

Chemical bonding heterocoagulation of nanoparticles onto polymeric spheres by two-step addition of polymerizable coupling agent

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Abstract Raspberry-shaped particles of a polymethylmethacrylate (PMMA) core chemically binding silica nanoparticles (NPs) could be synthesized with heterocoagulation in combination with two-step addition of a polymerizable silane coupling agent of 3-methacryloxypropylmethoxysilane (MPTMS) before and after the heterocoagulation, respectively. Submicron-sized PMMA particles were prepared in soap-free emulsion polymerization in the presence of MPTMS that was introduced into the PMMA particles as a scaffold for the chemical bonding. The PMMA particles were mixed with silica NPs under an acidic condition of pH=2 to cause electrostatic heterocoagulation of the PMMA cores and the silica NPs. Then, MPTMS was added to the acidic suspension, and the suspension pH of heterocoagulated particles was raised to 8 to generate strong chemical bonding between the PMMA and silica NPs in stable particle dispersion. The strong interaction between the PMMA cores and silica NPs was demonstrated in sonication experiments where desorption of silica NPs from the PMMA cores was drastically suppressed by the two-step MPTMS addition.

Keywords Desorption · Heterocoagulation · Nanoparticle · Silane coupling agent · Sonication

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Introduction

Coagulation between different particles, which is called heterocoagulation in colloid science, can provide an effective way to prepare well-designed, functional composite particles, because it is widely applicable to various component particles with different substances and sizes. Raspberry-shaped particles are a typical example of the well-designed particles prepared by the heterocoagulation. They can be defined as particles composed of a single large core particle and a lot of surrounding small particles. In a common heterocoagulation for preparation of raspberry-shaped composite particles, small particles are selectively coagulated onto large particles with specific interactions including electrostatic [1], hydrophobic [2], and hydrogen bonding interactions [3] and chelating [4]. The size ratio of small particles to large ones is important to selectively coagulate the small particles onto the large particles. It was reported that size ratios of $D_{\text{large}}/D_{\text{small}}$ higher than 3 were required for completely covering large silica particles with small polymer particles [5, 6]. Another important factor is the specific interactions between the large and small particles. It was experimentally indicated that weak specific interaction readily caused desorption of small particles from the surface of large particles under physically stressful environments such as centrifugation and sonication [7–10]. In some expected applications of raspberry-shaped particles, including surface coating to hydrophobized [11], catalytic supports [12] and external additives used for toners in printers and photocopiers [13, 14], the desorption of small particles is not allowed to use them in a repetitive way or in a long time scale.

Thus, we here propose a practical method for preparing raspberry-shaped organic-inorganic composite particles firmly fixing inorganic nanoparticles (NPs) on their polymeric surfaces by using a coupling agent to introduce chemical bonds between the NPs and polymeric surfaces. In the present

work, silica NPs were used as model inorganic NPs because silica particles with a narrow size distribution can be synthesized even for sizes less than 100 nm in a simple, modified sol-gel method [15]. Monodisperse polymethylmethacrylate (PMMA) particles were chosen as polymeric supports for the silica NPs. A silane coupling agent of methacryloxypropyltrimethoxy (MPTMS) was employed because of its methacrylic group highly affinitive to PMMA. Electrostatic heterocoagulations between the PMMA particles and the silica NPs with the aid of MPTMS were conducted to form heterocoagulates composed of a single PMMA particles and a lot of silica NPs. The MPTMS molecules added before and after the heterocoagulation were employed as scaffolds to chemically support silica NPs and as anchors for the silica NPs to be chemically fixed on the PMMA particles, respectively. To suspensions of the silica-PMMA heterocoagulates, a combined washing process of centrifugation and redispersion by sonication was applied several times to remove silica NPs that were not absorbed onto the PMMA particles. The amounts of silica NPs firmly fixed on the PMMA particles in iterative washing process were measured by thermal gravimetric analysis (TGA) to find heterocoagulation condition suitable for the silica NPs firmly fixed on the PMMA particles with MPTMS amount as small as possible. The present approach using the double addition of silane coupling agent will be applicable to other oxide NPs such as titania and magnetite NPs, which is allowed to functionalize various polymer particles by the NP decoration.

