A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 60 2015 Issue 2
DOI: 10.1515/amm-2015-0102

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FABRICATION OF COLLOIDAL CLUSTERS DECORATED WITH DYE MOLECULES FOR POTENTIAL APPLICATION AS PHOTONIC MOLECULES

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In this study, colloidal clusters decorated with fluorescent dyes were fabricated by evaporation-driven self-assembly using emulsion droplets as confining geometries. Silica microspheres were synthesized by Stober method followed by the modification with dye molecules through additional surface sol-gel reaction for the formation of thin silica shell. The surface of the resultant dye-doped silica microspheres was modified with hydrophobic silane coupling agent to disperse the particle suspension in organic solvent such as hexane. The fluorescent silica microspheres were self-assembled inside oil-in-water emulsions by evaporation-driven self-assembly for the formation of colloidal clusters, potentially applicable for photonic molecules. The clusters with fluorescent emission were observed using confocal microscope.

Keywords: Colloidal clusters, Fluorescent dyes, Photonic molecules, Particle self-assembly

1. Introduction

Over the past decades, growing attentions have been paid to the synthesis and applications of particulate sytems such as nanopowders and colloidal dispersions [1-4]. Among the various applications of such systems, monosized colloidal particles as building block materials for collidal crystals or colloidal clusters have been studied intensively in the field of colloidal science and nanochemistry, since the colloidal particles with uniform diameter and shape can be self-organized into regular ordered structures with two or three dimensional architectures [5, 6].

Colloidal clusters or molecules can be defined as the aggregates of colloidal particles which possess specific geometric structures with small constituent number of particles from $N = 2$ to 15. After recent development on the synthesis methods, colloidal clusters have been recognized as model systems for the researches of optimal packing of building block particles [7]. For instance, the dense packing of monodisperse polystyrene microspheres has been studied and two or three dimensional colloidal clusters with various polyhedral structures have been obtained by assembling colloidal particles inside oil-in-water emulsions [7, 8]. The research areas related with densely packed structures of colloidal particles are versatile, including scientific studies on nucleation and growth of atoms, optimization of interparticle potentials between spheres, and novel complex building blocks of colloidal photonic crystals [9-11].

Recently, some industrially important applications of colloidal clusters are suggested, and the most conventional application of colloidal clusters is additives of latex paint to maintain high viscosity of the product. Compared to usual latex paints with spherical colloidal particles, lobed polymeric particles can increase the viscosity of suspension with the same volume fraction of spherical particles according to Einstein's equation on viscosity of suspension [12]. Another application of colloidal clusters is antireflective coating motivated by moth eye structures. Dimer particles with snowman shape have been coated on glass substrate with the aid of contact printing method to increase the transmitance of the coating film [13-15]. The third application of colloidal clusters is building block particles of colloidal crystal [16]. Once dimer particles are assembled into face centered cubic (fcc) structure and the longitudinal direction of dimers is aligned with (111) of fcc lattice, diamond lattice of single spheres can be obtained. It is known that colloidal crystals with this kind of structure show complete photonic band gap regardless of the direction of incident electromagnetic waves. This omnidirectional photonic band gap has not been achieved from colloidal self-assembly yet, and the use of dimer particle for diamond lattice remains just potential application in the present time.

Another possible application of colloidal clusters is photonic molecules. Several research groups have tried to observe whispering gallery mode of photonic molecules, which have been fabricated by optical tweezers [17-20]. When the microspheres of photonic molecules are doped with dyes or semi-

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conducting nanocrystals, fluorescence emission can be enhanced or inhibited on the spherical microcavity (microsphere) due to the boundary conditions of surfaces on the propagation of radiation leading to resonances in the emission called whispering gallery mode [21]. However, most photonic molecules have been fabricated using optical tweezers resulting in the low yield with just laboratory scale. Thus, it is important to establish more efficient routes for the synthesis of photonic molecules in controlled manner. Novel approaches using self-assembly may lead to convenient way for photonic molecules since such methods do not need time-consuming artificial assembly of doped microspheres. The purpose of this study is finding the way to prepare photonic molecules with efficient manner using colloidal self-assembly, which enables to obtain sufficient amount of samples. The originality of this study can be found from this point, although other approaches have been tried to prepare photonic molecules with relatively inconvenient way.

