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Electrochemical polymerization of water-soluble and insoluble monomers in supercritical carbon dioxide-in-water emulsion

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Abstract

Dense carbon dioxide is an environmentally benign solvent, but its non-polarity limits the use of carbon dioxide as a reaction medium for electrochemical reactions. We have previously reported that the electrochemical polymerization in a carbon dioxide-in-water (C/W) emulsion proceeds to form conductive polypyrrole films [Jikei M, Saitoh S, Yasuda H, Itoh H, Sone M, Kakimoto M, et al. Polymer 2006;47:1547—54]. In this study, the effect of reaction conditions of the electrochemical polymerization on the resulting polypyrrole films was systematically investigated in order to reveal the features, flexibility and limitations of the C/W emulsion as a medium for electrochemical reactions. Other monomers, such as aniline and 3,4-ethylenedioxythiophene, were also examined for the electrochemical polymerization in the C/W emulsion. We have found that water-soluble monomers, such as pyrrole and aniline, are suitable for the electrochemical polymerization in the C/W emulsion that form films with a fine uneven texture.
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1. Introduction

Dense carbon dioxide is one of the promising reaction media for chemical reactions due to its non-toxic, non-flammable and virtually inert properties. Many successful organic reactions and polymerizations in dense or supercritical carbon dioxide have already been reported in the literature [1—5]. It is also known that carbon dioxide can penetrate into polymeric materials and often reduces interchain interactions. Therefore, exploring the new polymerization method using supercritical carbon dioxide may open the door for new materials, innovative reaction processes, and unexpected discovery induced by supercritical carbon dioxide. Despite the good solubility of many non-polar organic compounds, highly polar compounds, ionic species and polymeric materials show a limited solubility in dense carbon dioxide due to its inherent non-polar property. The limited solubility hampers the potential of carbon dioxide for the use in a broad range of applications. There

are mainly two strategies in order to increase the polarity of dense carbon dioxide. One is the use of additives or cosolvents in order to increase the polarity of the carbon dioxide. However, the addition of such organic compounds may diminish the advantage of carbon dioxide as an alternative to harmful organic solvents. The other solution is the use of surfactants to form a water-in-carbon dioxide (W/C) or carbon dioxide-in-water (C/W) emulsion. Many primary research studies to determine the nature and its possible use in emulsions have already been reported in the literature [6—9].

Electron-conductive polymers have been investigated since the 1980s and still deserve much attention from academic or industrial view points [10—15]. Among the many electron-conductive polymers reported in the literatures, polypyrrole, polyaniline and polythiophenes have been commercialized or examined for commercial applications due to their good balance of high conductivity and good stability in an atmospheric environment. Chemically oxidative polymerizations and electrochemical polymerizations can be used for the preparation of conductive polymers. There are several papers describing the preparation of conductive polymers in supercritical or dense carbon dioxide. The chemical oxidative

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polymerization of pyrrole in supercritical carbon dioxide was first reported in 1997 [16]. The conductivity of the resulting polypyrrole was two to three orders of magnitude lower than those of the polypyrrole prepared in conventional solvents. The chemically oxidative polymerization of thiophene derivatives was also applied for the preparation of conductive composite materials and CO_2-soluble semiconducting polythiophenes [17−19]. Due to its non-polar nature, pure carbon dioxide is not a suitable medium for electrochemical reactions. Electrochemical polymerization in supercritical carbon dioxide in the presence of acetonitrile as a cosolvent was reported in 2002 [20,21]. The addition of the polar solvent is essential for the electrochemical polymerization since the inherent polarity of supercritical carbon dioxide is low. The conductivity of the resulting polypyrrole films was reported to be 4.4 S/cm and unique film morphology on an ITO electrode was observed. We have recently reported that electron-conductive polypyrrole films can be prepared by electrochemical polymerization in a C/W emulsion on platinum electrodes [22]. A unique fine and uneven texture was observed for the polypyrrole films prepared in the C/W emulsion, which is more homogeneous and rougher than the surface of the films prepared in the absence of carbon dioxide. Since most highly conjugated polymers are essentially insoluble in most organic solvents, the morphology control in situ is of prime interest to improve the surface-related properties, such as adhesion, self-healing and sensing properties. This paper describes our extensive investigations to reveal the features, flexibility and limitations of electrochemical polymerization in a C/W emulsion. The effect of the reaction conditions, such as the reaction medium, electrode, reaction pressure and temperature, on the electrochemical polymerization of pyrrole was examined in detail. The electrochemical polymerization of aniline or 3,4-ethylenedioxythiophene was also carried out in the same manner as the electrochemical polymerization of pyrrole.

2. Experimental

2.1. Materials and high-pressure equipment

Pyrrole and aniline were purchased from Kanto Chemical Co., Inc., Tokyo, Japan, and were purified by distillation before use. 3,4-Ethylenedioxythiophene (EDOT) was purchased from the Sigma−Aldrich Japan Co., and was used without further purification. *p*-Toluene sulfonic acid monohydrate was purchased from Tokyo Kasei Co., Ltd., Tokyo, Japan, and was used without further purification. Sulfuric acid and tetraethylammonium perchlorate were purchased from Kanto Chemical Co., Inc., Tokyo, Japan, and were used without further purification. The poly(oxyethylene) lauryl ether $(C_{12}H_{25}(OCH_2CH_2)_{15}OH)$ solution in water (25%) was a kind gift from Toshin Yuka Kyogo, Inc., Tokyo, Japan, and was used without further purification. Critical micelle concentration of the poly(oxyethylene) lauryl ether, measured by the solubility change of 1,4-diaminoanthraquinone, was 0.17 mmol/L in water and 0.14 mmol/L in acetate buffer (0.1 M, pH = 3.6). The perfluoropolyether surfactant

$(F(CF(CF_3)CF_2O)_3CF(CF_3)COO(CH_2CH_2O)_7CH_3)$ was prepared by the procedure reported in the literature [23]. Carbon dioxide (purity: 99.9%, dew-point temperature: −65 °C) was purchased from Syusan Kogyo Co., Ltd., Akita, Japan, and used as received. De-ionized water was used in all the experiments. A platinum plate (thickness: 0.7 mm) was purchased from Tanaka Kikinzoku Kogyo K.K., Tokyo, Japan. The platinum plate was cut into a rectangular piece (1×2 cm) and then polished with aluminum oxide (0.05 μm) in a water suspension for use as an electrode. A nickel plate (thickness: 1 mm, 1×2 cm) was a kind gift from YP system Co., Ltd., and used for the electrochemical polymerization after polishing with an aluminum oxide suspension. An indium tin oxide (ITO) plate (<10 Ω/sq.) was purchased from Kinoene Kogaku Kogyo Co., Ltd., Japan, and was cut into a rectangular piece (1×2 cm) for use as an electrode.

