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Preparation and Electrochemical Characterization of Ferrocenyl-coated Polystyrene Monodispersed Latex Particle

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The mono dispersed redox-active latex particle with 0.90 μm in diameter was prepared by immobilizing ferrocenylmethanol acrylate on a surface of a polystyrene latex core through the emulsion copolymerization reaction. The aqueous suspensions exhibited stable voltammetric waves at 0.271/0.207 V vs Ag|AgCl. The anodic and the cathodic peak currents were diffusion-controlled, as if it were huge redox molecules with 3.8×10^7 electrons.

Redox reactions at large particles such as enzymes,[1] proteins,[2] fullerene,[3] complex cluster,[4] metal nanoparticles,[5] and colloids[6] often show dull electrochemical responses; i.e., broad voltammetric waves, largeover potentials, large irreversibility, and slowly responding current. Possible reasons for exhibiting dull responses are chemical complications via a mediator, geometrical blocking of redox sites, sluggish charge propagation within a particle, complicated transport of a particle by aggregation or adsorption. It is not easy to specify a definite reason, because there are no data that describe relation of electrode behavior with size and geometry of large particles, to our knowledge. In order to obtain a relation between charge transfer and particle size, colloidal particles with simple mass transport have been synthesized, e.g., polyaniline-coated latex,[7] vinylferrocene-coated latex,[8] and ferrocenyl polyallylamine-coated latex,[9] aiming at immobilization of redox sites on latex particles. Unfortunately, the polyaniline-coated latex exhibited voltammetric irreversibility because of slow propagation of the conducting zone.[7] The redox site in the vinylferrocene-coated latex was dissolved readily in redox cycles,[8] because it was adsorbed in the polystyrene mother latex. The ferrocenyl polyallylamine-coated latex was unstable in aqueous solution and hence the application was limited.[9]

We here synthesize the more stable redox-active latex by use of hydrophobic ferrocenyl moiety than the previous water-dissolved ferrocenyl moiety.[9] The charge-transfer reaction at the electrode is discussed voltammetrically.

The polystyrene latex (PS)[10] and ferrocenylmethyl acrylate (FMA)[11] were synthesized by a similar method to be documented in refs 10 and 11. FMA was purified by chromatography[12] and identified by FT-IR (KBr) and ^{1}H NMR.[13]

Seventy milliliters of suspension including 0.90 g of dried PS latex was diluted with 50 mL of water in 200 mL round-bottom flask under the N_2 atmosphere. In order to facilitate absorption of FMA and styrene on the PS latex surface, 2 mL of 2-propanol solution including 60 mg (0.18 mmol) of FMA and 0.5 cm^3 of styrene (4.5 mmol) was added dropwise to the suspension. The initiator, α,α'-azoisobytyronitrile (0.05 g) in 5 mL of water was dropped into the suspension. Polymerization was carried out at 70 °C for 24 h to change the white suspension into the yellow. Its supernatant was replaced by the mixture solution of 2-propanol/water (1:2, volume) by centrifugation and redispersion. This centrifugation–redispersion cycle was repeated several times, until the trace of ferrocene unit in supernatant disappeared from UV spectra. The precipitate was FMA-coated PS latex (FMA-PS) as demonstrated by FT-IR. The carbonyl frequency in FMA-PS, 1734 cm^{-1} is close to that in FMA, 1724 cm^{-1}. Especially, the band at 817 cm^{-1} is due to the out-of-plane bending of the CH groups at the cyclopentadiene ring. Various bands from 1000 to 1100 cm^{-1} can be assigned to the monosubstituted ferrocenyl derivatives. These bands were not found in the spectrum of PS latex. Therefore, ferrocenyl moiety was immobilized with high stability on to FMA–PS latex.

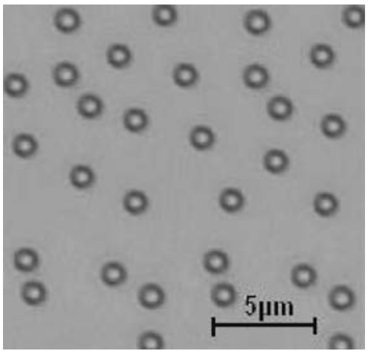

Figure 1. A photograph of the FMA-PS suspension by optical microscopy.

The aqueous FMA–PS suspension was milky yellow and was stable for at least three months without appreciable sedimentation, as shown in the photograph (Figure 1) by optical microscopy. The particles were nearly monodispersed, as shown in Figure 1 which was demonstrated by a light scattering instrument (Malvern Zetasizer Nano-ZS). The average diameters were 0.90 ± 0.01 μm. An amount of ferrocene per FMA–PS particle was determined quantitatively with UV spectroscopy in the following: The dried FMA–PS was dissolved in dichloromethane to get a transparent, yellow solution. The UV spectra showed the band at 435 nm specific to the Fc moiety. Concentrations of the Fc moiety in the latex suspension were evaluated from the comparison with that of FMA. By combining the concentration with the mass of one particle, the number of the Fc moiety per FMA–PS particle, n_{uv}, was estimated to be 3.8×10^7. The density of the whole FMA–PS particle is almost the same as the density of polystyrene (1.05 $g\,cm^{-3}$). Then, the volume and mass of one particle are 3.82×10^{-13} cm^3 and 4.01×10^{-13} g, respectively.