In this study, colloidal clusters decorated with dye molecules were prepared for the potential application of photonic molecules. Commercial or synthesized monodisperse silica microspheres were modified with dye molecules, and silica outer layer was formed additionally to protect the dyes from the surrounding solvents. These dye-doped particles were modified with hydrophobic silane coupling agent to disperse the particulate system in organic medium such as hexane. Then, hexane-in-water emulsions containing the fluorescent particles were obtained, and evaporation-driven self-assembly resulted in the formation of micro-clusters decorated with dye molecules. The resultant clusters were observed using confocal microscope and light emission from the dye-doped clusters was observed by fluorescent spectrum measurement.

2. Experimental

2.1. Materials

The suspension of monodisperse silica microspheres with 3 μm in diameter was purchased from Bangs Laboratory co. ltd. Dye molecules such as tetramethylrhodamine isothiocyanate (TRITC) or fluorescein isothiocyanate (FITC) and silane coupling agent such as OTMOS (octadecyltrimethoxysilane, 90 %) and APS ((3-aminopropyl)trimethoxysilane, 97%) were bought from Aldrich. TEOS (tetraethylorthosilicate, 99%) and ammonium hydroxide (28 – 30%) for the formation of silica shell were purchased from Aldrich and Junsei, respectively. Pluronic P104 (Sigma-Aldrich) was used as emulsion stabilizer for the formation of hexane-in-water emulsion droplets containing the dye-doped silica microspheres.

2.2. Synthesis of Fluorescent Silica Microspheres

The aqueous silica suspension with 3 μm in diameter was redispersed inside ethanol by repetitive centrifuge and washing procedure. Uniform dispersion of silica particles was prepared by sonication for enough time. Then, 25-ml silica suspension was mixed with 2.15-ml aqueous NH_4OH solution (29%), followed by the addition of 0.066-mg TRITC, 0.004-ml APS, and 0.187-ml TEOS under vigorous stirring for 6 hours. The addition of APS and TEOS can be explained for the improvement of dye stability and hetero-nucleation of coating layer on the silica seed particles, respectively.

Although covalent binding of TRITC on the surface of the silica suspension can be induced by the above reaction, 0.2-ml TEOS was added for the formation of thin silica shell to prevent the dye molecules from desorbing into the dispersion medium. After the reaction with additional TEOS for 2 hours, the resulting particles were washed by centrifugation and washing procedure.

For the synthesis of silica nanospheres with 870 nm in diameter, seeded growth method was adopted to prepare monodisperse particle suspension. The detailed synthesis procedures are as follows: 0.5-ml TEOS diluted with 2 ml-ethanol was mixed with 100-ml ethanol and 20-ml NH_4OH solution under vigorous stirring for 2 hours for the synthesis of silica particles. Further growth of silica for the size enlargement was performed by the addition of 8-ml TEOS diluted with 32-ml ethanol, and the reaction was continued for additional 2 hours.

The surface of the silica nanospheres were decorated with green dye molecule, FITC through the similar approach with the case of silica microspheres with 3 μm in diameter coated with TRITC except using FITC as dye molecules instead of TRITC.

Since the surface of the dye-doped silica microspheres is hydrophilic, the surface modification was performed using OTMOS to prepare organic suspension of the silica particles. The reaction of the particles with hydrophobic molecules such as OTMOS was performed under vigorous stirring for 2 hours and the resultant hydrophobic silica powders were collected by centrifugation, followed by the redispersion in hexane.

2.3. Fabrication of colloidal clusters of fluorescent silica particles by self-assembly.

Hexane-in-water emulsions containing dye-doped silica microspheres were prepared by mechanical homogenization of hexane suspension of the particles and aqueous solution of Pluronic P104 (1 wt. %) using homogenizer. The resultant complex fluid system was heated at 70°C for the evaporation of the hexane droplets, and the shrinkage of the droplets resulted in the formation of colloidal clusters of fluorescent silica particles.

