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Size-Controlled Synthesis of Conducting-Polymer Microspheres by Pulsed Sonoelectrochemical Polymerization**

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Conducting polymers exhibit not only electroconductivity but also unique optical and chemical properties. The diversity of the properties exhibited by conducting polymers suggests that these materials can be used in numerous technological applications.[1] However, the practical realization of many applications has been restricted by the poor processability of conducting polymers. Over the last two decades, excellent progress in improving the processability of these polymers has been made.[2] The preparation of colloidal dispersions of conducting polymers is an attractive approach for improving their poor processability.[3] The use of colloids enables film casting from aqueous or nonaqueous solutions, either as stand-alone conducting polymers or as composite materials with other polymers.

In general, the properties of conducting-polymer colloids originate from their morphological structure and size.[4] Therefore, it follows that the structure and size of the colloid particles should be controllable in order to tailor them to the purposes of their utilization. Although either a granular or fibrillar morphology is usually obtained by a simple oxidative polymerization method in the bulk,[5] spherical polymers can be synthesized by using steric stabilizers.[6] On the other hand, Wallace et al.[7] and Harima et al.[8] reported that spherical conducting polymers, such as polypyrrole and poly(*N*-methylaniline) (PNMA), could also be synthesized without the need for stabilizers by using electrochemical polymerization. However, an electrochemical method is not an effective means for preparing large numbers of the polymer spheres. In addition, the fine-tuning of the size of the spheres still needs some improvement.

The potential benefit of combining both sonochemistry and electrochemistry is being increasingly studied.[9] The particular beneficial effects include the promotion of mass transfer and continuous cleaning and activation of the electrode surface. Recently, pulsed sonoelectrochemical synthesis involving alternating sonic and electric pulses has been employed in the shape- and size-controlled synthesis of metal and semiconductor particles.[10] The sonoelectrochemical formation of these particles was accomplished by applying an electric pulse to nucleate and grow the electrodeposit, followed by a burst of ultrasonic energy to remove the deposited particles (see Figure 1). Therefore, the particle size can be controlled by adjusting the width of the ultrasonic and electric pulses; moreover, large amounts of the particles can be obtained by repeated application of the pulses.

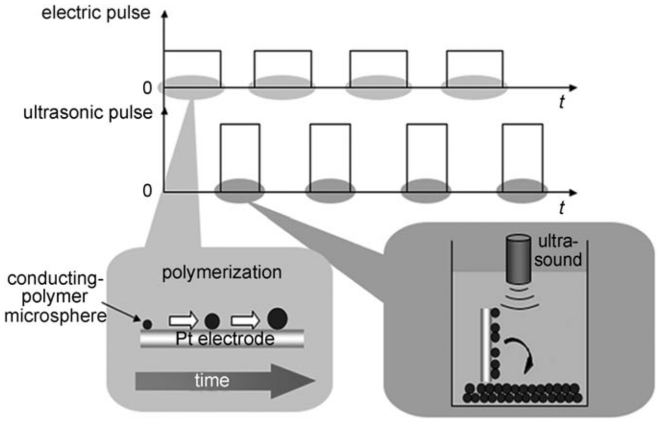

Figure 1. Pulsed sonoelectrochemical method for the production and recovery of conducting-polymer microspheres.

Herein, we report the preparation of size-controlled microspheres of conducting polymer by the use of a pulsed sonoelectrochemical method. In addition, we also report the redox properties of their solution-cast film on an indium tin oxide (ITO) electrode. As mentioned above, the shape of the PNMA electrodeposited from $HClO_4$ aqueous electrolyte was found to be spherical, and hence we chose this reaction as a model for the present demonstration.

Figures 2a–e shows scanning electron microscopy (SEM) images of the as-deposited PNMA microspheres obtained on an anode surface by applying a square-wave electric (potential) pulse. It can be seen that spherical particles are deposited and the average diameter of the microspheres increases with the pulse width. On the other hand, Figures 2f–j shows SEM images of the PNMA microspheres obtained by the application of alternating electric and sonic pulses. Although these samples were removed from the anode surface by a burst of ultrasonic energy (31 $W\,cm^{-2}$ power, 5 s duration), their shapes and sizes never changed from those of the as-prepared PNMA microspheres obtained on an anode surface by applying only an electric pulse. In other words, the subsequent sonication had the sole role of ablating the microspheres from the anode surface and did not break them.