The suspension of FMA–PS including 0.1 M $(C_2H_5)_4NCl$ was electroactive at a platinum disk electrode, as shown in Figure 2a. A pair of the redox waves at 0.271/0.207 V is ascribed to a couple of the electrode reaction of the ferrocenyl moieties by

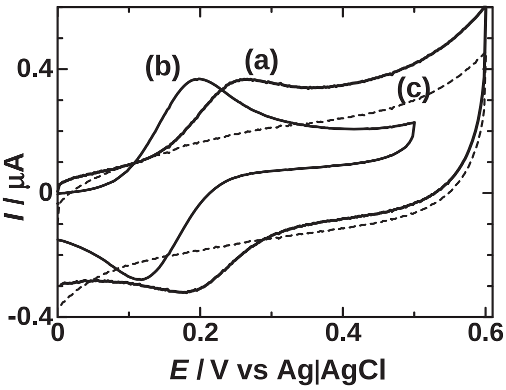

Figure 2. Cyclic voltammograms of (a) FMA–PS suspension including 23 mg/cm^3 dried latex, (b) FMA in the surfactant (1.5 g/dm^3 PVP)-contained aqueous solution, and (c) the supernatant of the suspension by the centrifugation. They were obtained in the 0.05 M aqueous $(C_2H_5)_4NCl$ solution on Pt disk electrode 1.6 mm in diameterat scan rate of 0.1 V s^{-1}.

comparing Figure 2a and 2b. The supernatant obtained from the suspension by centrifugation showed no redox wave (Figure 2c). Therefore, the redox wave (a) is not due to free ferrocenyl moiety released from the latex but due to the immobilized one. FMA-PS in the bulk ought to be in the reduced state, as can be confirmed by the zero value of the current in wave (a) at the forward scan near 0.0 V. Figure 3 shows the variation of the peak currents of the Figure 2a with the square-root of the potential scan rate. The proportionality implies that the anodic and cathodic currents should be controlled by the diffusion of particles. The anodic and cathodic peak potential did not vary with the scan rate, indicating the electrode reaction of FMA-PS was reversible reaction without complication.

A diffusion-controlled peak current of the succeeding n-electron reaction is expressed by[14]

$$I_{\mathrm{p}} = 0.446nF^{3/2}c^{*}A(D\upsilon/RT)^{1/2}, \tag{1}$$

where c^* is the bulk concentration of FMA-PS, A is the electrode area, and D is the diffusion coefficient of FMA-PS. The value of D can be estimated from the Stokes–Einstein relation,[15] $D = k_{\mathrm{B}}T/6\pi\eta a$ on the assumption of a hard sphere model, where η is the viscosity and k_{B} is Boltzmann's constant. We obtain $D = 5.5 \times 10^{-9}\ \mathrm{cm^2\,s^{-1}}$. The value of n in equation (1) corresponds to the number of redox sites per particle and should be close to 3.8×10^7 obtained by the UV analysis, if all the Fc units react simultaneously at collision with the electrode. When the known values of $n = n_{\mathrm{uv}}$, c^*, A and D in to eq 1, the calculated value of $I_{\mathrm{P}}\upsilon^{-1/2}$ was 3.70 times larger than the value of calculated from slope of Figure 3. Therefore, only the 1/3 of n_{uv} is voltammetrically active. The partial charge transfer is ascribed to the thickness of the double layer smaller than the diameter.[14]

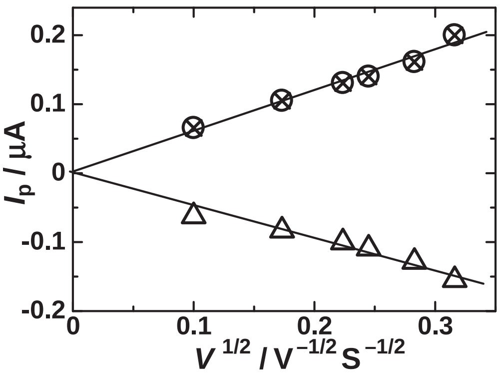

Figure 3. Variation of the peak currents of the Figure 2a with the square-root of the potential scan rate. ⊗ is anodic peak current and Δ is cathodic one.

In summary, the electroreactive spherical particles were synthesized by forming the core polystyrene and the ferrocenyl-coated copolymer-shell. The voltammetry demonstrated the diffusion control of the particles and the partial charge transfer.

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12 J. Kuwabara, D. Takeuchi, and K. Osakada, *Organometallics*, **24**, 2705 (2005).
13 Analytic Data: FT-IR (KBr) 3110, 2980–2860, 1724, 1625, 1635, 1460, 1400, 1385, 1280, 1190, 1115, 1050, 994, 820, 740 cm^{-1}. ^{1}H NMR (300 MHZ $CDCl_3$) δ 6.41 (dd, 1H, $C{=}CH_2$), 6.11 (dd, 1H, $C{=}CH_2$), 5.71 (dd, 1H, $CH{=}C$), 4.90 (s, 2H, $-CH_2-$), 4.10 to 4.75 (9H, Cp-H).
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