Advanced Powder Technology 27 (2016) 448–453

Contents lists available at ScienceDirect

Advanced Powder Technology

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

Original Research Paper

Synthesis of phosphor-free luminescent, monodisperse, mesoporous silica nanoparticles in the co-presence of double- and single-chain cationic surfactants

Haruyuki Ishii, Shunsuke Kawai, Daisuke Nagao *, Mikio Konno *

Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki-aza, Aoba-ku, Sendai 980-8579, Japan

ARTICLE INFO

Article history:
Received 19 September 2015
Received in revised form 6 January 2016
Accepted 12 January 2016
Available online 2 February 2016

Keywords:
Phosphor-free luminescence
Monodisperse mesoporous silica nanoparticle
Double chain cationic surfactant
UV irradiation

ABSTRACT

Phosphor-free luminescent, mesoporous silica nanoparticles (MSNs) were synthesized with a sol–gel method in the presence of cetyltrimethylammonium bromide (CTAB) and/or didodecyldimethylammonium bromide (DDAB). The surfactants were employed to play double roles as a template to form mesopores and as an organic compound to introduce luminescent centers in calcination step. The incorporation of DDAB produced MSN that was better in luminescent properties than the CTAB-incorporated nanoparticles. A low molar ratio of CTAB to DDAB in their coexistence system could produce highly monodisperse MSN that showed emission intensity higher than that of a conventional phosphor-free luminescent silica nanoparticle having no mesopores.

1. Introduction

Mesoporous silica is widely used as catalysts, catalytic supports, and adsorbents because of its high specific surface area and tunable pore structures. A common method to prepare mesoporous silica is soft-template synthesis in which the silica formation occurs around regularly ordered micelles of surfactants [1,2]. The porosity and morphology of the mesoporous silica are precisely controlled by surfactant species and reaction conditions [1–5].

Particulate mesoporous silica is a functional material that has porous properties suitable for transportation to specific targets [6]. The transportation of mesoporous silica can be visualized by introducing phosphors, which is usable for drug carriers [7] and bioimaging markers [8–11]. In these applications, highly monodisperse small particles (<200 nm) are often required for precise targeting and labeling as designed [12]. Fluorescent dyes [8–11] and rare earth ions [7,13] have been commonly employed as phosphors to provide mesoporous silica particles with luminescence properties. These phosphors, however, have some drawbacks: fluorescent dyes easily suffer photobleaching under irradiation of excitation light, and rare earth ions are expensive and neighbored to supply risk.

Metal oxides incorporating atomic defects or carbon impurities can be promising luminescent materials because of high chemical and optical stabilities, low toxicity, and facile preparation without phosphors nor expensive substances [14–18]. Monodisperse, particulate silica with the phosphor-free luminescence has commonly been synthesized in sol–gel methods in the presence of organosilanes, typically with 3-aminopropyl triethoxysilane (APTES) [16,17]. Calcination of the particulate silica incorporates atomic defects and carbon impurities in pore-free silica particles. This incorporation technique with APTES for phosphor-free luminescence was also applied to mesoporous silica particles that had been prepared in advance in a sol–gel method with cetyltrimethylammonium bromide (CTAB) [19,20]. The method employed the organosilane to introduce luminescent center into silica matrix.

The present work proposes a direct, facile synthesis of phosphor-free luminescent mesoporous silica nanoparticles (MSNs) with high monodispersity without any organosilanes. The synthesis is based on the use of cationic surfactants that act not only as templates for formation of mesopores but also as organic compounds to introduce luminescence center into MSNs by calcination. Commercial cationic surfactants with a quaternary ammonia salt, didodecyldimethylammonium bromide (DDAB) and CTAB, are employed for exploring an optimal system to produce the functional MSNs. Both mesoporous and luminescent properties are characterized with the silica particles calcined at high temperatures to pyrolyze the surfactants. The luminescent

* Corresponding authors. Tel.: +81 22 795 7239; fax: +81 22 795 7241.
E-mail addresses: nagao@mickey.che.tohoku.ac.jp (D. Nagao), konno@mickey.che.tohoku.ac.jp (M. Konno).

http://dx.doi.org/10.1016/j.apt.2016.01.010
0921-8831/

properties of the MSNs prepared are also compared to a conventional phosphor-free silica nanoparticle formed in the presence of an organosilane, APTES.

2. Materials and methods

2.1. Materials

Didodecyldimethylammounium bromide (DDAB, 99%), cetyltrimethylammounium bromide (CTAB, 95%) and tetraethyl orthosilicate (TEOS, 95%) were purchased from Wako Pure Chemical Industries (Osaka, Japan). 3-Aminopropyl triethoxysilane (APTES, 99%) was purchased from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). The other chemicals of analytical grade were purchased from the Wako Pure Chemical Industries.