Materials and methods

Materials Tetraethyl orthosilicate (TEOS, 95 %), methylamine aqueous solution (40 %), ethanol (99.5 %), acetonitrile (99.5 %), methyl methacrylate (MMA, 98.0 %), *p*-styrenesulfonic acid sodium salt (NaSS, 80 %), potassium persulfate (KPS, 95.0 %), hydrochloric acid solution (HCl, 1 M), and sodium hydroxide solution (NaOH, 1 M) were purchased from Wako Pure Chemical Industries (Osaka, Japan). 3-Methacryloxypropyltrimethoxysilane (MPTMS, 95.0 %) was obtained from Shin-Etsu Chemical (Tokyo, Japan). The inhibitor for monomers of MMA was removed by an inhibitor removal column. The other chemicals were used as received.

Preparation of silica particles Silica particles were prepared by hydrolysis and condensation of TEOS at 35 °C with a basic catalysis of methylamine in a mixed solvent of ethanol and acetonitrile (60:40 wt%). The concentrations of TEOS, H₂O, and methylamine were 0.20, 1.0, and 0.05 M, respectively [15].

Preparation of PMMA particles incorporating MPTMS molecules Water was deoxygenated by bubbling with

nitrogen for 30 min and used as a solvent for polymerization. MMA and NaSS were added to the deoxygenated water at 65 °C under stirring. NaSS is an anionic co-monomer to electrostatically stabilized PMMA particles during the polymerization [16]. After 15-min stirring, a solution of KPS was added to the mixture to initiate polymerization. MPTMS was added to the reactant mixture 40 min after the initiation of polymerization. The addition timing was adopted to enhance the MPTMS surface composition of resultant PMMA particles (see Figure S1 in Electronic Supplementary Material). The polymerization was performed with KPS initiator at 65 °C for 2 h under nitrogen atmosphere. The concentrations of MMA, NaSS, KPS, and MPTMS were 0.50 M, 0.5 mM, 5 mM, and 10 mM, respectively. All the concentrations are based on the volume of aqueous phase.

Electrostatic heterocoagulation A suspension of silica NPs was mixed with a suspension of PMMA particles with or without incorporation of MPTMS, and the mixed solution was heated up to 35 °C under stirring. Table 1 shows agent concentrations to prepare heterocoagulates of the silica NPs and PMMA particles. The pH value of the mixed suspension was lowered to pH 2 by HCl addition at 10 mM. Two hours later, MPTMS was added at the concentrations in Table 1. In run A1-4, the suspension was stirred for 12 h without any agent addition. In run B1-4, the MPTMS addition was followed by NaOH addition (9.3 mM) that raised pH to 8 to promote condensation between MPTMS and silica NPs. The slightly basic suspensions were stirred at the pH of 8 for 6 h.

Characterization The particles obtained before and after the heterocoagulation were observed with scanning transmission electron microscopy (STEM, Hitachi, HD-2700B). Zeta potentials of particles were measured with electrophoresis light scattering (ELS, Otsuka Electronics, ELS-Z). The Smoluchowski equation was used to convert electrophoretic mobilities into the zeta potentials. Colloidal stabilities of the particles were measured with dynamic light scattering (DLS,

Table 1 Concentrations of MPTMS and NaOH to prepare heterocoagulates of silica nanoparticles and PMMA particles

Run	MPTMS (mM)	NaOH (mM)
A-1	0	0
A-2	5.4	0
A-3	10.7	0
A-4	16.1	0
B-1	0	9.3
B-2	5.4	9.3
B-3	10.7	9.3
B-4	16.1	9.3

Before the MPTMS addition, pH was lowered to 2 by the addition of HCl at 10 mM in all runs