2.4. Instruments for Characterization

The oil-in-water emulsions encapsulating silica microspheres were prepared using homogenizer (DIAX900, Heidolph) and observed by optical microscope (Nikon, TE 2000). The morphology of the silica clusters was also observed using scanning electron microscope (FE-SEM, XL305FEG, Philips).

3. Result

In this study, fluorescent silica microspheres were synthesized by attaching the dye molecules such as TRITC or FITC on the surface of the silica particles, followed by the additional formation of thin silica shell, as summarized in the work flow chart in Fig. 1. Since silica particles are nonfluorescent, the attachment of dye molecules is necessary step

for the formation of light-emitting microspheres by surface modification procedures.

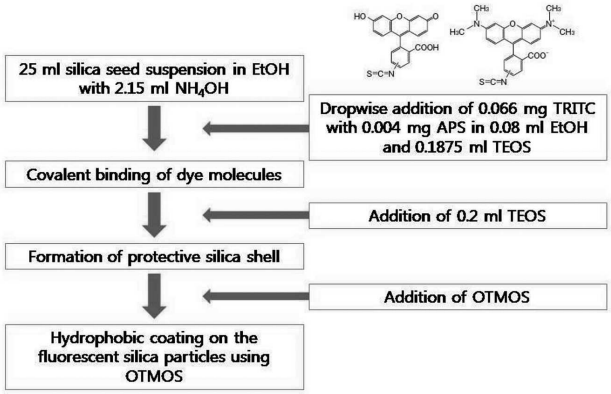

Fig. 1. Synthesis procedure of dye-doped silica microspheres

The structure of the silica particles with dye molecules on their surface and outer silica shell is represented as schematic figure in Fig. 2. The original silica microspheres are modified using dye molecules and the outer silica shell is formed additionally to protect the dye components from dispersion such as alcohol or other organic solvents. Finally, surface modification using proper silane coupling agent such as OTMOS can lead to the formation of hydrophobic fluorescent silica microspheres, which can be dispersed in oil medium such as hexane due to the hydrophobic nature of alkyl group in OTMOS molecule. The alkyl groups are represented as hairy lines on the surface of the particles in the schematic diagram of Fig. 2.

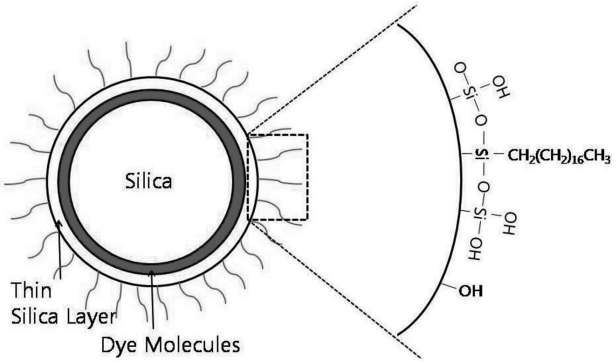

Fig. 2. Schematic figure of silica particle with surface dye molecules and outer silica shell with hydrophobic surface molecules

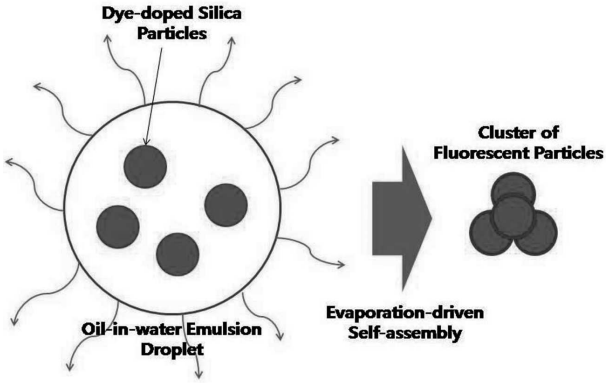

Fig. 3. Schematic figure for the formation of colloidal clusters of dye-doped silica microspheres by evaporation-driven self-assembly

Fig. 3 contains the evaporation-driven self-assembly process of the fluorescent silica microspheres schematically. Since the fluorescent silica particles are hydrophobic, the suspension of the particles can be prepared in hexane medium and the suspension can be emulsified in aqueous dispersion containing suitable emulsifier such as Pluronic P104. The resultant complex fluid system can be heated for the removal of hexane droplets, resulting in the self-organization of the fluorescent silica microspheres by the capillary force due to the shrinkage of the emulsion droplets containing the silica particles. Thus, silica micro-clusters with fluorescent properties can be synthesized by evaporation-driven self-assembly process.