The high-pressure equipment reported in our previous paper [22] was used for the high-pressure experiments. A visible high-pressure view cell (24 mL) equipped with sapphire windows (Taiatsu-Glass Kogyo Inc., Tokyo, Japan) was used to monitor the emulsion formation and the solubility test of reagents in supercritical carbon dioxide (35 °C, 12 MPa). A commercially available reactor (JACSO EV-3, 50 mL) was modified for the electrochemical polymerizations.

2.2. Monitoring of emulsion formation

The high-pressure view cell was charged with water (15 mL) and poly(oxyethylene) lauryl ether (0.45 mL, 9 mmol/L) or a perfluorinated surfactant (0.10 mL, 14 mmol/L). The sealed view cell was immersed in a water bath (35 °C), then carbon dioxide was introduced into the cell using an HPLC pump (JASCO SCF-Get) to 12 MPa. After 30 min, the solution was stirred using a magnetic stirrer (1100 rpm). The emulsion formed in the cell was visually monitored through the sapphire windows.

2.3. Electrochemical polymerization

The electrochemical polymerization of pyrrole in the C/W emulsion was carried out using the procedure described in our previous report [22]. Typically, the solution of pyrrole (0.21 mL, 0.003 mol), *p*-toluene sulfonic acid monohydrate (2.85 g, 0.015 mol), and poly(ethyleneoxide) lauryl ether (0.9 mL) in water (30 mL) was charged into the high-pressure reactor. The reactor was immersed in a water bath and carbon dioxide was introduced with a pressure of 12 MPa. After stirring (1100 rpm) for 30 min, the electrochemical polymerization was started by applying a constant voltage between the two electrodes placed at the distance of 2 cm.

When the reaction temperature was 5 or 20 °C, the reactor was first pressurized to 20 MPa at 35 °C by the introduction of CO_2, and then, cooled to the desired temperature. The pressure of the reaction medium decreased to 4 MPa at 5 °C and 11 MPa at 20 °C.

As the control experiments, the electrochemical polymerization in water was carried out using the same reaction setting

without adding CO_2. The amount of water was increased from 30 to 45 mL in order to completely immerse the electrodes in the electrolyte. The electrochemical polymerization in the hexane/water emulsion was also carried out as a control experiment. In this case, hexane (15 mL) was added to the solution of pyrrole, *p*-toluene sulfonic acid monohydrate and poly(ethyleneoxide) lauryl ether (0.9 mL) in water (30 mL) before sealing the reactor. The electrochemical polymerization was carried out in the same manner as the polymerization in the C/W emulsion without adding CO_2.

The electrochemical polymerization of aniline in the C/W emulsion was carried out by the same procedure described above. Sulfuric acid was used as the supporting electrolyte instead of *p*-toluene sulfonic acid. The applied voltage between the electrodes was 1.5 V.

The electrochemical polymerization of EDOT in the C/W emulsion was carried out by the same procedure described above. Tetraethylammonium perchlorate was used as the supporting electrolyte and the applied voltage between the electrodes was 1.5 V.

2.4. Measurements

The thickness of the film was determined by a Surfcom 1400A surface texture measuring instrument (Tokyo Seimitsu, Japan). The film prepared on the Pt electrodes was partially removed and the difference in the height between the polypyrrole film and the bare electrode surface was measured to determine the thickness of the film. The resistance of the film on the other side was measured by a 4-point probe method using a Loresta-GP with a MCP-TP06P probe (Mitsubishi Chemical Co.). The resistance of the film was determined by the average of at least five data points. A constant resistivity correction factor (4.532) was used for the calculation of the conductivity (S/cm). The IR spectra were obtained using an FTIR SPECTRUM 2000 spectrophotometer (Perkin−Elmer) by the KBr-pellet method. The AFM images were obtained using a SPA300 Scanning Probe Microscope (SII). The contact mode was used for the measurements. SEM pictures were obtained using a JSM-5900LV Scanning Electron Microscope (JEOL). Confocal scanning microscopic images were obtained using a Laser Microscope 1LM21 (Lasertec Co., Japan). The surface roughness, Ra, was calculated by Salt 1.09 software (Mitani Corporation). The Ra value calculated by the deviation of the data point from a standard surface level was averaged from five different positions. A small Ra suggests a flat and smooth surface. The outer surface of the film was examined for all the microscopic measurements.

3. Results and discussion

3.1. Electrochemical polymerization of pyrrole in the C/W emulsion

As previously reported [22], poly(oxyethylene) lauryl ether works as an effective surfactant to form a uniform carbon dioxide-in-water (C/W) emulsion. The poly(oxyethylene) lauryl ether is a highly hydrophilic surfactant and its hydrophilic−lipophilic balance (HLB) is known to be 14. Fig. 1a shows the mixture of water and carbon dioxide (12 MPa) in the high-pressure view cell at 35 °C with agitation at 1100 rpm in the presence of the surfactant at a concentration of 0.03 mmol/L. Although the emulsified white phase was formed, a continuous clear water phase was also observed through the windows. It is obvious that the homogeneous C/W emulsion is not formed at that surfactant concentration. At the concentration of 9 mmol/L, a homogeneous C/W emulsion was observed, as shown in Fig. 1b. The C/W emulsion is not thermodynamically stable and a boundary between the carbon dioxide and water gradually appeared after stopping the agitation. Due to the instability of the emulsion, the size of the CO_2 droplets was not directly determined. The white and homogeneous cloudy appearance of the C/W emulsion suggests the formation of droplets in the range sub to several micrometers. The C/W emulsion can be used as a good homogeneous reaction medium for the electrochemical reactions. Fig. 1 c shows the mixture of water and carbon dioxide (12 MPa) in the presence of the perfluorinated surfactant. It is known that the perfluorinated surfactant works as a surfactant to form water in the supercritical carbon dioxide microemulsion [23]. Although an emulsified white phase was formed, large droplets were also observed through the sapphire windows of the view cell. The perfluorinated surfactant enhanced the solubility of the carbon dioxide in water but
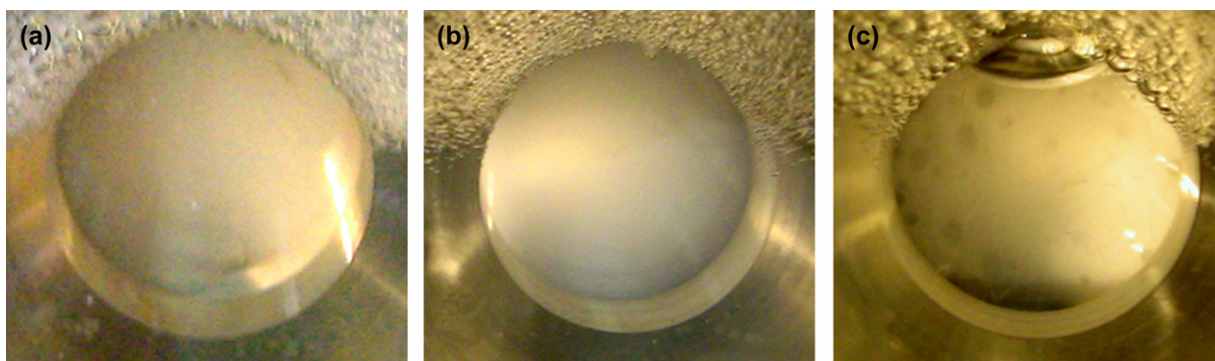

