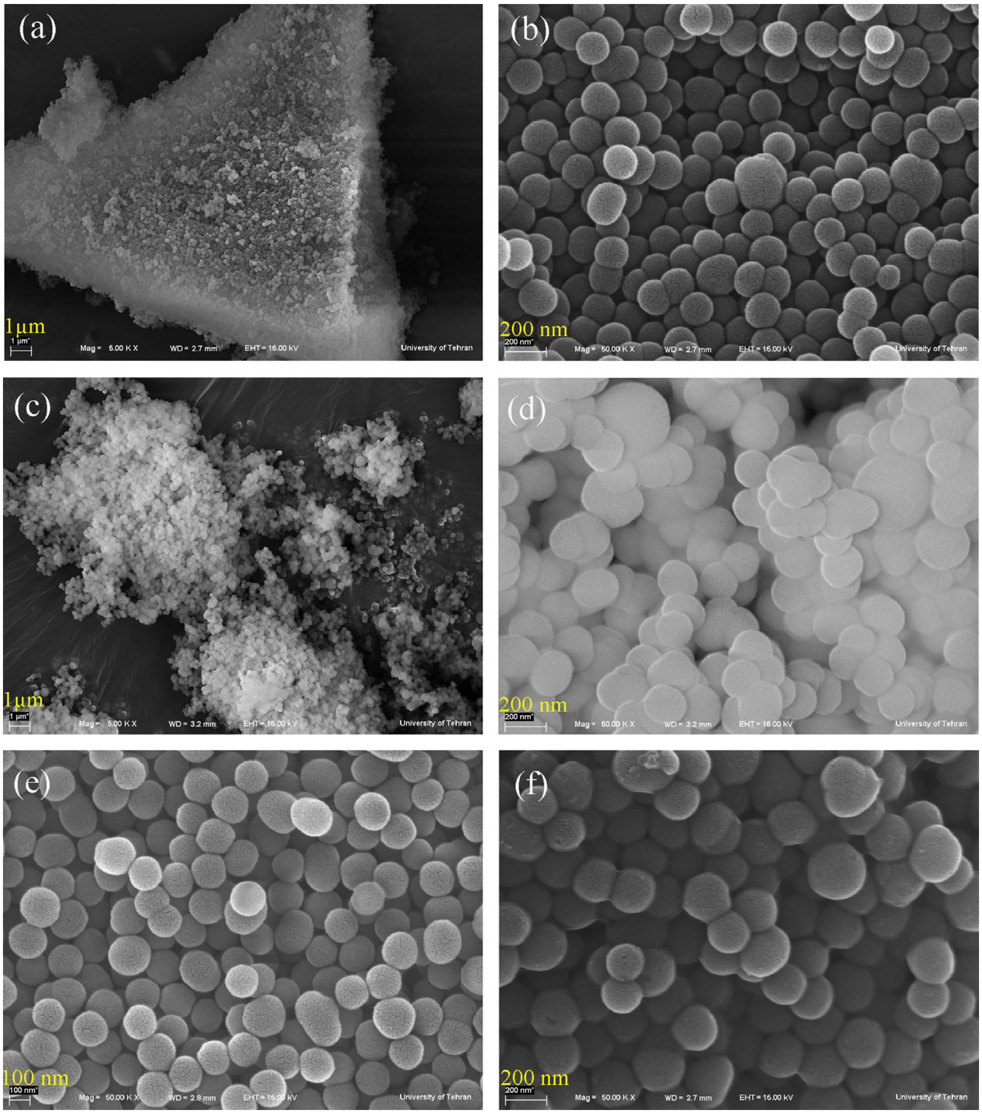

Fig. 4. SEM images of the SiO_2 nanostructure synthesized under applying of ultrasonic wave power of 60 W for (a, b) 40 min, (c, d) 60 min and at the power of (e) 50 W and (f) 70 W.

morphology of products was also examined. The result shows that nanoparticles were obtained at the power as low as 50 W (Fig. 4e). Increasing of the power to 70 W, causes more energetic bubbles which produces nanoparticles with more uniform distribution (Fig. 4f).