Fig. 4(a) and 4(b) contain the SEM image of monodisperse silica nanospheres with 870 nm in diameter and the confocal microscope image of the silica particles doped with green dye molecule such as FITC fabricated by the procedures shown in Fig. 1, respectively. The confocal image indicates the surface modification of the particles was successfully performed since the light emission from the particle surface can be observed clearly.

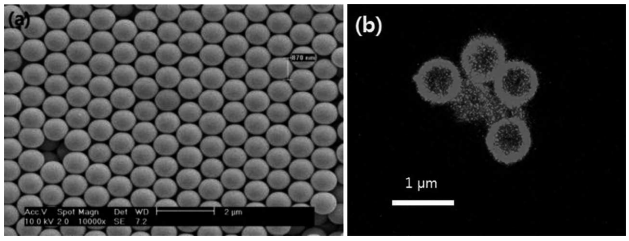

Fig. 4. (a) SEM image of silica nanospheres with 870 nm in diameter synthesized by seeded growth method. Scale bar indicates 2 μm. (b) Confocal microscope image of silica particles modified with FITC dyes. Scale bar indicates 1 μm

Fig. 5(a) and 5(b) shows the optical microscope images of the fluorescent silica microspheres with 3 μm in diameter, which are encapsulated inside hexane emulsion droplets. The particles are trapped inside the droplets, located near the fluid/fluid interfaces of the complex fluid and the escape of the particles into continuous phase was not observed. The number of the silica particles per an emulsion was varied for every droplet, implying the containment of the particles can be interpreted as purely stochastic process [22]. The polydisperse nature of the size of emulsion droplets also contributes to the non-uniform distribution of the particle number in the emulsion system, causing the generation of polydisperse clusters after the evaporation of hexane droplets.

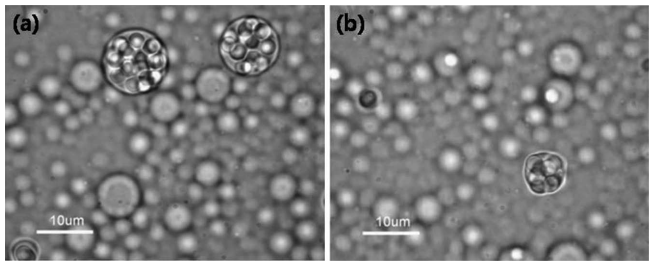

Fig. 5. (a) and (b) Optical microscope images of the dye-doped silica microspheres with 3 μm in diameter encapsulated inside hexane-in-water emulsion droplets. Scale bars indicate 10 μm

Fig. 6 contains the optical microscope images of the clusters composed of the fluorescent silica microspheres with 3 μm in diameter, fabricated by the removal of the hexane droplets by heating, which causes the size reduction of the emulsion droplets and increase of the capillary force to induce the close packing of the microspheres. The polydisperse nature of the clusters was also confirmed by observing the samples using scanning electron microscope, as contained in the microstructures of the clusters in the SEM images of Fig. 7.

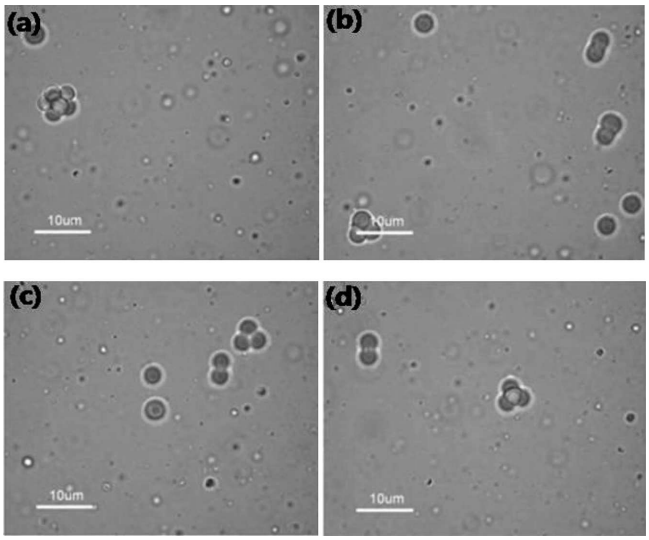

Fig. 6. (a) to (d) Optical microscope images of the colloidal clusters of the dye-doped silica microspheres with 3 μm in diameter. Scale bars indicate 10 μm