Fig. 1. Monitoring the mixture of water and carbon dioxide (12 MPa) in the presence of a surfactant. (a) Poly(oxyethylene) lauryl ether, 0.03 mmol/L; (b) poly-(oxyethylene) lauryl ether, 9 mmol/L; (c) perfluorinated surfactant ($F(CF(CF_3)CF_2O)_3CF(CF_3)COO(CH_2CH_2O)_7CH_3$), 14 mmol/L.

was not effective enough to form a homogeneous carbon dioxide-in-water emulsion. We have attempted the electrochemical polymerization of pyrrole at 35 °C in the mixture of water and carbon dioxide (12 MPa) in the presence of the fluorinated surfactant. The resulting film was rough and showed visible voids or pinholes on its surface. It is clear that the emulsion formed in the presence of the perfluorinated surfactant is not a suitable reaction medium for the electrochemical polymerization. It seems that the hydrophilic surfactant, which can effectively lower the surface tension of water, is suitable for the formation of the homogeneous C/W emulsion.

Fig. 2 shows the effect of the reaction medium used for the electrochemical polymerization on the morphology of the resulting polypyrrole films. As previously reported [22], a fine nodular texture was observed for the film prepared in the C/W emulsion (Fig. 2a) which was in contrast with the film prepared in water (Fig. 2b). Since hexane is known as a non-polar solvent similar to dense carbon dioxide, the electrochemical polymerization in a hexane/water emulsion was

also attempted in order to clarify the unique effect of carbon dioxide on the morphology. The formation of the hexane/water emulsion in the presence of the surfactant was initially confirmed using a high-pressure view cell. Fig. 2c shows the 3D images of the film prepared by the electrochemical polymerization in the hexane/water emulsion. It is clear that the surface is rough and irregular in comparison with Fig. 2a and b. During the electrochemical polymerization in the C/W or hexane/water emulsion, the current should flow when the water phase in the emulsion contacts to the electrode surface. Therefore, the electrochemical polymerization should proceed with continuous on/off mode, which resembles the pulse mode electrolysis. From that viewpoint, the mode of the electrolysis should be continuous in water and the on/off mode in the C/W emulsion and the hexane/water emulsion. Judging from the morphology of the film prepared by the polymerization in hexane/water, the on/off mode is not an important factor to produce the fine nodular texture. Therefore, carbon dioxide does influence the morphology of the resulting films that have a fine nodular texture.

Nickel and ITO electrodes can also be used for the electrochemical polymerization of pyrrole in the C/W emulsion. The formation of smooth polypyrrole films in the range of 0.8–11.5 μm was observed on the Ni electrodes. On the other hand, it was difficult to prepare thick polypyrrole films on the ITO electrodes since the film formed on the ITO electrodes was easily stripped by a weak force. The conductivity of the films prepared on Ni electrodes was in the same range (8–28 S/cm) as the film prepared on the Pt electrodes. It has been reported that the surface morphology of polypyrrole films is influenced by the nature of electrodes used for the electrochemical polymerizations [24–30]. Generally, a nodular morphology is often observed for the films on Pt electrodes and the formation of a wrinkle texture is reported for the film on ITO electrodes. A unique nodular morphology was also reported for the polypyrrole film on the ITO which was prepared in supercritical carbon dioxide in the presence of acetonitrile as a modifier and tetrabutylammonium hexafluorophosphate as an electrolyte [20]. The effect of the working electrode on the morphology of the polypyrrole films in the C/W emulsion was investigated, as shown in Fig. 3. Fig. 3b shows a wrinkle texture on the Ni electrode. The 3D image of the film indicated the presence of a fine nodular texture between the wrinkles. The 3D image of the film prepared on the ITO electrode (Fig. 3c) showed a similar nodular texture observed on the Pt electrode (Fig. 3a). However, the top view of the film clearly showed the presence of wrinkles. The width of the wrinkles observed for the film on the ITO electrode is narrower than that observed for the film on the Ni electrode. The width might be influenced by the thickness of the film. According to the morphology of the films on different electrodes, it seems that the resulting films prepared in the C/W emulsion typically have a nodular morphology. The reason for the wrinkled morphology is not clearly understood at this moment. Since the polypyrrole films prepared on the Ni or ITO electrodes were easily removed from the electrode surface in comparison with the films on Pt electrodes, we assume that
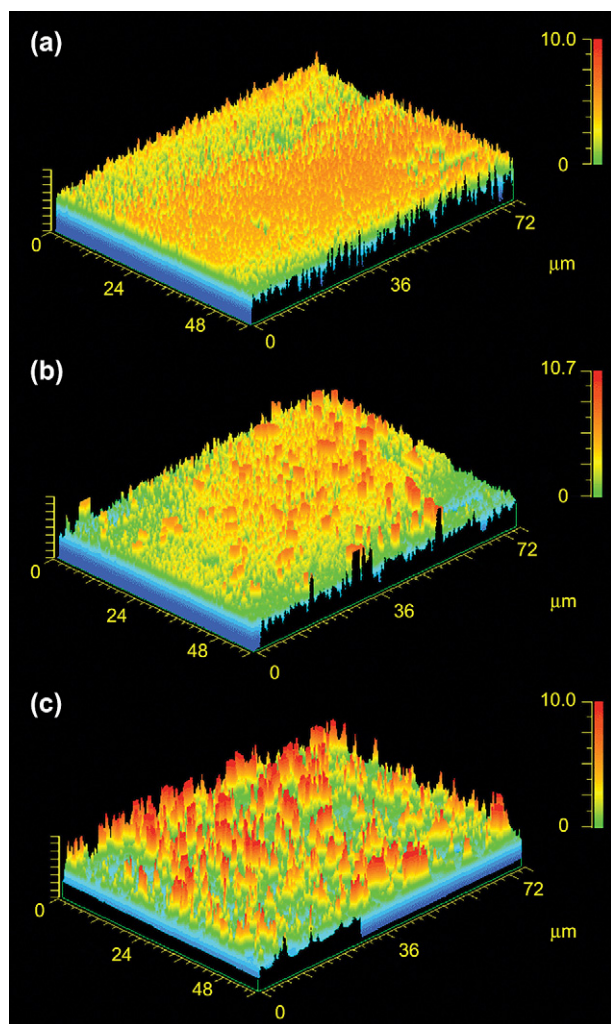