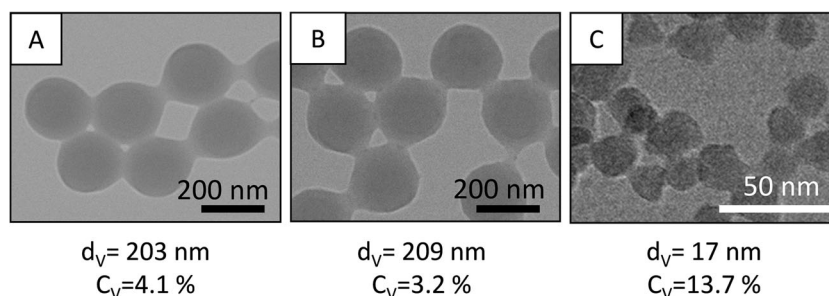


Fig. 1 TEM images of PMMA particles (a), MPTMS-PMMA particles (b), and silica nanoparticles (c) used in heterocoagulations. The PMMA and MPTMS-PMMA particles were prepared by MMA polymerization

with (a) and without (b) the addition of MPTMS 40 min after the initiation. The MPTMS concentration in the preparation (b) was 10 mM

Otsuka Electronics, ELS-Z). The number of silica NPs supported by polymer particles (N) was measured with thermogravimetric analysis (TG/DTA7200, Seiko Instruments). The surface coverage of silica NPs (θ %) was calculated by the following equations:

$$\theta \text{ [%]} = \frac{N}{N_{\max}} \times 100$$

$$N_{\max} = \frac{2\pi}{\sqrt{3}} \left(\frac{d_{\text{PMMA}} + d_{\text{silica}}}{d_{\text{silica}}} \right)^2$$

where d_{PMMA} and d_{silica} are the diameters of PMMA and silica particles, respectively. N_{\max} is the maximum number of NPs on the surface assuming hexagonal close packing [2]. The number of silica NPs added in the heterocoagulation was adjusted to the half of N_{\max} in the present work to obtain the raspberry-shaped particles with amphoteric surfaces of polymer and silica.

Results and discussion

The polymerizable silane coupling agent of MPTMS has double roles in the present heterocoagulation. One is a scaffold for silica NPs to be chemically bound onto the PMMA particles before the heterocoagulation. The other is an anchor to chemically bind the silica NPs to the PMMA particles after the heterocoagulation. TEM images of PMMA particles used in the heterocoagulation are shown in Fig. 1. Particles in Fig. 1a were prepared in the soap-free emulsion polymerization in the absence of MPTMS scaffold. They had an average size of 203 nm and a C_V value of 4.1 %. Particles in Fig. 1b were prepared with the addition of MPTMS to the polymerization system at a reaction time of 40 min. The incorporation of MPTMS molecules into PMMA particles was confirmed by XPS measurement in which a Si 2p peak attributed to tetravalent Si was observed at 102.5 eV (again see Figure S1 in Supporting Information). The PMMA particles were hereafter abbreviated as MPTMS-PMMA particles. The particles

shown in Fig. 1a, b had similar average sizes and low C_V values. Figure 1c shows silica NPs that had an average size of 17 nm. The size ratio of the MPTMS particles to the silica NPs was in a desirable range for particle heterocoagulation.

Zeta potentials of the three particles presented in Fig. 1 were measured to examine pH values suitable for the heterocoagulation. The potentials plotted at different pH values are shown in Fig. 2. Both the polymer particles had no isoelectric points and exhibited negative charges in the pH range of 2–7.5, which was caused by the anionic initiator of KPS used in their syntheses. On the other hand, the silica NPs had an isoelectric point between pH 2 and 3 and was found to be slightly cationized at pH 2.

According to the potential profiles in Fig. 2, heterocoagulation experiments were conducted at pH 2 using both the PMMA and MPTMS-PMMA particles with the silica NPs. The resultant particles obtained with the heterocoagulations were shown in the SEM images of Fig. 3. In Fig. 3a, the silica NPs were inhomogeneously distributed on the PMMA particles and tended to be accumulated between the PMMA particles. In addition, a lot of the silica NPs free from the PMMA particles were observed on the SEM grid. The observations suggested that the silica NPs

