



Construction of composite particles with monolayered poly(styrene-co-acrylic acid) spheres on gold surface via heterocoagulation

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ABSTRACT

Composite particles are successfully fabricated in a shape of bead-on-bead through a heterocoagulation. Submicron poly(styrene-co-acrylic acid) (PSAA) spheres are prepared and used as guest materials of composite particles. The spheres adsorb on the gold surface of a host material in perfect monolayered form and the pH dependence of the adsorption degree is also investigated. At strong acidic condition, the spheres are effectively adsorbed on the host materials, while the adsorption efficiency dramatically decreases with increasing pH due to the deprotonation of carboxyl groups at the surface of the spheres. Even though the composite particles are immersed in good solvents of PSAA for 12 h, the particles exhibit excellent adsorption stability.

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1. Introduction

In recent years, composite particles consisted of host and guest materials have drawn much attention due to the interesting properties derived from their hybrid structure [1,2]. Especially, gold-polymer composite particles can play an important role in diverse fields such as optics, electronics, catalysis, and biotechnology [3–5]. Although many efforts have been concentrated on the novel and effective preparation method of the gold-polymer composite particles, few attempts have shown successful results except the use of gold-thiol interactions due to the inert nature of gold [6,7]. Because the materials containing thiol groups can, however, cause significant problems including the corrosion of metal parts when fabricating a device and consequently, alternative methods have been highly demanded.

Heterocoagulation is often observed in many industrial processes as well as in nature, which is defined as the aggregation between particles with different properties [8]. Since functional materials with hybrid structure can be easily prepared through heterocoagulation [9,10], the heterocoagulation has been expected to be a promising route to construct composite particles. In this study, we demonstrate the preparation of the gold-polymer composite particles in the shape of bead-on-bead through a simple heterocoagulation technique. Sub-

micron sized poly(styrene-co-acrylic acid) (PSAA) spheres and microspheres with a gold surface are used as the guest and host materials of composite particles, respectively. The pH effect on the adsorption efficiency of PSAA spheres on the host materials is confirmed and the stability of the composite particles against various solvents is also investigated.

2. Experimental

Microspheres (AUL-704, Sekisui Chemical) were employed as host materials in heterocoagulated composite particles which have an organic core-metallic shell structure. The metallic shell consists of an inner layer with nickel and an outer layer with gold. Crosslinked PSAA spheres were prepared by emulsifier-free emulsion polymerization. The 0.04 wt.% of PSAA spheres dispersed solution in water was used to construct the bead-on-bead composite particles. The pH of the dispersion solution was adjusted by using 0.1 N HCl and 0.1 N NaOH standard solutions. 0.05 g of host materials (microsphere) were mixed with the dispersion solution through sonication for 30 min and then vigorously shaken for 12 h to adsorb PSAA spheres on the host materials. The morphology of PSAA spheres and composite particles were analyzed by a scanning electron microscope. The size distribution and zeta potential of the spheres were determined by a dynamic light scattering spectrophotometer (ELS-8000, Otsuka Electronics) and a laser electrophoresis zeta potential analyzer (Zetasizer 3000HS, Malvern Instruments), respectively. The zeta potential value was taken as the average of five measurements at 25 °C. The amount of PSAA

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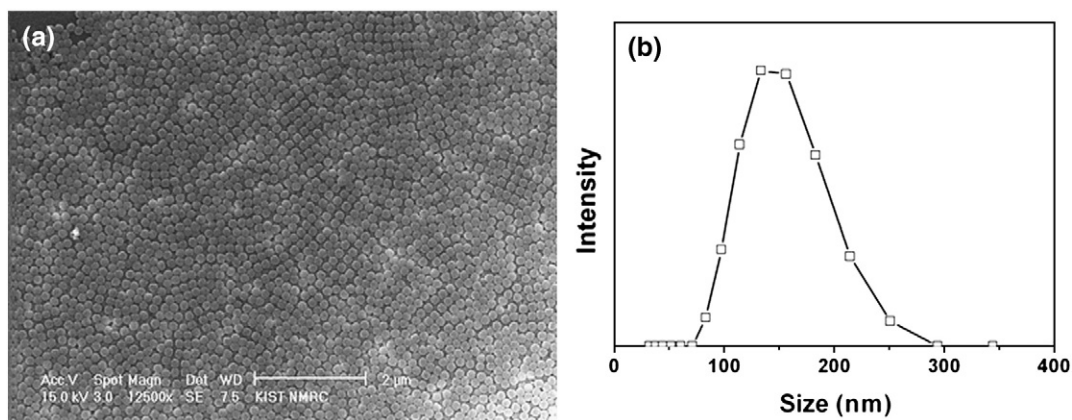


Fig. 1. (a) Morphology of PSAA spheres and (b) their size distribution.

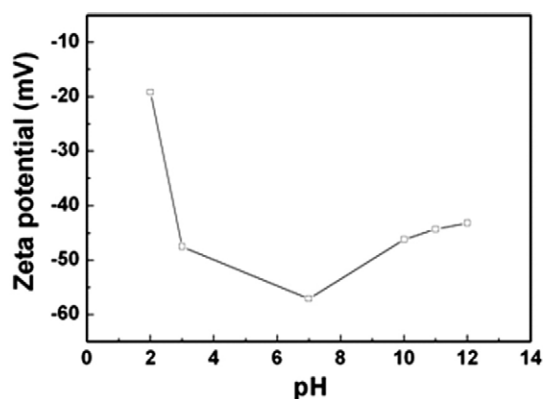


Fig. 2. Zeta potentials of PSAA spheres as a function of pH.

spheres desorbed by solvents was measured by a thermogravimetric analyzer.