Fig. 2. 3D image of confocal scanning micrographs for the polypyrrole film prepared by electrochemical polymerization on Pt at the applied voltage of 1.4 V. (a) Prepared in the C/W emulsion (CO_2: 12 MPa) by the accumulated charge of 5.2 C; (b) prepared in water by the accumulated charge of 5.2 C; (c) prepared in hexane/water emulsion by the accumulated charge of 5.4 C.
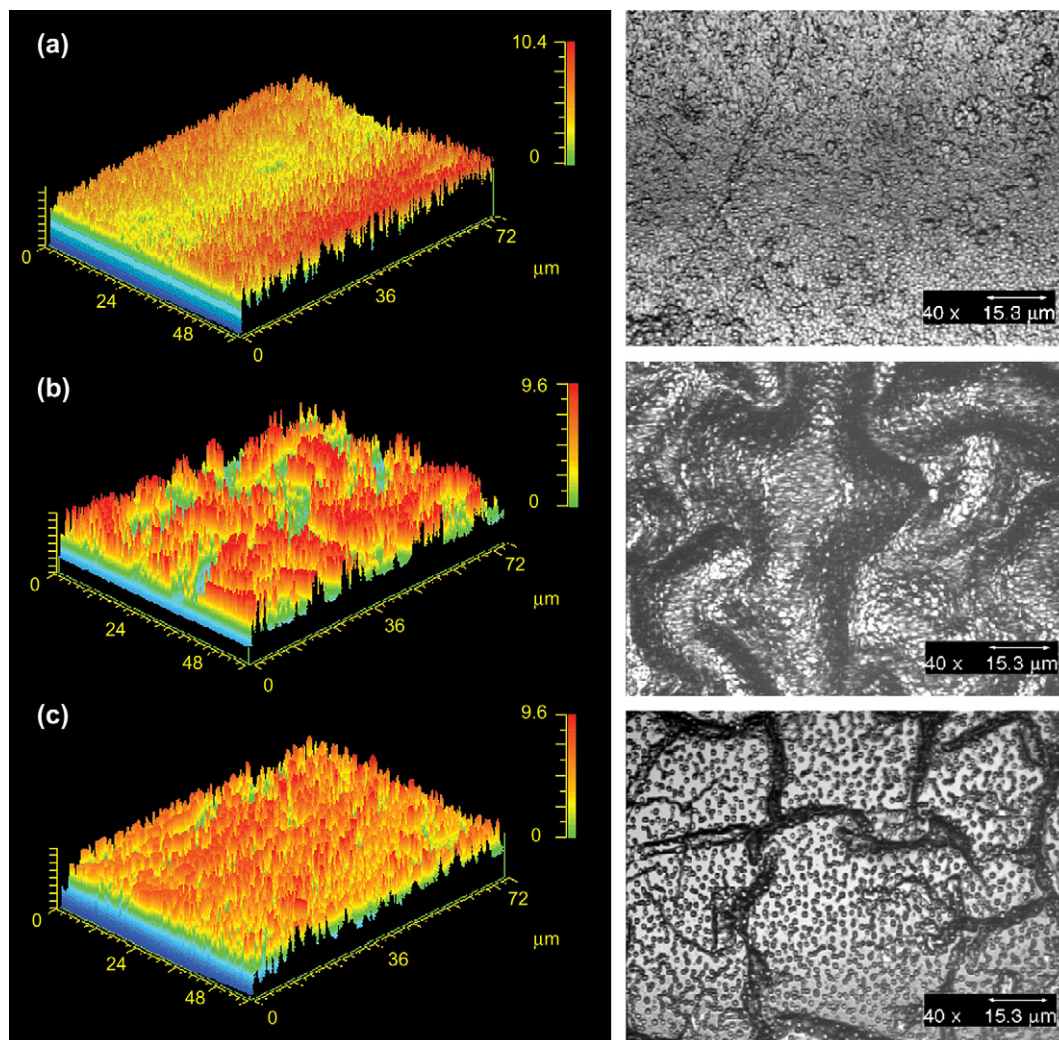
Fig. 3. Effect of the electrode on the morphology of the resulting polypyrrole films prepared by the electrochemical polymerization in the C/W emulsion at 35 °C and 12 MPa. (a) On Pt by the accumulated charge of 5.6 C; (b) on Ni by the accumulated charge of 5.5 C; (c) on ITO by the accumulated charge of 1.2 C.

the adhesion between the electrode and the resulting film significantly influences the formation of the wrinkles. During the electrochemical polymerization, carbon dioxide should have soaked into the resulting films. The release of the soaked carbon dioxide should occur during the pressure-releasing stage of the electrochemical polymerization. When the adhesion between the electrode and the resulting film is weak, the resulting film should have partially peeled from the electrode by the CO_2 release. This partial peeling might result in the formation of wrinkles.

The effect of the reaction pressure on the electrochemical polymerization of pyrrole in the C/W emulsion on the morphology is shown in Fig. 4. A fine nodular morphology was observed for the all 3D images and no noticeable difference in the morphology was observed in Fig. 4. Fig. 5 shows the effect of the reaction temperature on the morphology of the resulting films. Although a similar nodular texture was observed, each nodule on the film prepared at 5 °C became smaller. The roughness of the film (Ra) and the conductivity of the film are plotted versus the reaction temperature (Fig. 6). It is clear that the resulting film became smooth and conductive by lowering

the reaction temperature. It is reported that the conductivity of the polypyrrole films increased by lowering the reaction temperature [31]. The increase in conductivity is rationalized by minimizing the structural defects, such as α–β couplings. The same effect might influence the conductivity of the film prepared in this study.