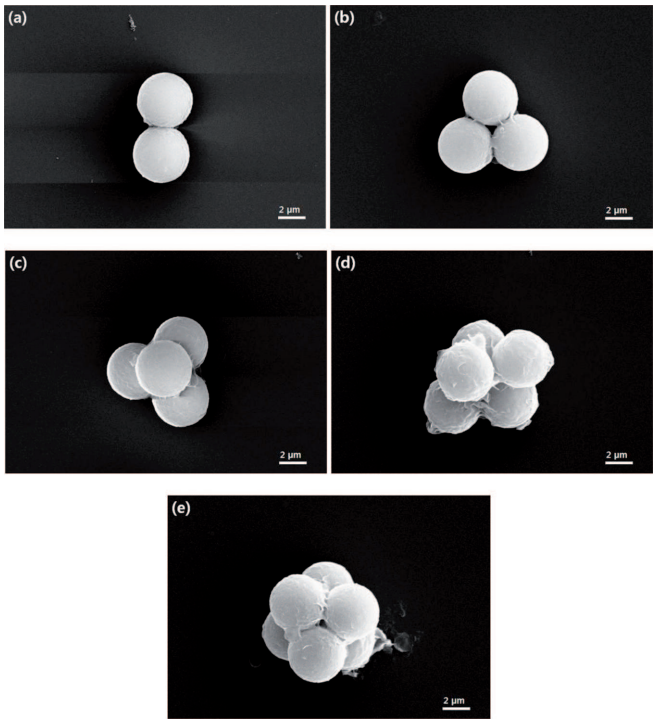

Fig. 7. (a) to (d) SEM images of silica micro-clusters (N = 2 to 6) generated from fluorescent silica microspheres with 3 μm in diameter. Scale bars indicate 2 μm

Fig. 7 contains the SEM images of colloidal micro-clusters made of the fluorescent silica microspheres with 3 μm in diameter. For these SEM images, the constituent number (N) of silica microshperes ranges from N = 2 to 6, corresponding to their unique polyhedral shapes. These cluster structures can be classified as the ones minimizing the second moment (M) of the microspheres:

$$M = \sum_{i=1}^{n} \|r_i - r_0\|^2 \tag{1}$$

where, r_i and r_o represents the central position of each microsphere and center of mass of the particulate system, respectively. It can be observed that the surface of the micro-clusters do not look clean and seem to be covered with some impurities, possibly due to the surface modification with dye molecules and outer silica shell shown in the steps in Fig. 1.

The fluorescent emission from the silica micro-clusters due to the presence of TRITC dyes on the cluster surface was observed using confocal microscope, as displayed in the confocal microscope images in Fig. 8. The presence of the dye molecules on the cluster surface could be recognized by observing the samples under confocal microscope, and the emission of light made the complex micro-clusters with colored morphologies as displayed in the images shown in Fig. 8. Since the emission strength of dye molecules can be decreased due to the interaction with solvent molecules, the additional protective shell was induced after covalent conjugation of dye molecules on the silica microspheres. Thus, we could observe the clear morphologies on the silica micro-clusters with stable attachment of dyes.

Since the clusters with various structures are mixed in one batch after the evaporation of emulsions, it is necessary to fractionate the clusters with identical number of constituent silica particles. In this study, we applied density gradient centrifugation technique for the purification of dimers and trimers composed of silica nanospheres modified with FITC dyes. For fractionation of the silica clusters, gentle centrifugation has been performed using 24 – 85 wt. % linear density gradient of glycerol, at 500 g for 15 minutes.

