

Electric Supplementary Information

Robust Platforms for Creating Organic-Inorganic Nanocomposite Microspheres: Decorating Polymer Microspheres Containing Mussel-Inspired Adhesion Layers with Inorganic Nanoparticles

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Appendix

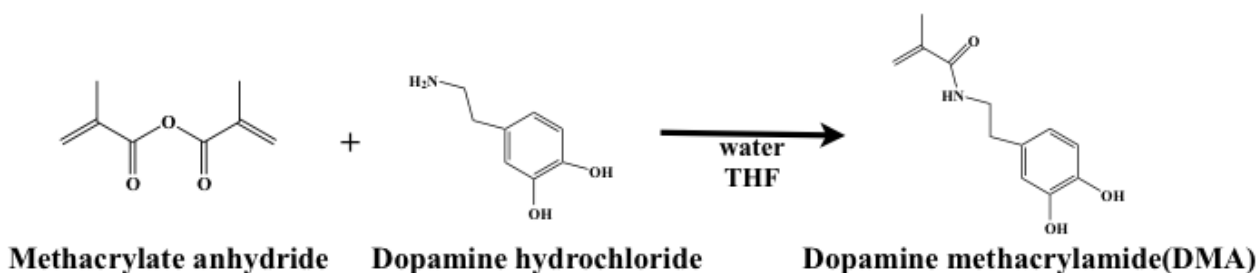
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S-1. Synthesis of mussel-inspired polymers

N-(3,4-dihydroxyphenethyl) methacrylamide (DMA) was prepared from dopamine hydrochloride and methacrylate anhydride, and then the amphiphilic copolymers, which contained the catechol group, were synthesized from DMA and *N*-dodecylacrylamide (DAA) by free-radical polymerization. DAA was synthesized according to the literature (M. Kojima, H. Yabu, M. Shimomura, Polym. J. **2009**, 41(8), 667).

Synthesis of DMA (Scheme S-1)

Dopamine hydrochloride (26.4 mmol) was dissolved in 500 mL of aqueous solution of sodium bicarbonate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 10 g) after 30 min of N_2 bubbling, and then, 25 mL of tetrahydrofuran solution of methacrylate anhydride (31.7 mmol) was added into the aqueous solution with stirring at room temperature and keeping around pH 8 with adding 1M NaOH aq. A solution of sodium bicarbonate and sodium borate was used to protect the dihydroxybenzene moiety. The mixed solution was stirred over night at room temperature, the product was extracted by ethyl acetate. After extraction, the product was recrystallized in ethyl acetate and hexane mixed solution. The crystallized product was corrected by filtration and dried under vacuum. The product DMA was yielded as a light brown powder (78.9%). ^1H 400-MHz NMR (400 MHz, MeOD) δ_{H} 6.71-6.67 (m, 2H, $\text{C}_6\text{H}_2(\text{OH})_2$), 6.56-6.54 (m, 1H, $\text{C}_6\text{H}_2(\text{OH})_2$), 5.65 (s, 1H, $-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CHH}$), 5.35 (s, 1H, $-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CHH}$), 3.42-3.34(m, 2H, $\text{C}_6\text{H}_3(\text{OH})_2-\text{CH}_2-\text{CH}_2(\text{NH})-\text{C}(=\text{O})$), 2.71-2.67(t, 2H, $\text{C}_6\text{H}_3(\text{OH})_2-\text{CH}_2-\text{CH}_2(\text{NH})-$), 1.93(s, 3H, $-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$) ppm.



Scheme S-1. Synthetic route of DMA.