The morphology of the polypyrrole films during the early stage of the electrochemical polymerization was investigated by AFM measurements, as shown in Fig. 7. The small nodules and their aggregates were observed for the film prepared by the electrochemical polymerization in the C/W emulsion for 5 ms (Fig. 7a). It is reported that small polypyrrole nodules are formed on a Pt electrode during the electrochemical polymerization at 1.3 V in an acetonitrile solution containing tetraethylammonium tetrafluoroborate during the initial stage (50 ms) [27]. The size of the small nodules in Fig. 7a is in the range of 100–200 nm. On the other hand, such small nodules were not observed on the film prepared by the electrochemical polymerization in water (Fig. 7c). Instead of the small nodules, the large aggregates about 1 μm were observed from the initial stage of the polymerization in water. When the
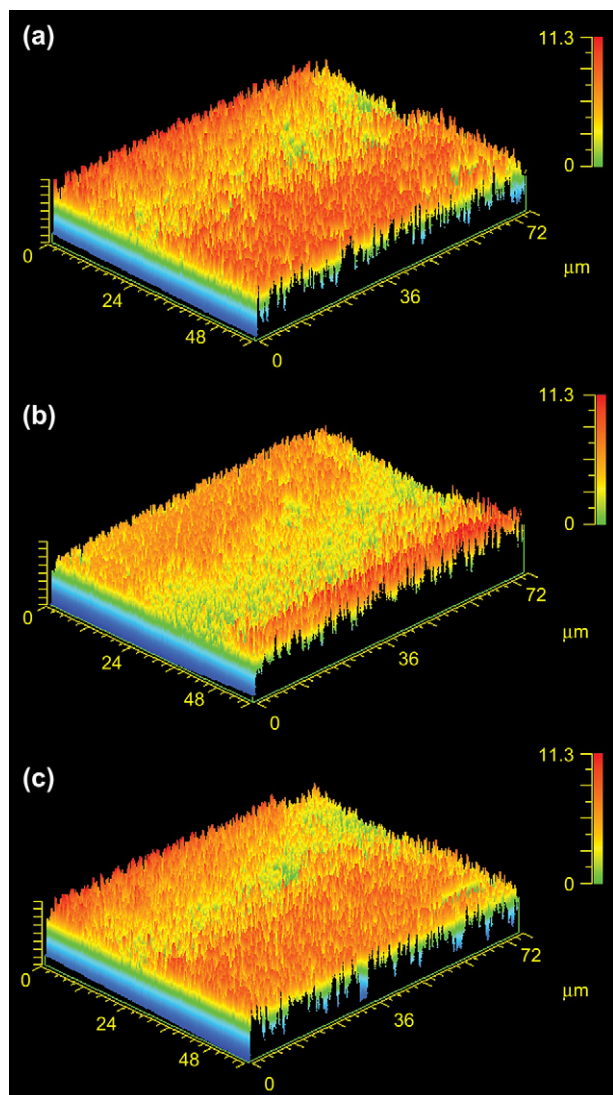
Fig. 4. Effect of the CO$_2$ pressure on the morphology of the resulting polypyrrole films prepared by the electrochemical polymerization on Pt in the C/W emulsion at 35 °C. (a) 8 MPa, 5.4 C; (b) 12 MPa, 5.4 C; (c) 20 MPa, 5.3 C.
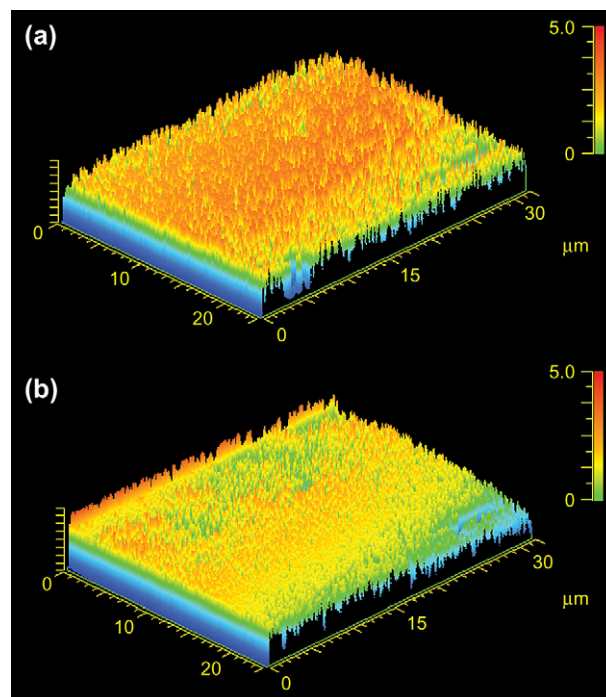

Fig. 5. Effect of the reaction temperature on the morphology of the resulting polypyrrole films prepared by the electrochemical polymerization on Pt in the C/W emulsion at 12 MPa. (a) 35 °C by the accumulated charge of 5.1 C; (b) 5 °C by the accumulated charge of 5.5 C.
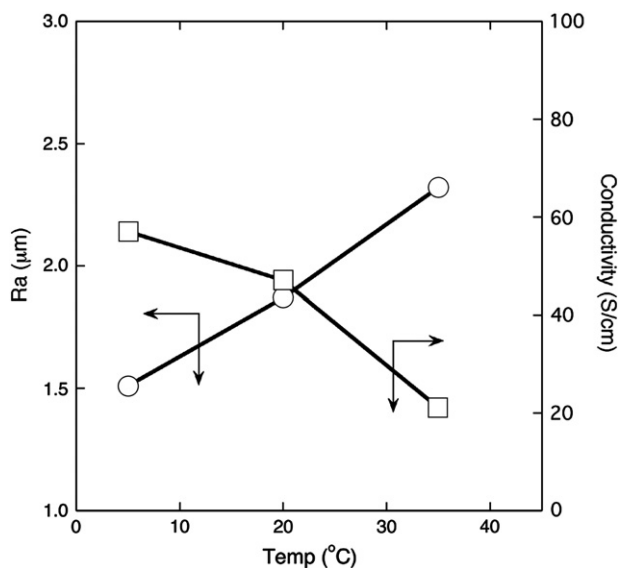

Fig. 6. Plot of the conductivity and the surface roughness (Ra) of the resulting polypyrrole films versus the reaction temperature for the electrochemical polymerization.

electrochemical polymerization was carried out for 10 s, the nodules were aggregated to form sub-micron to micron scale particles (Fig. 7b and d). The overall morphology seems to be similar to the cauliflower one reported in the literature [24–26]. The surface roughness (Ra) in Fig. 7b (32 nm) was higher than that of Fig. 7d (19 nm), which suggests that the film prepared in the C/W emulsion is rough in comparison with the film prepared in water. We assume that the formation of the small nodules during the early stage might influence the rough surface which finally results in the formation of the fine uneven texture, as shown in Fig. 2.