2.2. Preparation of mesoporous silica nanoparticles (MSNs)

The synthesis of MSNs used ethanol for cosolvent and a basic catalyst of ammonia [21,22]. An ethanolic solution of TEOS was added to an aqueous solution of cationic surfactants. The volume ratio of ethanol to water was one fourth, and the concentrations of ammonia and TEOS were 400 and 100 mM, respectively. The reaction mixture was stirred with a magnetic stir bar for 10 min and aged without stirring for 6 h at 80 °C. The nanoparticles obtained were washed with water and dried under vacuum at 60 °C, followed by calcination for 4 h to remove the cationic surfactants and organic compounds from the silica particles. The calcination was performed in a temperature range of 300–600 °C.

2.3. Preparation of phosphor-free luminescent silica nanoparticle without mesopores

APTES-incorporated silica nanoparticle was first prepared, according to the previous paper [16]. TEOS and APTES were used as silica sources, and APTES concentration (5.1 mM) was 2.9 mol % relative to the total concentration of the silica sources. The preparation was performed at 35 °C in ethanol–water mixture where concentrations of ammonia and water were 0.45 M and 7.2 M, respectively. The nanoparticle obtained was then washed with ethanol for three times and dried under vacuum at 60 °C. Phosphor-free luminescent silica nanoparticle without mesopores was finally obtained by calcination at 400 °C for 2 h [16].

2.4. Characterization

The nanoparticles obtained before and after the calcination were observed with a scanning transmittance electron microscope

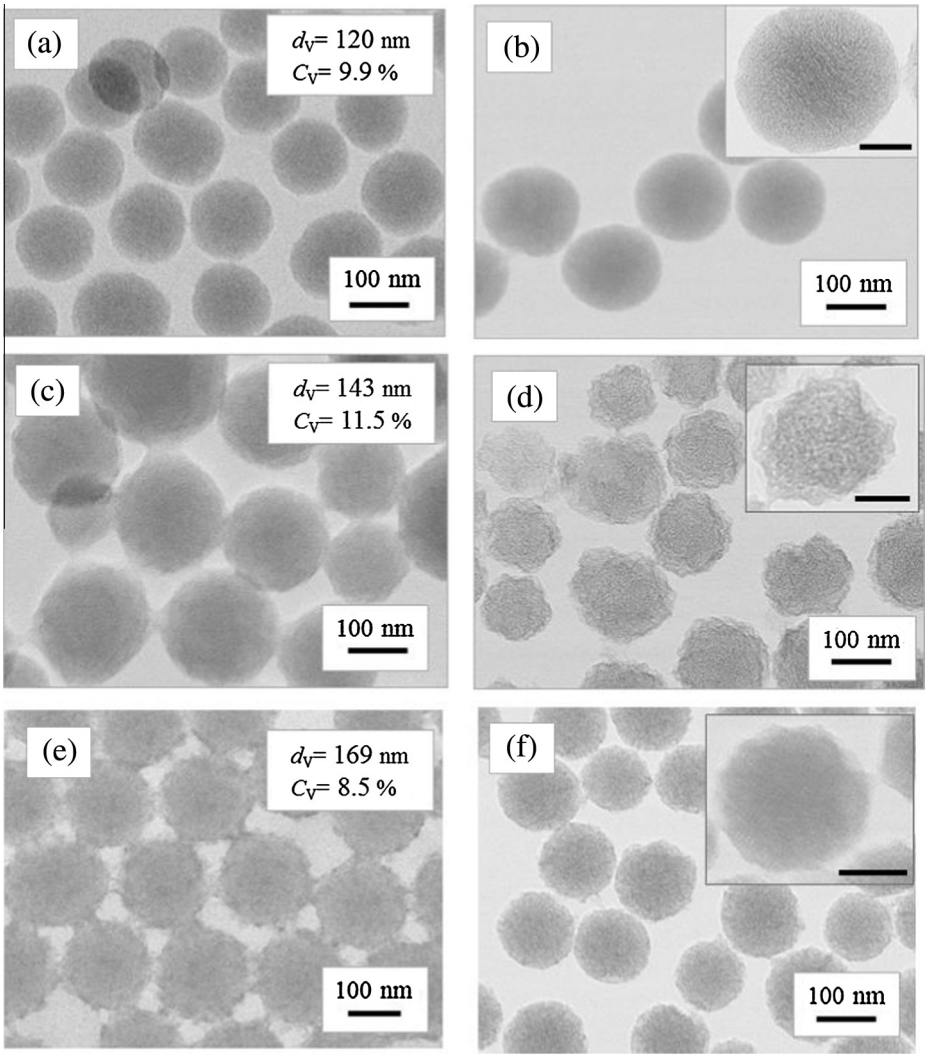

Fig. 1. TEM images of silica nanoparticles before (a, c and e) and after (b, d and f) calcination at 500 °C. The nanoparticles were synthesized in the presence of 50 mM CTAB (a and b), 50 mM DDAB (c and d) and 50 mM DDAB/10 mM CTAB (e and f). Scale bars in insets show 50 nm.