Polymerization of DAA and DMA

Azobisisobutyronitrile (AIBN) was purchased from Aldrich and used after purified by recrystallization in MeOH. The copolymerization ratios of DAA and DMA were shown in Table 1. DAA, DMA, and AIBN were dissolved in mixed solution of benzene and DMSO in a three-necked round-bottle flask equipped with a thermometer, a nitrogen cock and a reflux funnel. The solution containing DMA and DAA monomer and AIBN was degassed three cycles of freeze-evacuate-

thaw, and finally the atmosphere was filled with dry nitrogen. The polymerization was conducted at 72 °C for 5 h. After reaction, the polymer was purified by reprecipitation into a large amount of acetonitrile. The white powder was corrected by centrifugation and dried *in vacuo*. The chemical structures and molecular weights of the synthesized polymers were determined by size exclusion chromatography (HLC-8320GPC, Tosoh, Japan) and ¹H NMR (Bruker 400 MHz, MeOD), respectively. Typical assignments of the chemical shifts are as follows: δ_H 6.71–6.67 (m, 2H, C₆HH₂(OH)₂-), 6.56–6.54 (m, 1H, C₆HH₂(OH)₂-), 5.65 (s, 1H, -C(=O)-C(-CH₃)=CHH), 5.35 (s, 1H, -C(=O)-C(-CH₃)=CHH), 3.42–3.34 (m, 2H, C₆H₃(OH)₂-CH₂-CH₂(NH)-C(=O)), 2.71–2.67 (t, 2H, C₆H₃(OH)₂-CH₂-CH₂(NH)-), 1.93 (s, 3H, -C(=O)-C(-CH₃)=CH₂) ppm.

S-2. Synthesis of positively charged Au NPs

2-Aminoethanethiol hydrochloride (3.2 mg, Wako Pure Chemical Industries) was added to a 2.2 mM aqueous solution of HAuCl₄·4H₂O (40 mL; Wako Pure Chemical Industries). The solution was stirred for 20 min, 10 mM aqueous NaBH₄ (5 μL; Wako Pure Chemical Industries) was added, and then the solution was stirred for 3 h. The solution turned brown shortly after the NaBH₄ was added, and then deep red after 30 min. Transmission electron microscopy (TEM, H-7650, Hitachi, Japan) showed that the mean diameter of the Au-NH₂ NPs was 25 nm.

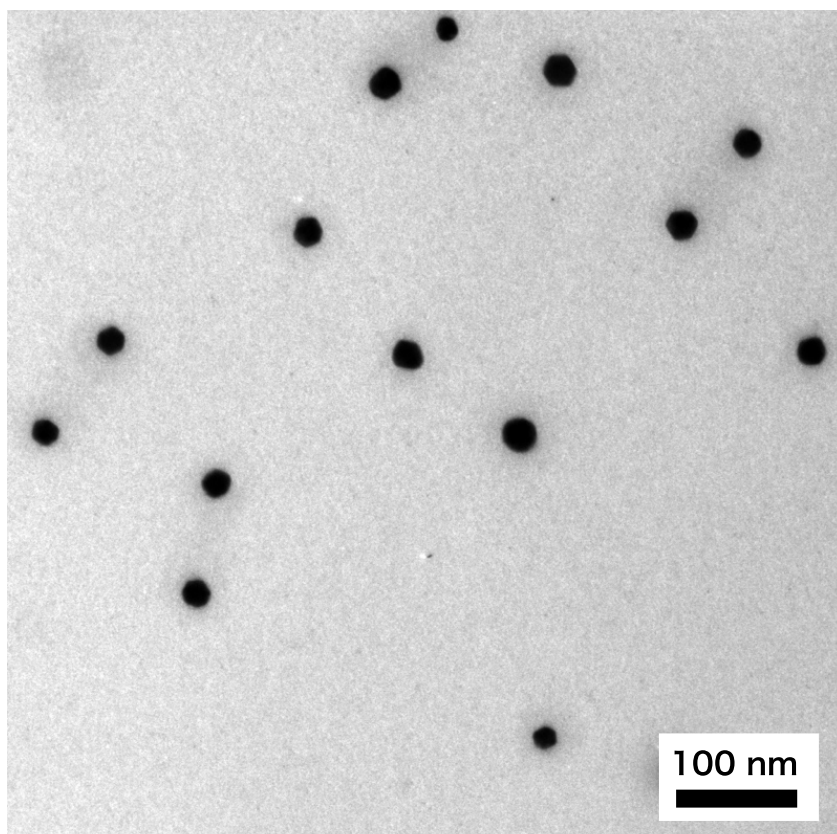


Figure S-1. TEM image of positively charged Au NPs.