The XRD pattern of spherical SiO_2 nanoparticles is shown in Fig. 5a. The pattern of the as-prepared SiO_2 nanoparticles is indexed as an amorphous phase which is very close to the literature values (JCPDS No. 82-1557). The crystallite size measurements were also carried out by using the Scherrer equation

$$Dc = K\lambda/\beta \cos\,\theta$$

where β is the width of the observed diffraction line at its half intensity maximum, K is taken about 0.9, and λ is the wavelength of X-ray source used in XRD. The average crystallite size is estimated to be around 6 nm.

The purity of the nanostructures was also confirmed by energy-dispersive X-ray spectroscopy. EDS analysis of SiO_2 nanoparticles is illustrated in Fig. 5b. The lines of Si and O are obviously observed. FT-IR spectrum of as-synthesized product is depicted in Fig. 5c. Absorption peak at 1076 cm^{-1} is related to stretching vibrations of Si–O bond. The result shows that the product does not have any major IR-active impurity. The optical absorption spectrum of SiO_2 nanostructures is given in Fig. 5d. An absorption peaks at 220 nm, is attributed to the quantum confinement of charge carriers in the nanostructures.

4. Conclusions

Spherical silica nanostructures have been prepared using the sonochemical method. The influence of different surfactants such as CTAB (cationic), SDS (anionic), PEG and PVP (polymeric), as well as a new Schiff base capping agent on

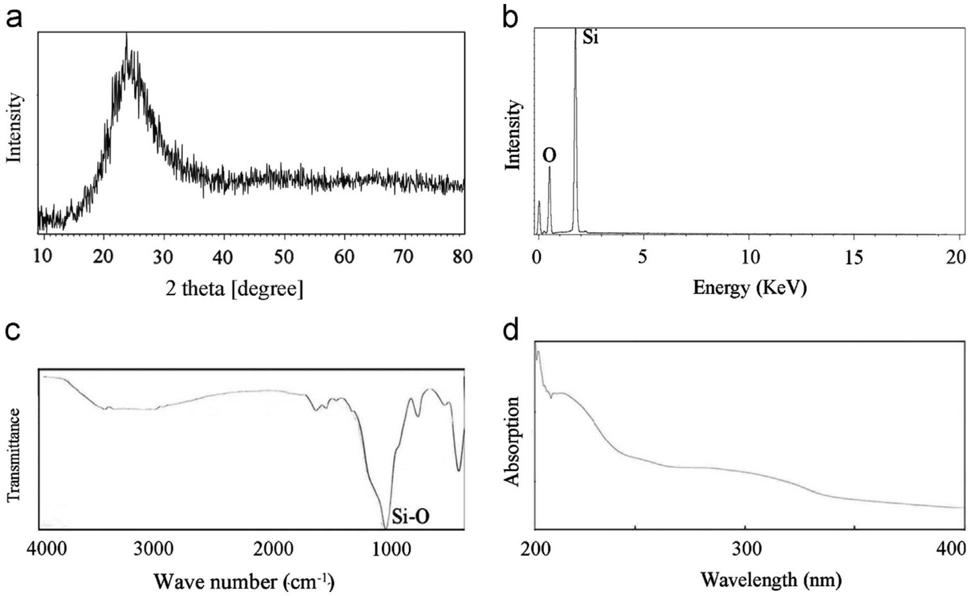

Fig. 5. (a) XRD pattern (b) EDS (c) FT-IR and (d) UV–vis spectra of SiO_2 spherical nanostructures.

the morphology of the silica has been investigated. Using cationic and anionic surfactants lead to synthesize of bulk products. Therefore we used a new Schiff base for obtaining nanostructures. Our results show that by using acetyl acetanato ethylene diimine as a new capping agent, nanostructure with appropriate size distribution can be obtained.

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