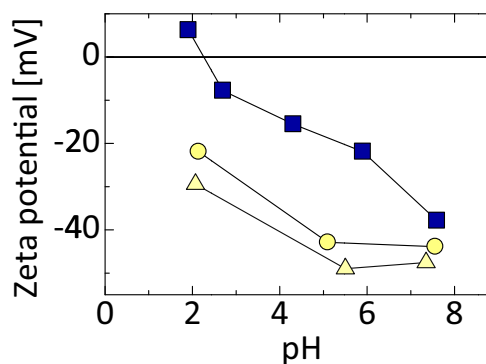
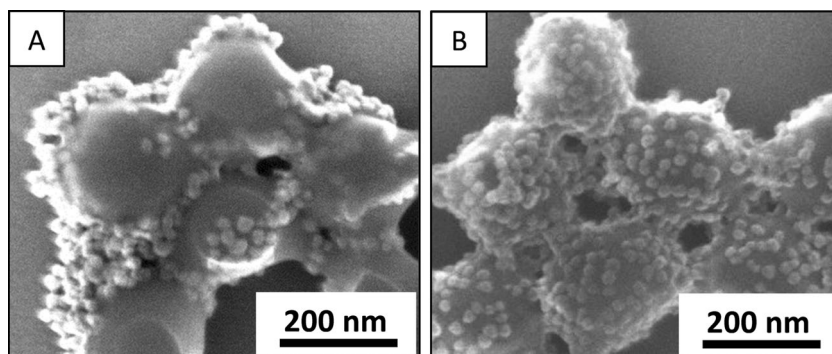


Fig. 2 Zeta potentials of particles shown in Fig. 1. PMMA particles, MPTMS-PMMA particles, and silica nanoparticles are indicated with circles, triangles, and squares, respectively. The pH values in the measurement of zeta potentials were varied in the range of 2–7.5 by hydrochloric acid

Fig. 3 SEM images of particles formed by the heterocoagulation at pH=2 using PMMA particles (a) or MPTMS-PMMA particles (b)



were weakly fixed on the PMMA particles mainly due to physical interactions. On the other hand, the silica NPs in Fig. 3b were distributed more homogeneously on the MPTMS-PMMA particles, and almost no free silica NPs were observed on the SEM grid.

For suspension of the heterocoagulates prepared in Fig. 3b, a combined washing process of centrifugation and redispersion with ultrasonication was performed three times to examine the amount of silica NPs supported onto the MPTMS-PMMA particles with thermogravimetric analysis (TGA). A SEM image of particles obtained in the washing processes is shown in Fig. 4a. Most silica NPs shown in Fig. 3b were, however, desorbed from the MPTMS-PMMA particles. The desorption of silica NPs was probably caused by shear stress in the iterative washing processes, especially in the ultrasonication (see Figure S2). Strong shear stress induced under ultrasonic irradiation redispersed the silica NPs from the MPTMS-PMMA particles. Weak electrostatic interaction between the MPTMS-PMMA particles and the silica NPs might be responsible for desorption of silica NPs.

To chemically bind the silica NPs onto MPTMS-PMMA particles, MPTMS was added after the heterocoagulation at the same pH of 2. SEM images of particles obtained by the iterative washing processes following the MPTMS addition are shown in Fig. 4b–d where MPTMS was added at different concentrations of 5.4, 10.7, and 16.1 mM, respectively.

According to the SEM images in Fig. 4, the number of silica NPs desorbed seems to be decreased by the MPTMS additions. However, it appeared that aggregates were formed by the MPTMS addition at the high concentration. The colloidal stabilities of the suspensions of Fig. 4a–d were examined in a simple dispersion test where the four suspensions were shaken and left for a short time as presented in Figure S3. The suspension at the MPTMS concentration of 16.7 mM did not reveal stable dispersion but caused rapid sedimentation of the aggregates.

To promote condensation between methoxy (or silanol) groups of MPTMS, the pH of heterocoagulated suspension after the MPTMS additions was raised to pH 8 with addition of NaOH aqueous solution [17] and further reacted for 6 h. Figure 5a–d shows SEM images of heterocoagulates obtained by the iterative washings following the 6-h reaction in the same concentration range of MPTMS. Simple dispersion tests were also conducted with these suspensions. The suspensions of B-3 and B-4 were not stably dispersed but revealed dense aggregations, as shown in Figure S4. An excess amount of MPTMS added probably promoted intermolecular reactions of MPTMS to induce aggregation of the heterocoagulates. Good dispersion stability was observed for B-1 and B-2, the former of which, however, lost most number of silica NPs from the surface after iterative washing in the SEM of Fig. 5a. On the other hand, the coagulated particles in