S-3 Structural analysis

The surface and interior structures of the polymer particles were observed by scanning electron microscopy (SEM; S-5200, Hitachi, Japan) and transmission electron microscopy (TEM; H-7650, Hitachi), respectively. Sample specimens were prepared by placing a drop of an aqueous dispersion of the polymer on a Si substrate or a Cu grid covered with a carbon membrane, and were then dried at room temperature.

To observe cross-sectional TEM images of core-shell microspheres, thin slices of microspheres embedded in epoxy resin were prepared by using an ultramicrotome (UC-6, Leica, Germany). The structure was observed without staining. The surface and interior structures of the polymer particles were observed by scanning electron microscopy (SEM; S-5200, Hitachi, Japan) and transmission electron microscopy (TEM; H-7650, Hitachi), respectively.

To reveal the surface structure before and after mixing a salt solution into composite microspheres, sample specimens were prepared by placing a drop of an aqueous dispersion of the polymer on a Si substrate or a Cu grid covered with a carbon membrane, and were then dried at room temperature. To observe cross-sectional TEM images of core-shell microspheres, thin slices of microspheres embedded in epoxy resin were prepared by using an ultramicrotome (UC-6, Leica, Germany). The structure was observed without staining.

S-4. Cross-sectional TEM images of MS-1, MS-3, and MS-4

Cross-sectional TEM images of MS-1, MS-3, and MS-4 were observed by using the same procedures of MS-2, which is shown in Figure 2 (b). Interior core-shell structures (PS cores and mussel-inspired copolymer shells) were clearly imaged.

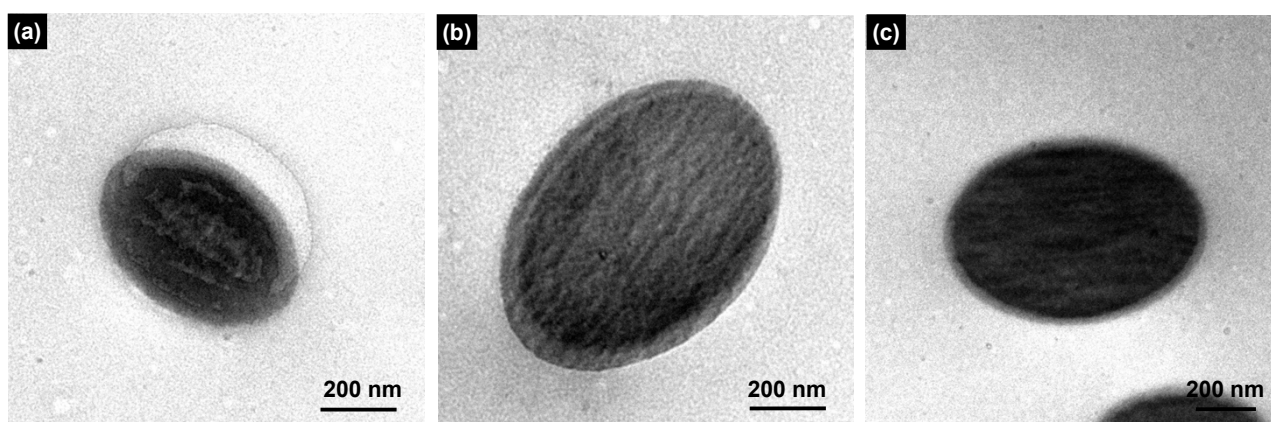


Figure S-2. Cross-sectional TEM images of MS-1 (a), MS-3 (b), and MS-4 (c), respectively.

