

Enhancement Of Electrochemical Activity By Small-Sizing The Vinylferrocene-Immobilized Polystyrene Latex Particles

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1. Introduction

It is microspheres or latex particles that are size-controllable materials. Polystyrene (PS) latex particles have been widely used as models of molecular ordering because they provide well-stabilized suspensions in a board range of size with sharp size-distribution. The nanometer-scaled PS particles have exhibited more rapid aggregation than micrometer-scaled ones at common mass concentration. We describe effects of particle size on the voltammetric electroactivity by use of vinylferrocene-immobilized PS (VFc-PS) microspheres in aqueous suspension. VFc is adsorbed hydrophobically in nearly mono-dispersed PS particles, of which size is synthetically controlled. Points of interest are (i) whether VFc is distributed on the particle surface or within the particle, (ii) in which process VFc is controlled for the electrode reaction, (iii) stability of the adsorbed VFc for the redox reaction, and (iv) the ratio of the amount of reacting VFc to the immobilized amount.

2. Results and Discussion

The average diameters of the particles, $2a$ (a : radius), and their diffusion coefficient evaluated from Stokes-Einstein equation are given in Table 1

	$2a / \mu\text{m}$ (SEM)	$2a / \mu\text{m}$ (optical mcrscp)	$n_{UV} \times 10^5$	$D_0 \times 10^8$ $/ \text{cm}^2 \text{s}^{-1}$	n / n_{UV}
1	0.16 ± 0.002	—	2.05	3.16	0.50
2	0.18 ± 0.02	—	3.14	2.72	0.51
3	0.24 ± 0.01	—	3.58	2.04	0.26
4	0.36 ± 0.02	0.39 ± 0.07	10.6	1.36	0.18
5	0.48 ± 0.01	0.51 ± 0.06	33.7	1.02	0.20
6	0.61 ± 0.05	0.62 ± 0.07	52.1	0.82	0.14
7	0.85 ± 0.08	0.87 ± 0.07	77.5	0.58	—
8	1.08 ± 0.06	1.09 ± 0.07	308	0.45	—

The loading of the ferrocene units per particle, n_{UV} , was estimated from the absorbance at 440nm of particle-dissolved dichloromethane solution and the concentration of the particles. For example, one particle 1 μm in diameter had $n_{UV} = 3 \times 10^7$ VFc units. Since this particle is composed of 4×10^9 styrene units estimated from the weight of the styrene unit, it is not necessary to take into account the contribution of the density of VFc. The values of n_{UV} increased with the increase in the particle size. The uniform distribution of VFc is supported by the proportionality of n_{UV} with a^3 . The slope of the line gives the concentration of VFc in PS particles, 70 mM. This concentration was achieved by immersing the PS particles in 5 mM VFc solution.

Figure 1 shows cyclic voltammograms of the aqueous suspensions of three sizes of the VFc-PS particles at the 1.6 mm platinum electrode. When particle size increased, voltammetric peaks disappeared (Figure 1(c)), even though the adsorption of particles on the electrode surface was observed by the optical microscopy,

as was found previously. The anodic peak current of the

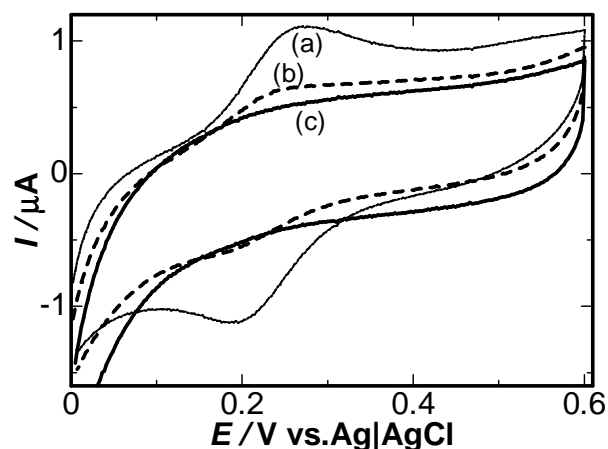


Fig. 1 Cyclic voltammograms of the water-suspended VFc-PS particles with $2a = 0.16 \mu\text{m}$ (a), $0.48 \mu\text{m}$ (b) and $0.84 \mu\text{m}$ (c) at the Pt electrode for the scan rate of 100 mV s^{-1} in 0.1 M KCl aqueous suspension.

small particle ($2a = 0.16 \mu\text{m}$) was proportional to $v^{1/2}$, suggesting diffusion control of VFc within the particle or of the particle itself in the suspension.

It is reported that big redox latex particles show partial charge transfer reaction, and hence values of the actually transferred charge, n , may be smaller than n_{UV} , the number of the latent charge per particle. We evaluated n from the slope of $I_{p,A}$ vs. $v^{1/2}$ for various particles, and listed values of n/n_{UV} in Table 1. The values of n/n_{UV} decreased with an increase in particle size. The variation of n/n_{UV} with the size is plotted on a logarithmic scale in Figure 2, showing a linear relation. The slope of the line gives $n/n_{UV} = h/a$, where h is a proportional constant, having a dimension of length, $0.07 \mu\text{m}$. The ratio, h/a , represents the partition of the electrochemical oxidation. If $a \leq h$, all the amount of VFc in the particle should be oxidized at the electrode reaction. Significance of h is a maximum distance of the electroactive domain from a contacting point of the particle with the electrode. VFc located only in the domain less than h from the contacting point can participate in the oxidation on the electrode. This type of the partial charge transfer is specific to hard big core redox particles, rather than soluble redox polyelectrolytes.

We shall express the anodic peak current in terms of the radii in order to specify the size effect as

$$I_{p,A} = (4\pi/3)0.446FAc_{in}hc_p a^{3/2} (vFN_A/6\pi\eta)^{1/2}$$

The anodic peak current should be proportional to $a^{3/2}$ for given values of c_p and v . We plotted values of $I_{p,A}/c_p v^{1/2}$ against $a^{3/2}$, and found proportionality. This proportionality is nothing but the quantitatively expressed size effect.