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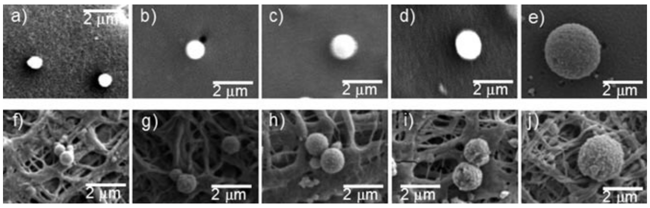

Figure 2. SEM images of PNMA microspheres a–e) as-deposited on the anode surface by applying a potential pulse and f–j) ablated from the anode surface by applying a subsequent sonic pulse. Experimental conditions: potential pulse: 0.75 V vs. saturated calomel electrode (SCE); ultrasonic pulse density: 31 $\mathrm{W\,cm^{-2}}$; duration of the ultrasonic pulse: 5 s; duration of the potential pulse: 10 (a,f), 20 (b,g), 30 (c,h), 40 (d,j), 90 s (e,j).

Figure 3 shows the size distributions of the PNMA spheres obtained by the pulse sonoelectrochemical method with different electric (potential) pulse widths. These samples were prepared by applying alternating electric and sonic pulses 100 times, and consequently about 10 mg of the PNMA spheres were obtained, regardless of the electric pulse width. Histograms of the size distribution of the spheres were calculated by counting 100 sphere sizes in the samples. When the electric pulse width was fixed during the sonoelectrochemical synthesis, the size of the spheres was well controlled and depended on the electric pulse width (Figure 3 a and b). This result suggests that the effective removal of the deposit from the anode by the sonic pulse occurs before the next electric pulse, thus preventing further growth of spheres. Figure 3 c shows the size distribution of the spheres obtained by sonoelectrochemical synthesis with the combination of different electric pulse widths. As we would expect, PNMA spheres with a broad size distribution were obtained in this case.

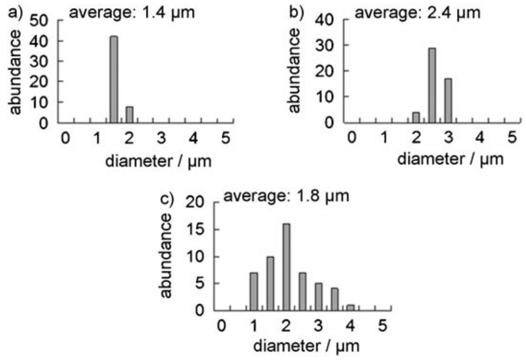

Figure 3. Size distribution of PNMA microspheres prepared by applying alternating electric and ultrasonic pulses 100 times. Preparation conditions for PNMA microspheres: potential pulse: 0.75 V vs. SCE; ultrasonic pulse density: 31 $\mathrm{W\,cm^{-2}}$; duration of ultrasonic pulse: 5 s; duration of potential pulse: a) 40 s, b) 90 s, c) a combination of different pulse widths (30, 60, 90, 120, 150, 180 s).

We next discuss the redox properties of cast films of the three samples used in the size distribution measurements. The cast films of PNMA spheres on ITO electrodes were prepared by spin-coating of an aqueous solution of the spheres.

Figure 4 shows cyclic voltammograms (CVs) of the cast films of PNMA spheres with various size distributions. The leucoemeraldine/emeraldine salt (LE/ES) transition could be clearly seen as very sharp redox peaks at $E_{\mathrm{p,a1}} = 0.12/E_{\mathrm{p,c1}} = 0.02$ V for the cast film of smaller spheres (Figure 4 a). In this voltammogram, a pair of smaller redox peaks was also observed at $E_{\mathrm{p,a2}} = 0.30/E_{\mathrm{p,c2}} = 0.22$ V. Taking into account their heights and potentials, this observation is attributable to the response of a side product generated during the polymerization process.[11] It was still possible to observe the LE/ES transition in the CV for the cast film of larger spheres, although the redox peaks became broad (Figure 4 b). On the other hand, very broad oxidation and reduction peaks were observed for the cast film of the size-uncontrolled spheres (Figure 4 c). It can therefore be stated that fine-tuning of the size of the spheres is necessary to observe the sharp LE/ES transition versus potential. Moreover, the redox peaks for the smaller spheres were apparently higher than those for the others. This finding can be ascribed to the effective charging and discharging of the smaller spheres, because the same amount of spheres was cast on the ITO substrate for the preparation of each modified electrode.