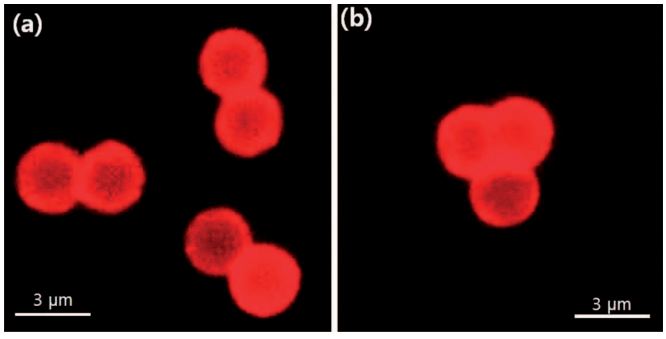

Fig. 8. (a) and (b) Confocal microscope images of silica micro-clusters generated from fluorescent silica microspheres with 3 μm in diameter. Scale bars indicate 3 μm

Fig. 9(a) and 9(b) contain the confocal microscope images of silica dimers and trimers modified with FITC dyes, respectively. The clusters composed of silica nanospheres having 870 nm in diameter can be observed with green light emission due to the presence of dye molecules on the particle surface. Fig. 9(c) shows the fluorescent spectrum of the resultant clusters for N = 2 and N = 3, indicating that the fluorescent

emission is derived from the FITC dyes on the cluster surface. Thus, it is possible to fabricate the assembled structures of dye-doped microspheres using self-organization strategy, and the fabrication of the samples will be more convenient than artificial routes using optical tweezers. The schemes in this article can be applied to study photonic molecules with sufficient amount of sample quantity.

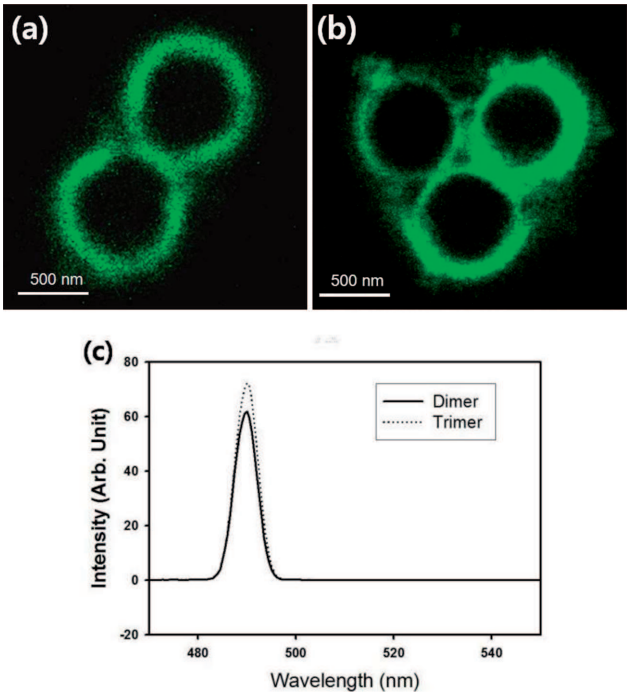

Fig. 9. (a) to (b) the confocal microscope image of silica dimers and trimers with 870-nm silica nanospheres modified with FITC molecules. (c) Fluorescence spectrum of colloidal clusters such as dimers and trimers isolated by density gradient centrifugation. The clusters were prepared using silica nanospheres decorated with FITC molecules. Scale bars indicate 500 nm

4. Summary

In this article, the fabrication method of colloidal clusters with dye molecules is presented by binding TRITC or FITC molecules covalently on the surface of the constituent silica particles, and the resultant fluorescent silica particles were self-organized inside oil-in-water emulsion droplets. After evaporation-driven self-assembly, the colloidal clusters doped with dye molecules were fabricated and identical clusters could be separated by density gradient centrifugation. The resultant clusters could be observed under confocal microscope and fluorescent spectroscopy for the potential application of photonic molecules.

Received: 20 November 2014.

Acknowledgements

This research was supported by a grant (14CTAP-C078865-01) from Infrastructure and Transportation Technology Promotion Research Program funded by Ministry of Land, Infrastructure and Transport (MOLIT) of Korea Government and Korea Agency for Infrastructure Technology Advancement (KAIA).

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