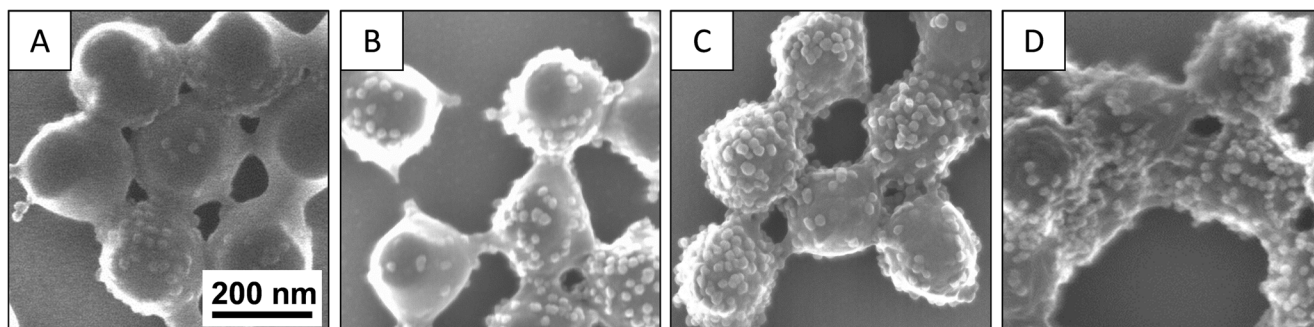


Fig. 4 SEM images of particles obtained in the iterative washing processes for heterocoagulates prepared in the presence and absence of MPTMS at a low pH of 2. The concentrations of MPTMS added were 0

(a), 5.4 (b), 10.7 (c), and 16.1 mM (d), respectively. The reactions of MPTMS added were performed at pH=2 for 12 h

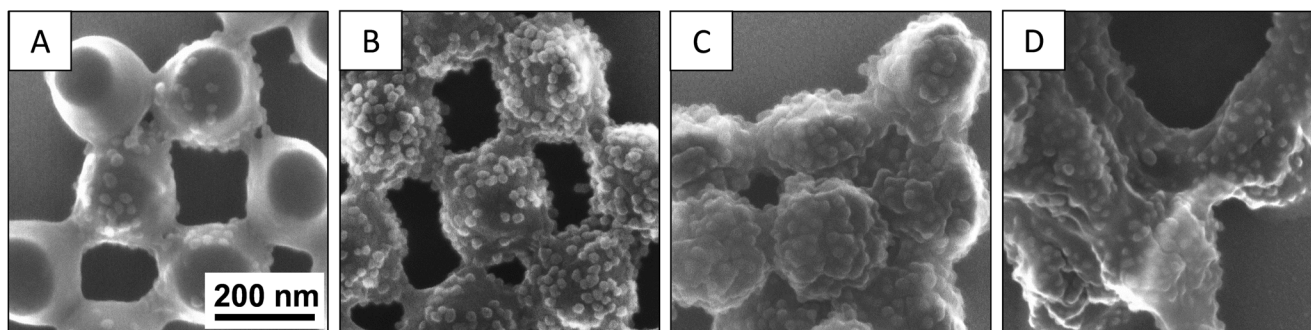


Fig. 5 SEM images of particles obtained in the iterative washing processes for heterocoagulates prepared in the presence and absence of MPTMS at a high pH of 8. The concentrations of MPTMS added were 0

(a), 5.4 (b), 10.7 (c), and 16.1 mM (d), respectively. The MPTMS added to heterocoagulate suspension was reacted at pH=2 for 12 h and further reacted at pH=8 for 6 h

Table 2 The effect of MPTMS post-addition at different pHs and MPTMS concentrations

Run	MPTMS (mM)	pH	Inorganic % before the washings (W_{before}) (wt %)	Inorganic % after the washings (W_{after}) (wt %)	$W_{\text{before}} - W_{\text{after}}$ (wt %)	Surface coverage of silica NPs (θ %)	Fixing percentage (F %)
A-1	0	2	11.5	4.4	7.1	3.2	19.3
A-2	5.4	2	12.1	8.1	4.0	9.0	54.5
B-2	5.4	8	13.6	11.5	2.1	12.6	76.1