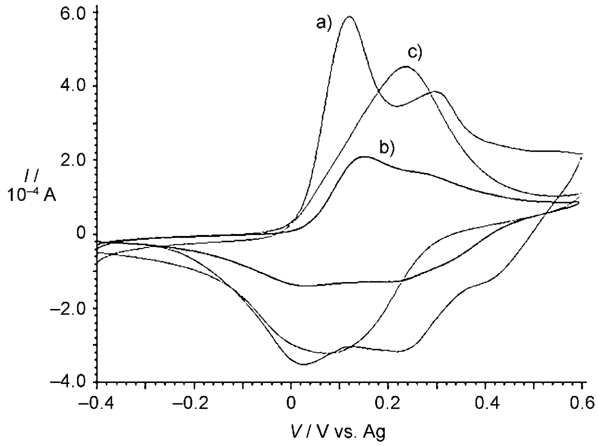

Figure 4. CVs of cast films of PNMA spheres with various size distributions. PNMA samples (a–c) in Figure 3 exhibited CVs (a–c), respectively. Scan rate: 0.1 $\mathrm{V\,s^{-1}}$.

Such a sharp redox response versus potential is required for the use of conducting polymers for electrochemical devices, such as electrochromic windows and displays.[12] As PNMA is an electrochemically coloring polymer,[13] small PNMA spheres may be applied to these devices. Figure 5 shows the UV/Vis spectra of PNMA microspheres with various size distributions on ITO electrodes, obtained at different time intervals after applying electrode potentials of $E = 0.6$ and -0.4 V versus Ag wire. The smaller PNMA spheres exhibited a rapid color change (Figure 5 a and d) compared to the other samples. Within the first 0.5 minutes, the color of the PNMA spheres was almost changed. As mentioned above, this may also be ascribed to the effective charging and discharging of spheres during electrochemical redox reactions. On the other hand, the larger PNMA spheres showed little color change (Figure 5 b and e). In this case,

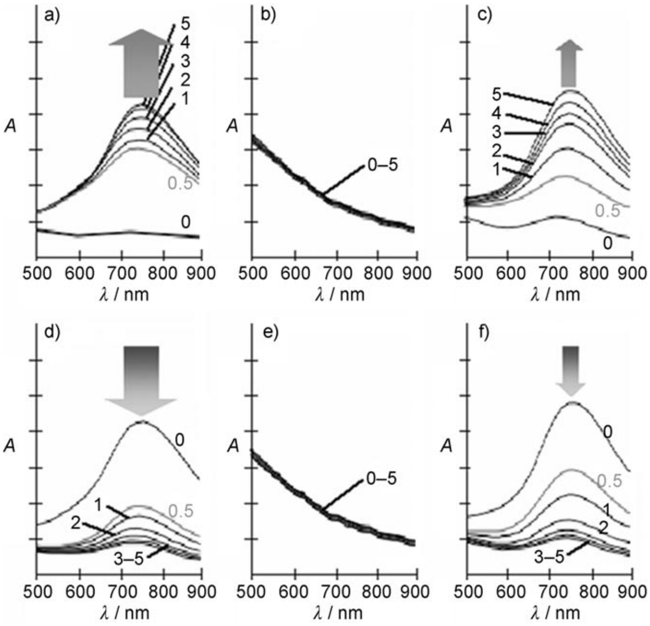

Figure 5. UV/Vis spectra of PNMA microspheres with various size distributions on ITO electrodes, obtained at different time intervals (in minutes) after applying electrode potentials of a–c) $E = 0.6$ and d–f) -0.4 V versus Ag wire. PNMA samples (a–c) in Figure 3 exhibited the spectra (a,d), (b,e), and (c,f), respectively.

probably only a small portion of the spheres was charged and discharged.