According to the data discussed in this section, it is clear that carbon dioxide influences the morphology of the resulting polypyrrole films. The widespread and fine uneven texture is typically observed for the film prepared in the C/W emulsion. The uneven texture was observed for the films prepared on different electrodes, at different pressures, and at different temperatures. The AFM image indicates the formation of small nodules during

the initial stage of the electrochemical polymerization in the C/W emulsion. During the electrochemical polymerization, the C/W emulsion continuously rinses the electrode surface. Therefore, the polymerization mixture can make good contact to the working electrode or the propagating film surface. It is also reported that the oxygen generated by the oxidation of water during the electrochemical polymerization significantly affects the morphology of the polypyrrole films [32,33]. Since carbon
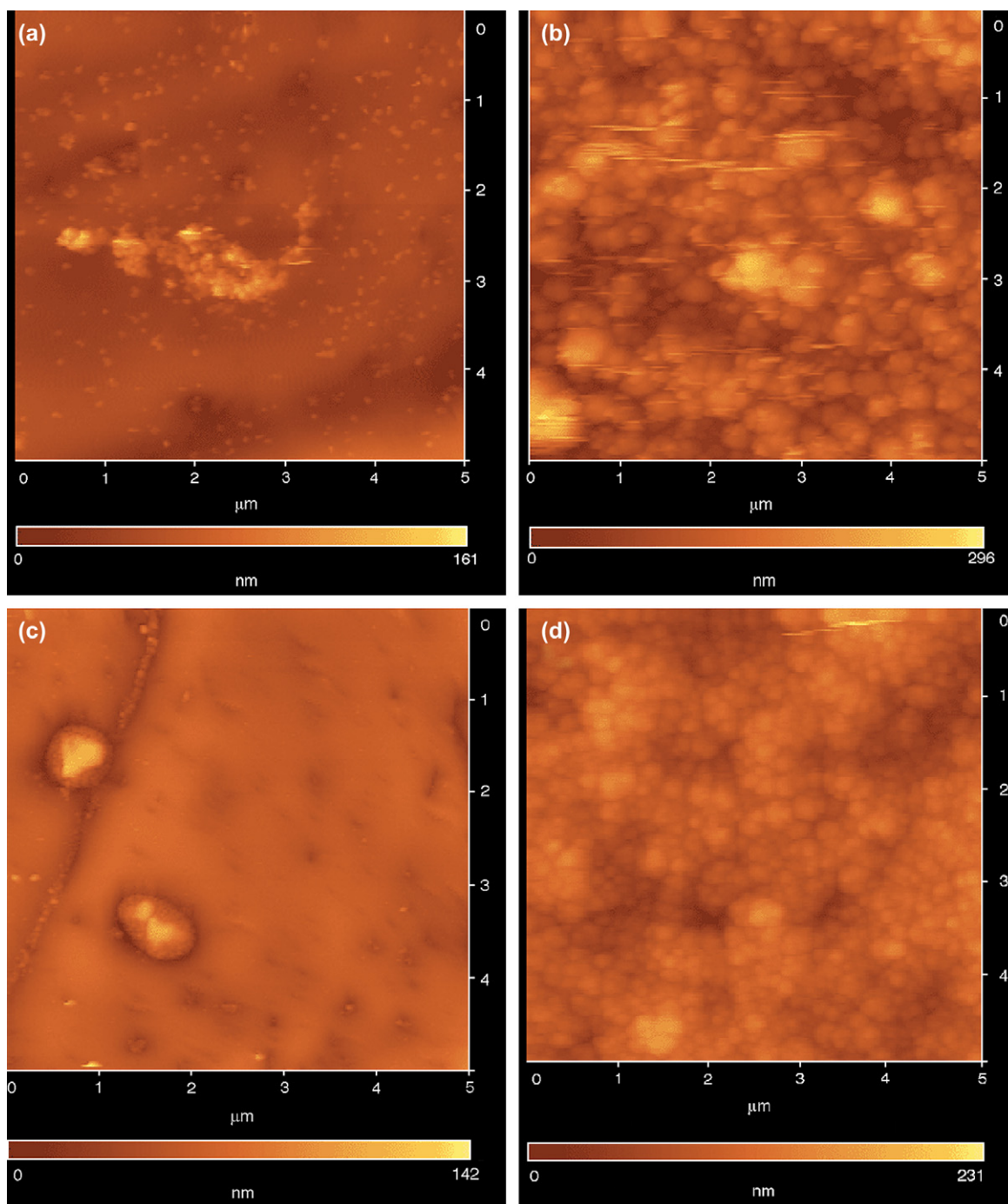
Fig. 7. AFM images of the polypyrrole films prepared on Pt in the C/W emulsion or in water for a different reaction period of the electrochemical polymerization. (a) In the C/W emulsion for 5 ms; (b) in the C/W emulsion for 10 s; (c) in water for 5 ms; (d) in water for 10 s.

dioxide is freely miscible with oxygen, the undesired effect by the oxygen can be minimized. As a result, small nodules formed during the initial stage can continuously propagate and aggregate to form the fine uneven texture. The same cleaning effect by carbon dioxide was also reported for the electroplating of nickel films in the C/W emulsion [34,35]. It cannot be ruled out that carbon dioxide influences the formation of nodules itself. It is reported that carbon dioxide plasticizes polymeric materials or accelerates crystallization of some polymers [36–42]. Unfortunately, we do not have any direct evidence if the carbon

dioxide in the C/W emulsion influences the nucleation and propagation reaction itself.

The conductivity of the resulting polypyrrole is typically in the range of 10–50 S/cm, which is higher than the conductivity previously reported using supercritical carbon dioxide as a reaction medium. The conductivity range in this study is comparable to the data reported for non-oriented polypyrrole prepared in conventional solvents. In other words, the enhancement of the conductivity of the resulting films by dense carbon dioxide was not observed. In fact, the pattern
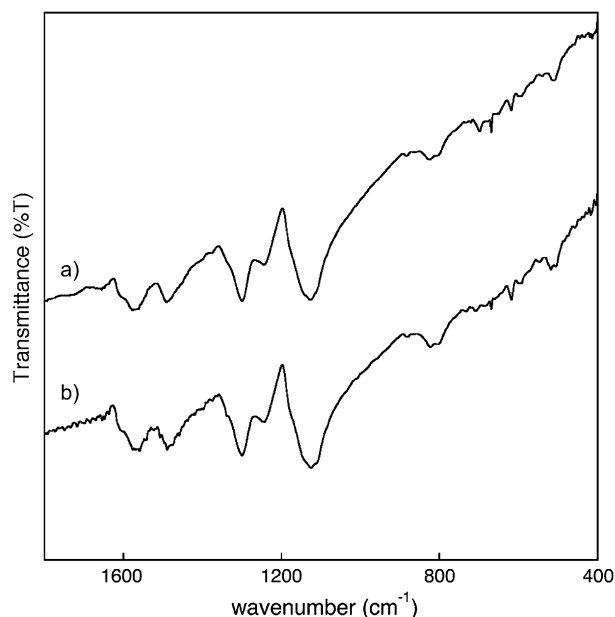
Fig. 8. IR spectra of the polyaniline prepared on Pt by the electrochemical polymerization at 35 °C. (a) In the C/W emulsion (12 MPa) by the accumulated charge of 6.1 C; (b) in water by the accumulated charge of 5.9 C.

of the wide angle X-ray diffraction for the film prepared in the C/W emulsion was consistent with the pattern for the film prepared in water. This consistency denies any additional orientation induced by the dense carbon dioxide.

