Applied Surface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Sonochemical synthesis of silica particles and their size control

Hwa-Min Kim [a], Chang-Hyun Lee [b], Bonghwan Kim [b,*]

[a] Advanced Materials and Chemical Engineering, Catholic University of Daegu, Gyeongbuk 38430, Republic of Korea
[b] Electronic and Electrical Engineering, Catholic University of Daegu, Gyeongbuk 38430, Republic of Korea

ARTICLE INFO

Article history:
Received 31 August 2015
Received in revised form 4 December 2015
Accepted 5 December 2015
Available online xxx

Keywords:
Sonochemical
Spherical silica
Ultrasound
Size control
Molar ratio

ABSTRACT

Using an ultrasound-assisted sol–gel method, we successfully synthesized very uniformly shaped, monodisperse, and size-controlled spherical silica particles from a mixture of ethanol, water, and tetraethyl orthosilicate in the presence of ammonia as catalyst, at room temperature. The diameters of the silica particles were distributed in the range from 40 to 400 nm; their morphology was well characterized by scanning electron microscopy. The silica particle size could be adjusted by choosing suitable concentrations of ammonium hydroxide and water, which in turn determined the nucleation and growth rates of the particles during the reaction. This sonochemical-based silica synthesis offers an alternative way to produce spherical silica particles in a relatively short reaction time. Thus, we suggest that this simple, low-cost, and efficient method of preparing uniform silica particles of various sizes will have practical and wide-ranging industrial applicability.

1. Introduction

Sonochemistry, the application of ultrasound for chemical synthesis and modified processes, has recently attracted increased interest. Several studies have reported the synthesis of various types of colloidal particles in the nanometer range, including Au, Pt, Fe, and CdS, which were produced due to the ultrasonically initiated reduction of the solutions [1,2]. In aqueous solution, hydrogen and hydroxyl radicals are produced under ultrasonic conditions. Several research groups have shown the possibility of increasing nucleation and growth rates with improved size distribution characteristics [2,3]. Among these various types of colloidal particles, in particular, silica has attracted extensive interest due to its structure, simple functionality, large surface area, and high demand for catalyst, optical, and biosensor applications [4–7].

Several synthetic techniques such as the surfactant template method and Stöber method [8], as well as sonochemical methods, have been proposed for the preparation of silica particles [8–17]. Gholami et al. reported the synthesis and characterization of spherical silica nanoparticles by a modified Stöber process assisted by organic ligands. They varied the ultrasonic treatment time and power, and the molar ratio of reactants. The average sizes of the nanoparticles ranged from 100 to 300 nm [10]. Bogush and Zukoski obtained monodisperse silica particle sizes ranging from 40 nm to few micrometers using a modified Stöber method [11]. Javidi and coworkers described the ball-milling synthesis of silica nanoparticles from rice husk ash for drug-delivery applications [12]. Masjedi-Arani et al. reported a sonochemically assisted synthesis of spherical silica nanostructures in the presence of a new capping agent. They investigated the influence of different surfactants [13]. Noori et al. described the synthesis and characterization of silica nanostructures in the presence of Schiff-base ligands via a simple sonochemical method. The method was based on a modified Stöber procedure using the reaction between tetraethyl orthosilicate (TEOS), ethylenediamine (en), and methanol in water [14]. Salavati-Niasari and Javidi synthesized silica nanoparticles from rice husk ash at room temperature by a sonochemical method [15]. Gholami et al. synthesized TiO_2@SiO_2 core/shell nanoparticles by a sol–gel method from tetraethyl orthotitanate and TEOS [16]. The Stöber and sonochemical methods are currently used for synthesizing silica nanoparticles. However, since there is scarcely any information among the several known methods regarding the control of dispersity, reaction time, and size, especially for producing nanometer-scale particles, there is an obstacle to practical application [18]. Limited research has successfully controlled the silica nanoparticle size to as low as tens of nanometers [11]. Sonochemical methods show some of the best potential because they are facile and capable of being operated under ambient conditions [13].

In this work, we report a novel approach for the synthesis and size control of silica particles using an ultrasound-assisted sol–gel

Abbreviations: DI, deionized; FE-SEM, field-emission scanning electron microscopy; TEOS, tetraethyl orthosilicate.

* Corresponding author. Tel.: +82 538503547; fax: +82 538503547.
E-mail address: bhkim@cu.ac.kr (B. Kim).

http://dx.doi.org/10.1016/j.apsusc.2015.12.048
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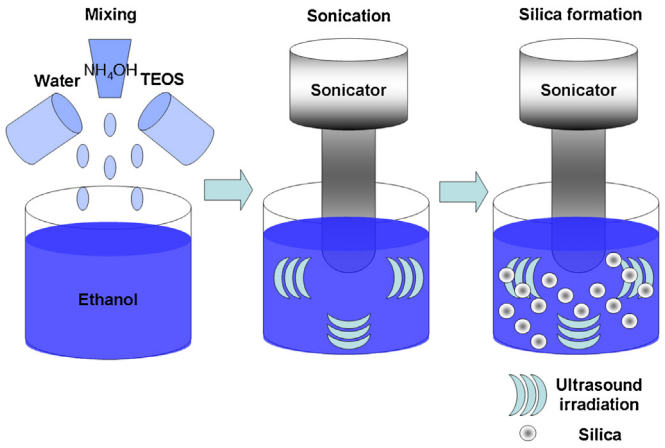

Fig. 1. Schematic illustration of silica formation using ultrasound.

method. This approach affords a significant improvement in the control of the silica particle size and shape uniformity, obtained by changing the molar ratio of the deionized (DI) water and ammonium hydroxide in the reaction medium. The successful control of the shape and size of the silica particles was confirmed through scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

TEOS (98.5%) and ammonium hydroxide (NH_4OH, 30 wt%) were purchased from Sigma Aldrich, and ethanol (99.9%) was obtained from Merck Inc. All reagents were used without further purification.