In summary, we have demonstrated a novel size-controlled synthesis of conducting-polymer microspheres by using pulsed sonoelectrochemical polymerization. This synthetic method enables the size of the microspheres to be controlled precisely by adjusting the width of the electric pulses during the polymerization process. We expect that this new methodology will make a significant contribution not only to polymer chemistry but also to various device technologies. The limitations and further application of this methodology are currently under investigation.

Experimental Section

Materials: All chemicals were used without further purification. *N*-Methylaniline was purchased from Wako Pure Chemical Industries and perchloric acid was purchased from Kanto Chemical. *p*-Toluenesulfonic acid was purchased from Tokyo Kasei Kogyo. Distilled and deionized water was used as solvent for the electrochemical polymerization and colloidal dispersion of PNMA microspheres.

Pulsed sonoelectrochemical polymerization: The sonoelectrochemical device employed in these experiments is illustrated in Figure S1 in the Supporting Information. A glass-beaker cell in a cooling bath was equipped with a Pt plate anode (1×1 cm^2), a Pt plate cathode (2×2 cm^2), a reference electrode (SCE), and an ultrasonic stepped horn (13 mm in diameter) connected to a 20 kHz ultrasonic processor (SONIFIER-250D, Branson Ultrasonics Co.). The platinum anode surface was positioned vertically to the propagating direction of ultrasonic waves. The electrolyte was an aqueous solution of 1.0 M $HClO_4$ containing 0.8 M *N*-methylaniline (100 mL volume). The pulsed sonoelectrochemical polymerization involved alternating electric (potential) and sonic pulses. The electric (potential) pulse was immediately followed by a sonic pulse. A pulse driver (WAVE FACTORY 1941, NF Co.) was used to control a potentiostat (HABF 501, Hokuto Denko). The electric (potential) pulse was 0.75 V versus SCE, with a duration of 10, 20, 30, 40, or 90 s. The ultrasonic processor was adapted to work in the pulse mode (5 s duration). The sonic pulse had a power of 31 W cm^{-2} with a duration of 5 s. The temperature during the reaction was controlled at 25 °C. After the polymerization, the PNMA microspheres were separated from their colloidal solution by filtration (membrane filter with pore size 200 nm), washed with water several times, and dried under vacuum. Dried spheres were subjected to SEM (VE-7800, Keyence Co.).

Preparation of the cast film of PNMA microspheres on an ITO electrode: Dried PNMA microspheres were redispersed in deionized water and a colloidal solution (1 wt %) was prepared. As illustrated in Figure S2 in the Supporting Information, the solution (30 mL) was then deposited dropwise onto a bare part of an ITO electrode (the electrode was covered with insulating tape such that it remained bare in the central part (0.8×0.8 cm^2)). Finally, cast films of PNMA spheres were prepared by spin-coating (300 rpm, 10 s) and these samples were then dried under vacuum at 80 °C. SEM images of the cast films of PNMA microspheres with various size distributions are shown in Figure S3 in the Supporting Information.

Cyclic voltammetry: Cyclic voltammetry was performed by a computer-controlled electrochemical system (ALS/CH Instruments 630C). CVs were recorded with a three-electrode system using an ITO working electrode covered with the cast film of PNMA spheres, a Pt wire counter electrode, and an Ag wire reference electrode in aqueous 1.0 M *p*-toluenesulfonic acid solution at 25 °C.

In situ UV/Vis measurements: As shown in Figure S4 in the Supporting Information, an ITO working electrode covered with the cast film of PNMA spheres was placed in a quartz cell for UV/Vis measurements. The cell was also equipped with a Pt wire counter electrode and an Ag wire reference electrode. The spectra were recorded first at open circuit potential in aqueous 1.0 M *p*-toluenesulfonic acid solution. Then, a potential of 0.6 V was applied and the spectra were recorded at different time intervals. After keeping the potential at 0.6 V for 5 min, it was changed to -0.4 V and the spectra were again recorded at different time intervals.

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