3.2. Electrochemical polymerization of aniline in the C/W emulsion

The electrochemical polymerization of aniline was carried out in the same manner as the case for pyrrole. Sulfuric acid was used as the supporting electrolyte. After applying voltage (1.5 V) between the electrodes, a continuous current flow was observed during the polymerization. Black polyaniline was coated on the working electrode after the electrochemical polymerization. The IR spectra of the resulting film are shown in Fig. 8. The IR spectrum of the polyaniline prepared in the C/W emulsion was consistent with that of polyaniline prepared in water. The absorption bands attributed to the C−N stretching (1300 cm^{-1}) and skeletal vibration (1577, 1492 cm^{-1}) modes are indicative of the aniline unit. The strong and broad absorption band at 1127 cm^{-1} is attributed to the S=O stretching mode of the sulfonate anion as a dopant. It is confirmed that any side reactions such as carboxylation by carbon dioxide does not occur during the electrochemical polymerization.
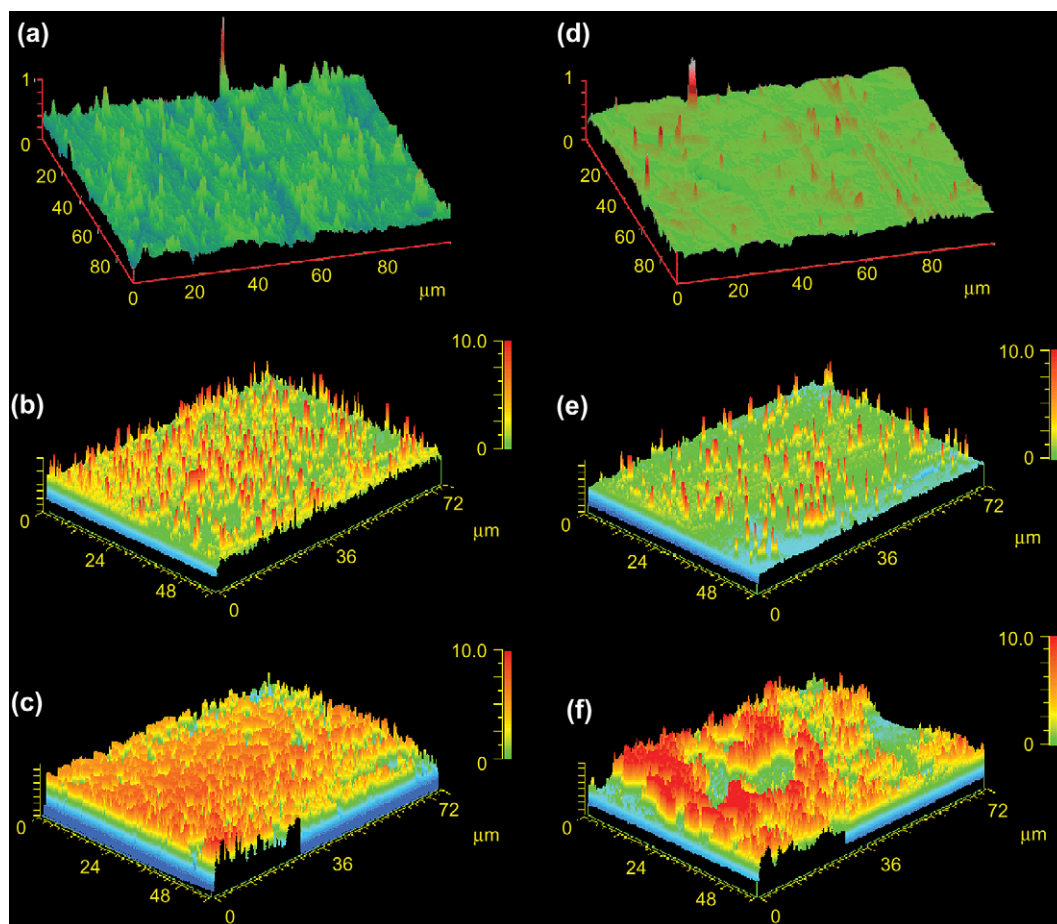

Fig. 9. AFM (a, d) and confocal scanning microscopic (b, c, e, f) images of the polyaniline films prepared on Pt in the C/W emulsion or in water by the electrochemical polymerization at 35 °C in the C/W emulsion for 100 ms (a); for 10 s (b); for 500 s (c); in water for 100 ms (d); for 10 s (e); for 500 s (f).
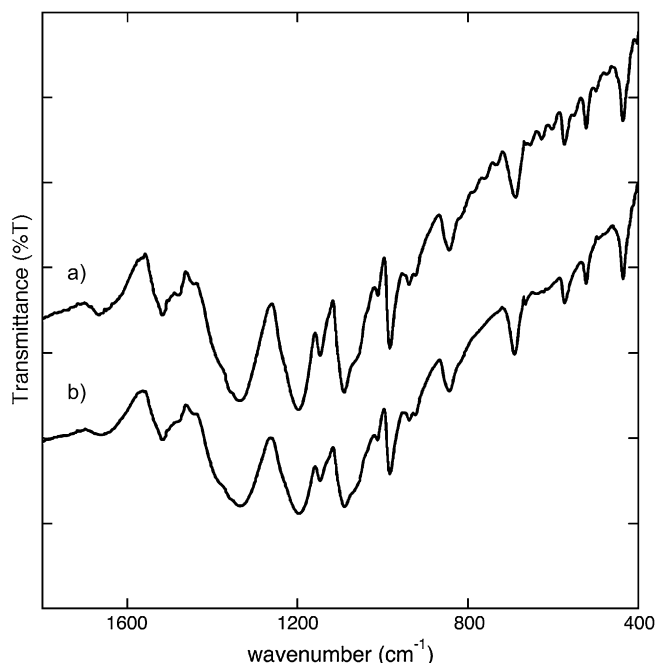
Fig. 10. IR spectra of the PEDOT prepared on Pt by the electrochemical polymerization at 35 °C. (a) In the C/W emulsion (12 MPa) by the accumulated charge of 5.9 C; (b) in water by the accumulated charge of 6.0 C.

