



## Fabrication of composite particles by attaching surface-modified nanoparticles to core particles by wet processing in organic solvents



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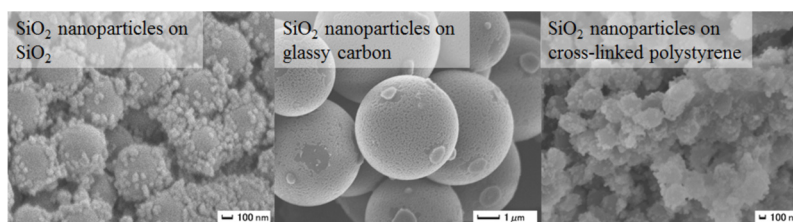
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### HIGHLIGHTS

- PEI and surfactant modified SiO<sub>2</sub> nanoparticles attached on core particles in toluene.
- The prepared SiO<sub>2</sub>/SiO<sub>2</sub> composite particles possessed improved stability in toluene.
- Long-range adhesive force was important for effective adsorption of nanoparticles.
- Compositing process can be applied to glassy carbon and polystyrene spheres.

### GRAPHICAL ABSTRACT

A simple wet processing route to form composite particles via the adsorption of highly dispersible nanoparticles onto the core particles in organic solvents has developed.



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### ABSTRACT

A simple wet processing route for the formation of composite particles via the adsorption of highly dispersible nanoparticles onto the core particles in organic solvents, without the formation of strong aggregates, was developed. The process involved a simple mixing procedure using core particles and surface-modified highly dispersible nanoparticles (shell nanoparticles) in organic solvents, assisted by ultrasonication. As a model study, submicron-sized (ca. 400 nm) and nano-sized (ca. 30 nm) SiO<sub>2</sub> particles, prepared by Stöber process, were applied as the core and shell materials, respectively. The surface of the shell SiO<sub>2</sub> nanoparticles was modified by a layer-by-layer process that involves the adsorption of cationic polyethyleneimine and an anionic surfactant comprising branched alkyl and polyethylene glycol chains for improving the stability in various organic solvents, as well as for controlling the interaction with the core material. The surface modified shell SiO<sub>2</sub> nanoparticles were found to be effectively adsorbed onto the core SiO<sub>2</sub> particles when mixed in toluene, while minimal adsorption was observed in ethanol. The obtained composite particles showed improved stability compared to raw core SiO<sub>2</sub> particles in toluene. The adsorption mechanism of the shell SiO<sub>2</sub> nanoparticles on the core particles in various organic solvents was proposed on the basis of surface-interaction measurements by atomic force microscopy colloidal probe methods. We believe that a long-range adhesive force between the shell SiO<sub>2</sub> nanoparticles and the core particles played an important role in promoting effective adsorption, allowing the formation of composite particles.

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## 1. Introduction

Composite materials comprising different types of fine particulate materials such as ceramic green sheets [1,2], electrodes

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for various battery systems (for example, Li-ion batteries), fuel cell systems, dye sensitized solar cells [3–5], and polymer nanocomposites [6] have become indispensable in industry owing to their uniquely designed electrical, magnetic, mechanical, optical, and chemical properties. While the preparation of these composite devices has been reported and developed by various researchers, a processing protocol to improve the final properties of the composite devices is yet to be designed. To control the properties of composite devices comprising different types of fine particulate materials, a method for controlling the dispersion and alignment states of the fine particles in the composite structure is crucial. For example, for ceramic green sheets with different particle components, a homogeneous dispersion of raw fine particles in the green sheet structure is essential to obtain highly reliable ceramics after the sintering process [7]. In the electrodes used for Li-ion batteries, the particle alignments in the electrode composite used to enhance the transport of Li ions and electrons plays an important role in the overall properties of the battery [8]. In polymer nanocomposite systems, which are designed for high conductivity and transparency, a uniform dispersion of conductive nanoparticles in the polymer device, as well as local alignment of filler nanoparticles, are important for obtaining a highly transparent device with enhanced electrical properties [9].

Among the various processing protocols reported, particle processing in nonaqueous systems is one of the most important choices for battery fabrication and nonoxide ceramic processing, which is required to prevent contamination with water that critically deteriorates the battery properties [10] and to control the overall oxygen content of the raw nonoxide material [11], respectively. Nonaqueous systems are also widely applied in the fabrication of polymer nano-composite materials because of the solubility of polymer-based compounds. Therefore, a processing protocol that can control the dispersion and alignment states of fine particles in nonaqueous systems is essential.

For controlling the dispersion and alignment state of fine particles in composite structures, fabrication of composite particles (such as nanoparticles aligned on core particles) is a potentially powerful technique, because the nanoparticles could form alignments based upon the morphology of the core particles. The layer-by-layer assembly of particles in aqueous systems [12–14], which alternately adsorbs positively and negatively charged particles (i.e., those that were designed by cationic and anionic surface modifiers, respectively), on core particles has been reported by many researchers. The use of mechanical processes that treat high-shear-mixing of a dry mixture of core and shell particles in a narrow gap system [15–17] can also produce composite particles that contain nanoparticles aligned to the core particles. In both the cases, to apply the prepared composite particles in material processing chains using nonaqueous systems, additional tailor-made surface modification of the prepared composite particles is necessary for improving their wettability and their stability in organic solvents and/or polymeric materials.