S-5. Mixing MS-2 with negatively charged Au NPs

To examine the effect of surface charges of IO NPs, 75 μL of aqueous dispersion of positively or negatively charged Au NPs were mixed into 150 μL of aqueous dispersion of MS-2, and then the mixture was incubated for 1 h at 25 $^{\circ}\text{C}$ in a water bath. After incubation, the dispersion was corrected by centrifugation (2,000 rpm, 15 min, 5 $^{\circ}\text{C}$) and supernatant was removed. After addition of membrane filtered water and sonication, a drop of dispersion was placed on a Cu grid with an elastic carbon membrane. Surface structures were observed by SEM after evaporation of water. Figure S-3 (a) and (b) shows MS-2 microspheres after mixing negatively charged Au NPs. Au NPs were aggregated among MS-2 microspheres. This result indicates that there is no specific adhesion of Au NPs onto MS-2 microspheres were obviously observed.

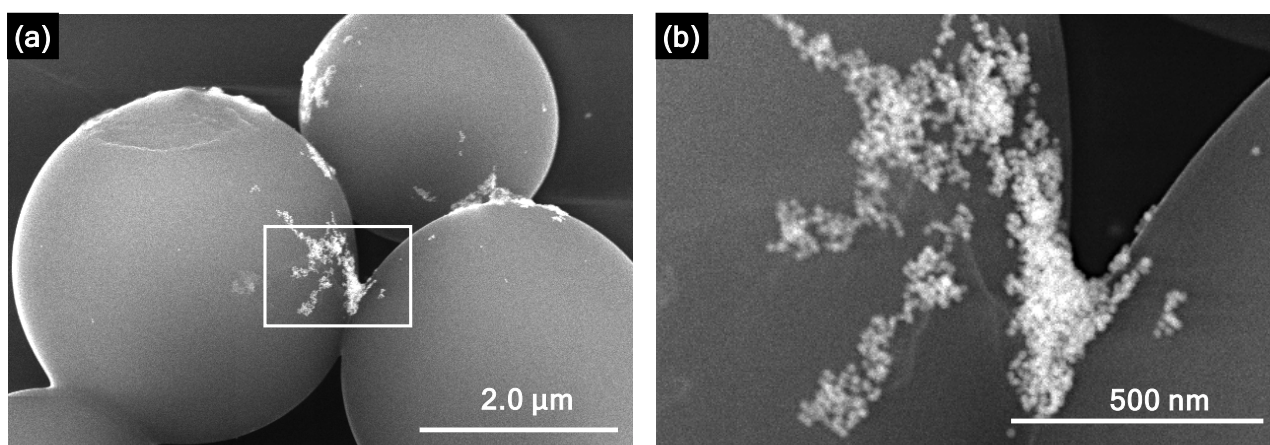


Figure S-3. SEM image (a) and close-up SEM image (b) of MS-2 and negatively charged Au NPs.

S-6. SEM images and UV-Vis spectra of composite particles

Figure S-4 shows absorption spectra of MS-1 (a) and MS-3 (b) before/after addition of KCl. In the case of MS-1, which contains high amount of catechol moieties in the shell part of the core-shell microspheres, there is no obvious color change. Plasmonic absorption of Au NPs was observed at $\lambda=540$ nm in each case. Note that there is no color change observed even though the composite particles aggregated in an aqueous media. From SEM images of MS-1 before/after addition of KCl, composite particles form three-dimensional aggregations in both cases (Figure S-5 (a) and S-5 (b)). These results indicate that Au NPs and core-shell microspheres strongly adhered each other, and Au NPs worked as cross-linkers of core-shell microspheres.

On the other hand, the plasmonic red color of MS-3 turned purple and plasmonic absorption peak at $\lambda=530$ nm clearly red-shifted to $\lambda=550$ nm in the case of MS-3 after addition of KCl. This result

implies that aggregation of Au NPs occurred. SEM images (Figure S-5 (c) and S-5 (d)) reveal that adhered Au NPs were removed from the surface of core-shell microspheres after addition of KCl as same as the PS/PS-OH case (Figure 4 (e) and 4(f)).

