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Size-dependent efficiency of electron transfer at suspended ferrocenyl jumbo particles

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Abstract

Ferrocenylmethanol acrylate (FcMA)-immobilized polystyrene latex particles were synthesized by copolymerizing FcMA and styrene in the presence of polystyrene latex suspensions with eight different diameters ranging from 0.084 to 1.7 μm. The amounts of the ferrocenyl moiety loaded on one particle were proportional to the radii, *a*. The proportionality suggests the uniform distribution of the ferrocenyl moiety over the particle, of which concentration was 0.18 M. The aqueous suspensions, which were stable in the presence of a surfactant, exhibited reversible voltammetric waves for the ferrocenyl moiety. The peak current was controlled by diffusion of the latex particles. The efficiency of the reaction was obtained from the ratio of the observed current to the theoretical one which was estimated from the number of the ferrocenyl moieties and the diffusion coefficient of the particle by the Stokes–Einstein relation. The ratio was proportional to $a^{-0.47}$, whereas it might be a^0 for an ideal particle without any size effect. This relation was explained in terms of the contribution of rotational diffusion of redox particles.

Keywords: Latex; Suspension; Ferrocenyl moiety; Diffusion-controlled current; Size effects

1. Introduction

Voltammetric work on large redox particles such as metal nanoparticles [1–5] and redox latexes [6–10] is interesting in that they may exhibit unusual properties owing to molecular interaction or assemblies. For example, thiolate ligand-stabilized clusters with Au cores have shown the quantum dot properties of monolayer-protected clusters [1], quantized double layer charging [2] and the appearance of a molecule-like bandgap [3]. The stabilities of silver alkylcarboxylate composing of the nanoparticles have decreased with an increase in the length of alkylchains owing to the interaction with the core silver metal [5]. Dispersed polyaniline latex at the microelectrode with similar size to the latex diameter has shown discretized currents [6]. Hemin-immobilized polyallylamine–polystyrene latex suspensions have shown higher catalytic activity for dioxygen [7] and carbon dioxide [8] than molecular hemin has. Polyaniline latex has protected strongly against corrosion [11,12]. Potential cycling of polypyrrole latex has varied a degree of adsorption of imidazole [13]. Advantages of voltammetry for jumbo particles have been demonstrated to be not only easy identification of redox sites by peak potentials [14] but also evaluation of transferring charge per particles [9,10,14].

Voltammetric measurements, however, have some technical difficulties in poor dispersion of particles in electrolyte solution [15], in less reactivity of owing to surfactants or hydrophobic surface of particles [16], and in purification of suspensions. Furthermore, an essential problem lies in the concept of which reaction actually occurs [17], $R_n \leftrightarrow O_n + ne^-$ or $n(R \leftrightarrow O + e^-)$ even in equilibrium. More complications can be included in currents owing to not only translational diffusion of particles but also

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rotational diffusion [18], partial electron transfer of the redox sites on the particle surface in contact with an electrode [9,10], detachment of redox sites from particles [9], and charge transport within particles. They ought to depend not only on size of particles but also distribution of redox sites within one particle. Consequently, it is necessary to control the distribution.

There are basically two types of distribution: one being the core–shell structure at which redox sites are included only in the shell, the other being uniform distribution of redox sites over the particle. The former has been realized in metal nanoparticles by coating metal core with surfactants [1,4]. The core–shell structure of redox latex particles has been formed by coating hydrophobic cores with hydrophilic shells [7,10,19]. In contrast, latexes with uniform distribution has been constructed by adsorbing redox sites into particles [9,16]. Unfortunately, the adsorbed redox sites were readily desorbed by redox reactions, like corruption of redox micelles after redox reactions [20,21]. It is necessary to immobilize the redox moiety with a sigma bond on polymers of the core in order to stabilize the redox sites against desorption. Although very hydrophobic redox moiety may make the redox distribution uniform in a polystyrene core, no redox reaction occurred in the strongly hydrophobic environment [16]. Moderate hydrophobicity may be required both to make the distribution uniform and to facilitate redox reaction. We select ferrocenylmethanol acrylate for a candidate of satisfying both conditions in the present work, and attempt to synthesize uniformly distributed latexes with various diameters. The voltammetric responses of the particles in aqueous suspensions are examined in the context of partial electron reactions [9,10].