3. Results and discussion

In the case of emulsion copolymerization with styrene (St) and acrylic acid (AA), the carboxyl groups are mostly localized at the surface of the spheres due to the hydrophilic nature of AA and thus the colloidal stability of the spheres is largely enhanced [11]. In addition, feeding AA in emulsion copolymerization facilitates the formation of primary particles such as oligomers or oligomer radicals and results in decreasing the size of the spheres [12]. Fig. 1 shows the morphology of prepared polymer spheres and their size distribution; their average size and standard deviation are 148 nm and 36 nm, respectively.

As shown in Fig. 2, PSAA spheres show zeta potential values in the range of -15 to -60 mV as a function of pH. At pH 2, the electrostatic repulsive force of PSAA spheres decreases due to the protonation of carboxyl groups, while the deprotonation of carboxyl groups at pH 7 makes the electrostatic repulsive force rise significantly. The electrostatic stability, however, decreases again when the pH is larger than 10, because

the electrical double layer around the spheres is contracted by excess amount of NaOH [13,14].

PSAA spheres successfully anchor on the gold surface of microspheres in a monolayered form as confirmed in Fig. 3. The stability of the PSAA spheres seems to be enough to prevent irreversible aggregation and to build monolayer on the host materials owing to their polar group of AA even though the electrostatic repulsion is not strong at low pH [13]. Based on this result, it is demonstrated that anionic polystyrene (PS) spheres can be effectively self-assembled on the gold surfaces of host materials via heterocoagulation in the same manner with the previous result that cationic PS spheres with active ester groups were well deposited on the hydrophobic PS surface without opposite charge [10].

Fig. 3 also exhibits that the adsorption degree is highly correlated with pH of medium. In acidic condition, large amount of PSAA spheres is adsorbed on the gold surface of the host materials whereas the spheres are hardly deposited in neutral condition, when the PSAA spheres are stable. As the pH decreases from 7 to 2, the stability of the spheres decreases due to the decrease of the electrostatic repulsive force by protonation of carboxyl groups. Accordingly, it can be considered that the spheres are gradually adsorbed on the microspheres to compensate the stability as the pH decreases. Moreover, when the pH increases over 10, the degree of adsorption is slightly recovered because the stability is decreased due to the shrinkage of electrical double layer.

The adsorption stability of gold-PSAA composite particles was investigated in toluene and ethyl acetate (EA), being well known as good solvents for PSAA. Adsorption stability was observed by immersing composite particles formed in acidic condition. After immersion in each solvent for 12 h, the amount of the desorbed spheres was measured by microscopic and thermogravimetric analysis (TGA). It is difficult to evaluate the amount of the desorbed PSAA spheres through micrographs because the spheres were swelled and distorted by solvents. A significant desorption of the spheres however, was not detected in both images (Fig. 4). TGA enables the accurate quantitative analysis, as shown in Fig. 5. The residual weights are almost equal regardless of the solvents; the residual weights of control, toluene and EA were 67.3, 67.3 and 67.1%, respectively. Therefore, it can be concluded that monolayered adsorption of PSAA spheres on gold surface through heterocoagulation has excellent stability against solvents.

4. Conclusions

We have demonstrated that an inert gold surface can be easily adsorbed with monolayered PSAA spheres via heterocoagulation. The



Fig. 3. Morphology of composite particles at various pHs. Each pH is (a) 2, (b) 7, and (c) 11.

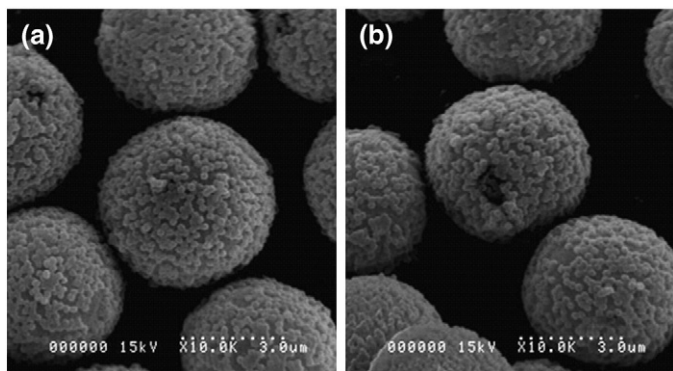


Fig. 4. Morphology of composite particles after immersion in (a) toluene and (b) EA for 12 h.

degree of absorption is highly affected by the pH of medium due to the electrostatic interaction of PSAA spheres. In addition, the composite particles show excellent stability against solvents. Consequently, the heterocoagulation technique controlled by electrostatic interaction can be a promising route to construct composite particles.

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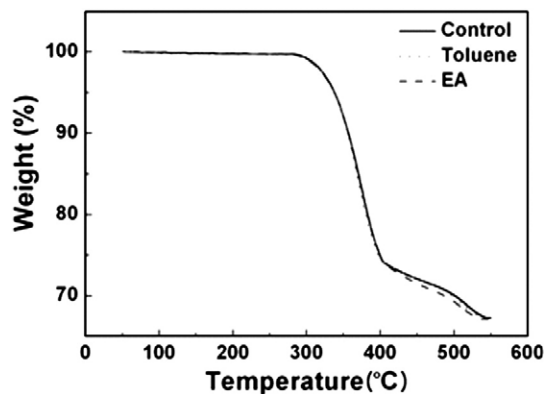


Fig. 5. TGA curves of composite particles after immersion in solvents. Heating rate is 10 °C/min.

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