From these results and results shown in Figure 4, adhesion force of core-shell microspheres to Au NPs increased with increased content of catechol moieties, which is equal to the copolymerization ratio of DMA.

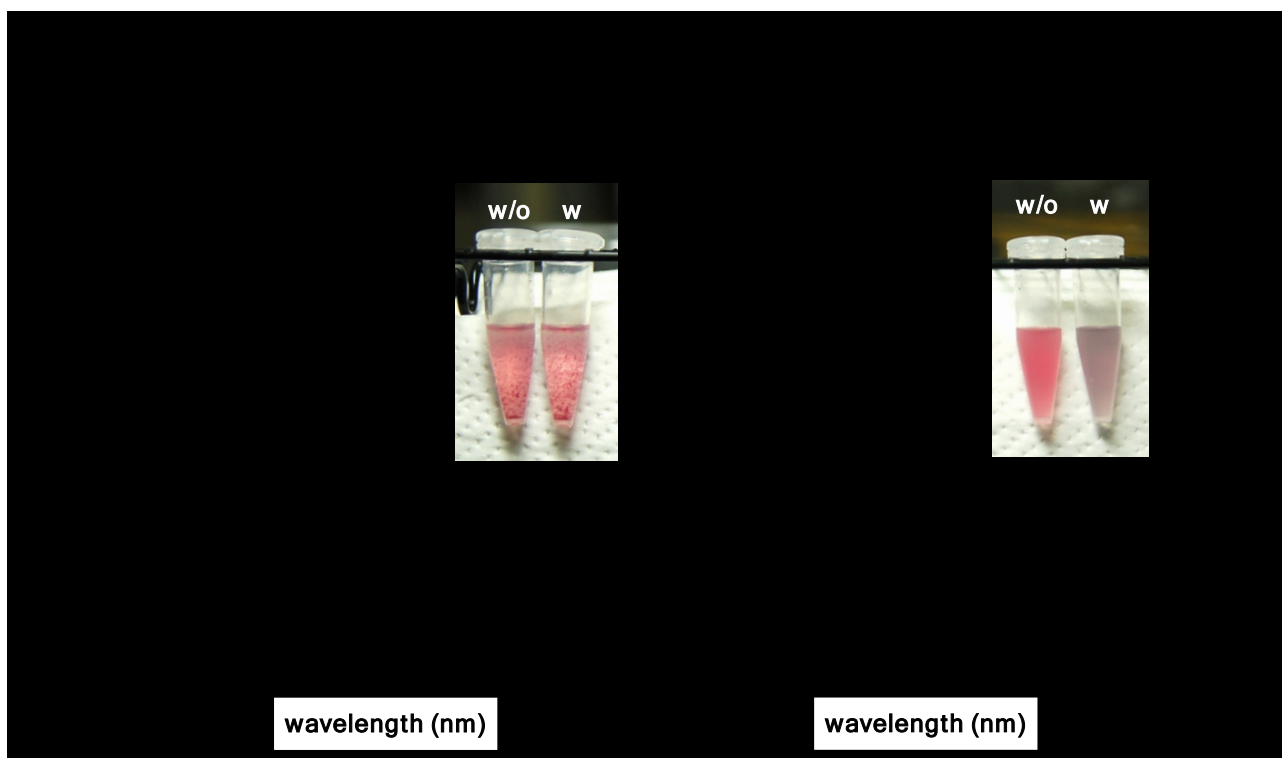


Figure S-4. Absorption spectra of MS-1 (a) and MS-3 (b) before/after addition of KCl. Inset images show photographs of respective samples.