2. Experimental

2.1. Chemicals

Styrene was purified with 5% aqueous NaOH solution and distilled water, dried with anhydrous $MgSO_4$ for one day, distilled under vacuum at 35 °C, and then stored in a refrigerator before use. Ferrocenylmethanol (TCI, Tokyo), acrylyl chloride (Wako), poly(*n*-vinylpyrrolidone) (PVP) with $360\ \mathrm{kg\ mol^{-1}}$ and α,α′-azoisobutyronitrile (AIBN) were used as received. All solvents were analytical grade and distilled before use. Aqueous solutions were prepared with ion-exchanged and twice-distilled water.

2.2. Synthesis of ferrocenylmethanol acrylate (FcMA)

The FcMA was synthesized through the Schotten–Baumann reaction [22], as is shown in Fig. 1. Ferrocenylmethanol (1.08 g, 5 mmol) and pyridine (1.4 cm^3) were added to anhydrous dichloromethane (50 cm^3) at 0 °C. Acrylyl chloride (0.48 cm^3, 6 mmol) dichloromethane solution (10 cm^3) was added drop-wise into the mixture. The mixture was stirred at 0 °C for 2 h to obtain pyridine chloride as white deposition of pyridine chloride. The deposition was filtered out and the filtrate was rinsed with saturated $NaHCO_3$, NaCl solution and water in turn, extracted by ethylacetate, and dried with $MgSO_4$. The product was purified by column chromatography of silica gel (200–400 mesh) with a mixture of hexane and dichloroethane (4:1 volume). The eluent was evaporated to produce an orange solid of ferrocenylmethanol acrylate (581 mg, 43% yield). The bands of FTIR on a KBr plate were 3110, 2980–2860, 1724, 1625, 1635, 1460, 1400, 1385, 1280, 1190, 1115, 1050,

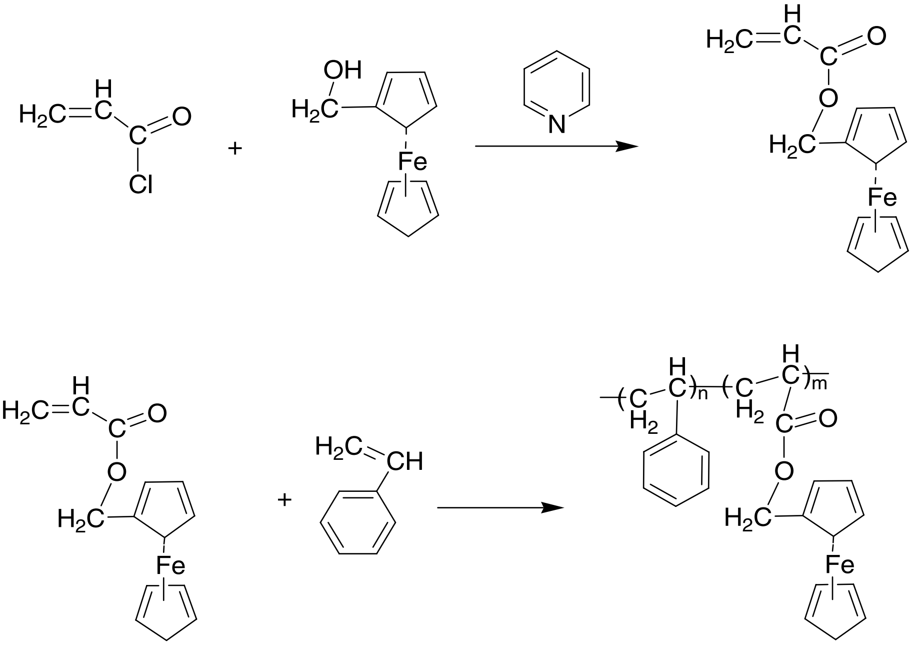

Fig. 1. Reaction scheme of synthesis of (upper) FcMA and (lower) ferrocenyl moiety-immobilized latex particles.