Herein, we report a simple wet processing route for the fabrication of composite particles, which contain nanoparticles adsorbed onto core particles in organic solvents without the formation of strong aggregates. The process involves a simple mixing procedure using core particles and surface-modified, highly dispersible nanoparticles in organic solvents assisted with ultrasonication. As a model study, submicron-sized (ca. 400 nm) and nano-sized (ca. 30 nm) SiO<sub>2</sub> particles, both prepared by the Stöber process, have been applied as the core and shell materials, respectively. The surface of the shell SiO<sub>2</sub> nanoparticles was modified via a layer-by-layer process involving the adsorption of cationic polyethyleneimine and an anionic surfactant comprising branched alkyl and PEG chains that was previously reported to stabilize nanoparticles in organic solvents with varying polarities [18,19].

The effect of the solvent used during the mixing process on the structure of the prepared composite particles was probed by FE-SEM and TG-DTA analyses, and surface interactions between the core and shell particles during the adsorption procedure were investigated by an atomic force microscopy (AFM) colloidal probe technique.

## 2. Experimental

### 2.1. Materials

Tetraethyl orthosilicate (TEOS, >95%), ethanol (95%), aqueous ammonia (28 wt%), sodium hydroxide (>97%), polyethyleneimine (PEI, average molecular weight 1800), toluene (99.5%), styrene (>99%), and potassium peroxydisulfate (KPS, 99%) were purchased from Wako Pure Chemical Industry Ltd., Japan. Divinylbenzene (*meta* and *para* mixture) was purchased from Tokyo Chemical Industry Co., Ltd. Glassy carbon spheres and quartz plates (ES grade) were purchased from Tokai Carbon Co., Ltd. and TOSOH Quartz Corporation, respectively. Anionic surfactant (**1**), comprising a phosphoric head group and an organic chain that branches into a hydrophilic PEG unit and a hydrophobic alkyl unit, was prepared by a previously reported method (where the chemical structure can also be found) [18]. Styrene was washed thoroughly with a 0.1-M sodium hydroxide aqueous solution to extract the polymerization inhibitor before use. Other materials were used without further purification.

### 2.2. Synthesis of core particles (SiO<sub>2</sub> and cross-linked polystyrene) and shell nanoparticles (SiO<sub>2</sub> modified with PEI and anionic surfactant (**1**))

SiO<sub>2</sub> particles (ca. 400 nm and 30 nm in diameter) were prepared by the Stöber method in a manner similar to the one previously reported [20]. For the synthesis of 400-nm SiO<sub>2</sub> particles, which will be applied as core particles, a mixture of 5.25 g of TEOS in 30 mL of ethanol was rapidly added into a mixed solution of 8.19 g of ammonia solution, 5.92 g of water, and 60 mL of ethanol under stirring, and was kept stirred at 25 °C for 24 h. After stirring, the prepared particles were washed twice with ethanol during a centrifugation and redispersion process, and collected as a powder by drying the cake obtained after the final centrifugation. Throughout the preparation process of core particles and shell nanoparticles, 1–2 min. of ultrasonication (300 W, NIHONSEIKI KAISHA Co., US-300 T, Japan) was applied to redisperse the synthesized particles into the solvent from the cake. To prepare the 30-nm SiO<sub>2</sub> particles, which will be applied as shell nanoparticles, 50 g of TEOS was rapidly added into a mixture of 3.8 g of ammonia solution, 60 g of water, and 590 g of ethanol, and the resulting mixture was stirred for 72 h. The prepared SiO<sub>2</sub> nanoparticles were then modified with PEI and surfactant (**1**) on the basis of our previous report [19]. To a 50-g suspension of as-prepared SiO<sub>2</sub> nanoparticles, 1.1 mL of 20 wt% PEI aqueous suspension was added, and the resulting mixture was stirred for 1.5 h. The SiO<sub>2</sub> nanoparticles, which became weakly flocculated, were collected by centrifugation, rinsed with deionized water, and then redispersed into 200 g of deionized water with sonication. The obtained suspension was treated with 3.2 mL of a 40-wt% aqueous solution of surfactant (**1**). After stirring for an hour, the flocculated SiO<sub>2</sub> nanoparticles were collected by centrifugation, rinsed with water, and dried under vacuum at 80 °C.

Cross-linked polystyrene particles (ca. 400 nm, which will be applied as core particles) were also prepared through a soap-free emulsion polymerization process in a manner similar to the one previously reported [21]. To a four-necked round-bottom flask, 2.1 g of styrene and 90 g of water were added and nitrogen gas

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