2.2. Preparation of silica particles

Silica particles were prepared using an ultrasound-assisted sol–gel method. Ethanol and DI water were mixed for 10 min, and then TEOS was added for pre-hydrolysis. After mixing for 5 min, NH_4OH was added into the pre-hydrolyzed solution and stirring was continued for 5 min. The mixture was exposed to ultrasonic waves generated by a Sonics and Materials VCX-750 ultrasonic generator for 1 h. The molar ratio of the reactant mixture was $TEOS:C_2H_5OH:H_2O:NH_4OH = 1:75.9:x:y$, where $x = 61.6$ or 12.3 and $y = 2.85$, 5.7, or 8.54. The molar ratios of water and ammonia were varied to investigate the effects on the silica particles' shapes and sizes. The produced silica particles were washed with DI water several times and collected by centrifuging at 8000 rpm for 15 min. After centrifugation, the silica particles were placed in a drying oven for 4 h at <80 °C. The detailed experimental procedure is illustrated in Fig. 1. The morphology of the silica particles including their size and distribution was analyzed using field-emission scanning electron microscopy (FE-SEM, Hitachi, S4800). The silica particle diameter was determined as an average of the sizes of 20 randomly selected particles as determined by SEM.

Table 1
Silica preparation parameters and results.

Sample	Ethanol:DI water:TEOS:NH_4OH (molar ratio)	Average particle size (nm)
A	75.9:61.6:1.0:2.85	285 ± 27.0
B	75.9:61.6:1.0:5.7	316 ± 22.9
C	75.9:61.6:1.0:8.54	430 ± 48.4
D	75.9:12.3:1.0:2.85	39 ± 3.4
E	75.9:12.3:1.0:5.7	110 ± 8.7
F	75.9:12.3:1.0:58.54	415 ± 61.7

3. Results and discussion

3.1. Formation of silica particles via highly intense irradiation

The test samples were prepared using varying $TEOS:C_2H_5OH:H_2O:NH_4OH$ molar ratios. Very uniformly shaped and monodispersed silica particles were successfully synthesized by ultrasonication. Table 1 shows the influence of the water and ammonia molar ratio on the particle size; the average particle size was controllable within the range from 40 to 400 nm under these conditions.

The typical morphology and various sizes of the silica particles are shown in Fig. 2. Spherical silica particles were always generated regardless of the reagent concentrations. As the molar ratio of the ammonia solution is increased, the particle size increases, as shown in Fig. 2 (cf. Table 1). This can be explained by the change in the reaction rate, which is mainly controlled by the amount of catalyst, i.e., NH_4OH, in this process.

The silica particle size decreases with a decreasing molar ratio of DI water, as shown in Fig. 3 (cf. Table 1). The DI water provides OH radicals to the reaction to form silica particles. Thus, the decrease in the silica particle size due to the lower DI water concentration may be related to the limited availability of OH radicals.

Fig. 4(a) shows the silica particle size as a function of the NH_4OH molar ratio for the two different water molar ratios (61.6 and 12.3). It is clear from Fig. 2(a) that the silica particle size is significantly affected by the water molar ratio. The effect is more pronounced with smaller amounts of NH_4OH. On the other hand, Fig. 4(b) shows the effects of the NH_4OH molar ratio on the silica particle size.

There is a significant difference in the particle size as water molar ratio increases from 12.3 to 61.6 for NH_4OH molar ratios of 2.85 and 5.7. However, when the ammonia molar ratio is 8.54, there is almost no difference in the silica particle size for water molar ratios between 12.3 and 61.6.

The ammonia and water ratios were varied over the reaction and their effects are clearly shown in Table 1 and Fig. 4. From the results of Figs. 2 and 3, it is evident that the average silica particle size can be controlled within the range from 40 to 400 nm by varying the reagent molar ratios. We, therefore, suggest that the silica size can

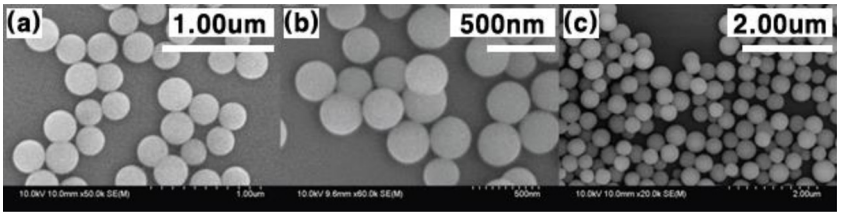

Fig. 2. SEM images of changes in silica particle size synthesized in mixed solutions of water (molar ratio 61.6) and different ammonium hydroxide concentrations (molar ratios of (a) 2.85, (b) 5.7, and (c) 8.54).

Please cite this article in press as: H.-M. Kim, et al., Sonochemical synthesis of silica particles and their size control, Appl. Surf. Sci. (2015), http://dx.doi.org/10.1016/j.apsusc.2015.12.048