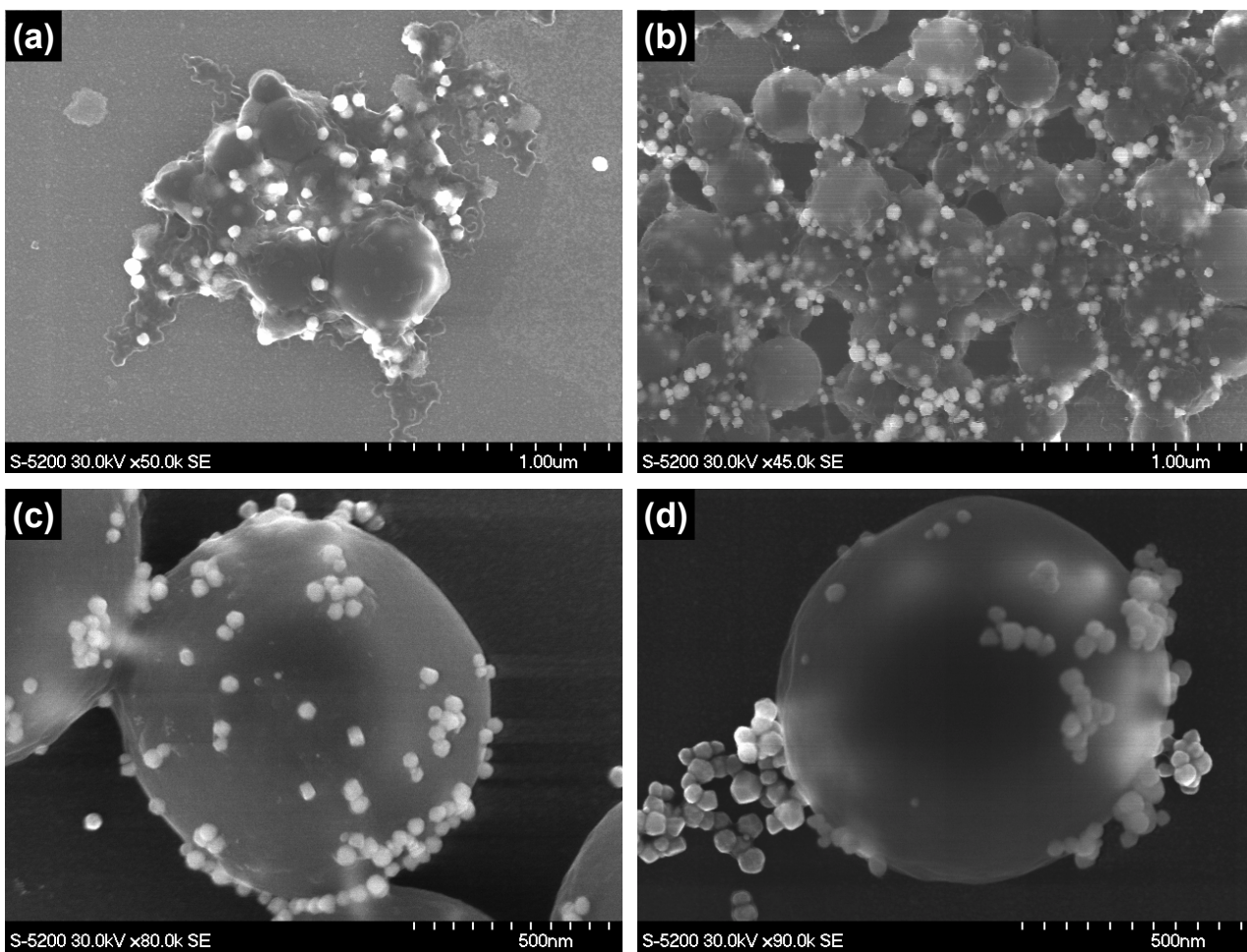


Figure S-5. SEM images of MS-1 before (a) and after (b) mixing of KCl and MS-3 before (c) and after (d) mixing of KCl, respectively.