Fig. 5b could retain concentrated number of the silica NPs homogeneously distributed over the surface of PMMA particles. Homogeneity of the silica NPs distribution in Fig. 5b was better than that of Fig. 4b, c. The dispersion size distribution of Fig. 5b measured by DLS (see Figure S5) had a sharp distribution around 300 nm. The dispersion size distribution had no significant difference from the ones of the other suspensions (Figs. 4a–c and 5a) with high stability of dispersion (see Figures S3 and S4). The dispersion sizes in colloidal range observed by DLS are thought to attain dispersion stability.

To examine the high fixation of NPs at pH=8, an additional experiment in which the same amount of MPTMS was added to heterocoagulate suspensions in a pH range of 2–8 was conducted. SEM images of the heterocoagulates obtained by the iterative washing are shown in Figure S6. The comparison of the SEM images indicates that the slightly basic condition of pH=8 could effectively suppress desorption of NPs whereas the other conditions caused apparent desorption of NPs by the iterative washing process. A high pH in sol-gel reactions generally increases condensation rates of hydrolyzed silicon alkoxides more than hydrolysis rates of silicon alkoxides [17]. The high rate of condensation at pH=8 could contribute to the fixation of NPs on MPTMS-PMMA particles.

The effect of MPTMS addition was quantitatively characterized by TGA in which the weight percentage of inorganic component in the heterocoagulates was measured before and after the iterative washing for runs (A-1), (A-2), and (B-2) (see TGA profiles shown in Figure S7). According to the TGA profiles in Fig. S6, surface coverage of silica NPs (θ %) and fixing percentage (F %) were calculated and are summarized in Table 2. The method for calculation of the fixing

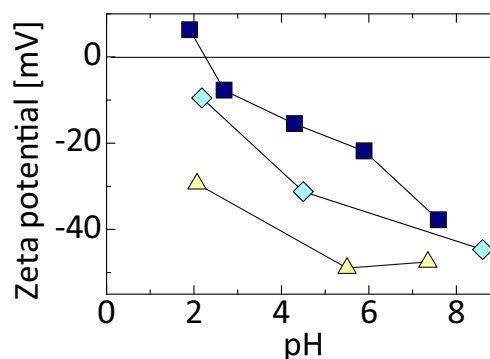


Fig. 6 Zeta potential profiles of heterocoagulates (Fig. 5b, diamonds), MPTMS-PMMA particles (Fig. 1b, triangles), and silica nanoparticles (Fig. 1c, squares)

percentage, which is defined as a criterion to evaluate the effect of the second MPTMS addition on the NP fixing, is described in Figures S8 and S9. The values of θ % and F % presented in Table 2 revealed that an appropriate amount of MPTMS added at pH=8 could fix silica NPs firmly enough to withstand the iterative washing processes. The high fixing percentage of 76.1 % was attained in the treatment of B-2.

Zeta potential of the heterocoagulates in Fig. 5b was measured at different pH values to examine their surface composition. The potential profiles are presented in Fig. 6 where zeta potentials of MPTMS-PMMA particles and silica NPs are also presented. It should be noted that the present zeta potentials of heterocoagulates were between the ones of MPTMS-PMMA particles and silica NPs. The intermediate potentials indicated that the heterocoagulates had both the surface of the silica and the MPTMS-PMMA particles.

Conclusions

Sonication-resistant heterocoagulates composed of inorganic NPs and PMMA particles were successfully prepared in the present work. The polymerizable silane coupling agent of MPTMS was added twice to firmly fix the NPs to PMMA particles. The first role of MPTMS incorporated into PMMA particles was scaffolds to support silica NPs onto PMMA particles in the heterocoagulation. The second one of MPTMS was fixers to chemically bind silica NPs on the polymeric particles. The double roles of MPTMS successfully prepared heterocoagulates firmly supporting silica nanoparticles resistant against ultrasonic irradiation and also provided the heterocoagulates with both surface compositions of polymer and silica.

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