The 3D images of the polyaniline films prepared on Pt electrodes are shown in Fig. 9. The film prepared in the C/W emulsion was homogeneously rough and small nodules were observed from the early stage of the polymerization (100 ms). On the other hand, the initial film prepared in water showed some spikes and a flat surface, and an irregular rough morphology was observed for the grown films. The morphological tendency of the polyaniline films is similar to the case for polypyrroles described in the previous section.

3.3. Electrochemical polymerization of EDOT in the C/W emulsion

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most attractive π-conjugated polymers because of its good conductivity and stability in an atmospheric environment [43,44]. It should be noted that 3,4-ethylenedioxythiophene (EDOT) is soluble in organic solvents but almost insoluble in water. A preliminary solubility test revealed that EDOT was soluble in supercritical carbon dioxide at 35 °C and 12 MPa. Therefore, EDOT should be supplied to the electrode surface from the CO_2 phase in the C/W emulsion during the electrochemical polymerization.

The electrochemical polymerization of EDOT was carried out in the same manner as the case for pyrrole. Tetraethylammonium perchlorate was used as the supporting electrolyte and the applied voltage between the electrodes was 1.5 V. A continuous current flow was observed during the polymerization, which suggests the formation of a conductive film on the working electrode. Blue PEDOT films were formed on the Pt or ITO electrode by the electrochemical polymerization in the C/W emulsion. Fig. 10 shows the IR spectra of the resulting PEDOT films. It was confirmed that the IR spectrum of the PEDOT prepared in the C/W emulsion was consistent with that of PEDOT prepared in water. The absorption bands attributed to the skeletal vibration modes (1518 and 1400 cm^{-1} (shoulder)) are indicative of the thiophene ring. The
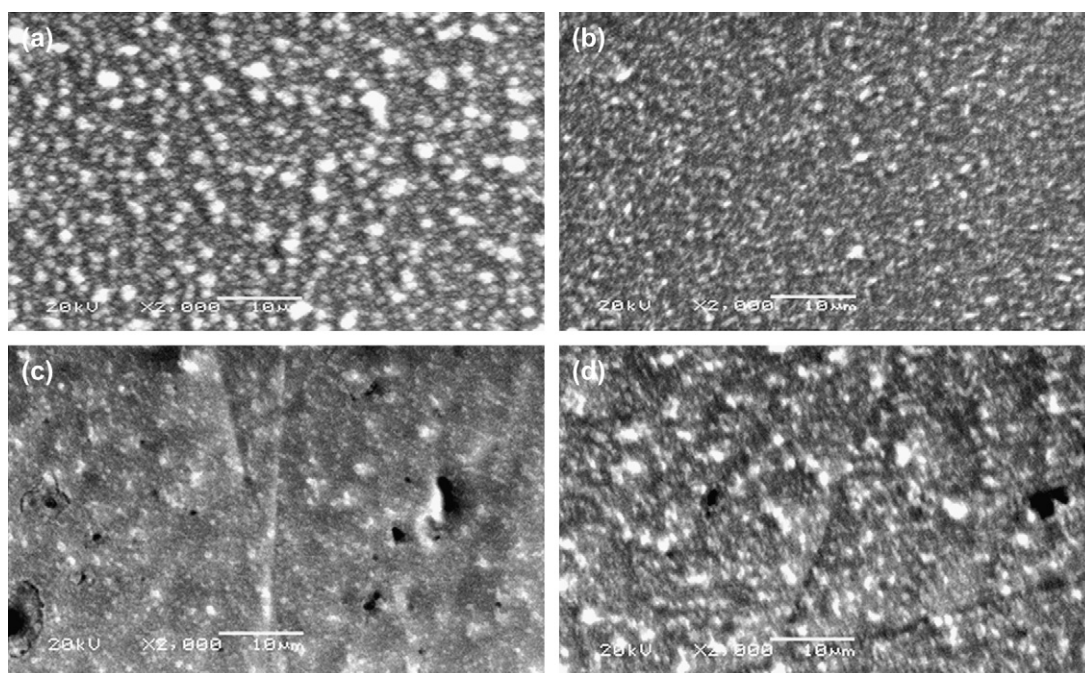

Fig. 11. SEM images of the PEDOT films prepared by the electrochemical polymerization at 35 °C in the C/W emulsion or in water. (a) In the C/W emulsion on ITO by the accumulated charge of 250 mC; (b) in water on ITO by the accumulated charge of 220 mC; (c) in the C/W emulsion on Pt by the accumulated charge of 250 mC; (d) in water on Pt by the accumulated charge of 210 mC.

absorption bands at 1147, 1091, and 688 cm^{-1} are attributed to the perchlorate anion as a dopant. Similar to the case for the polymerization of pyrrole and aniline, no side reactions, such as carboxylation by carbon dioxide during the electrochemical polymerization, were observed.

The SEM images of the PEDOT prepared in the C/W emulsion or water are shown in Fig. 11. When ITO was used as an electrode, a nodular morphology was observed on both films (Fig. 11a and b). The size and distribution of the nodules observed on the film prepared in the C/W emulsion are greater in comparison with the film prepared in water. Therefore, the film prepared in the C/W emulsion is rough and irregular. When Pt was used as the electrode, both films showed nodules and pinholes on the surface (Fig. 11c and d). Therefore, the morphological tendency of PEDOT films is quite different from that of polypyrrole and polyaniline films. Presumably, the solubility of the monomers influenced this different tendency. EDOT is soluble in supercritical carbon dioxide, but almost insoluble in water. Therefore, the EDOT should be supplied from the CO_2 phase in the C/W emulsion and the supply might not be efficient enough to form homogeneous films. In other words, water-soluble monomers, such as pyrrole and aniline, might be suitable for the formation of conductive polymer films with a fine uneven texture by the electrochemical polymerization in the C/W emulsion.

4. Conclusion

The electrochemical polymerization of pyrrole was investigated in order to characterize the features of the C/W emulsion as a reaction medium. The polymerization efficiently proceeds in the presence of a hydrophilic surfactant to form polypyrrole on Pt, Ni and ITO electrodes. One of the distinct features is the fine uneven texture of the resulting films. Small nodules were observed during the initial stage of the electrochemical polymerization in the C/W emulsion. Presumably, carbon dioxide in the emulsion continuously cleans the electrode surface, which allows it to propagate and to aggregate the initial nodules to form the fine uneven texture. The conductivity of the polypyrrole prepared in this study is comparable to the polypyrroles prepared in conventional solvents, and no enhancement in conductivity induced by the dense carbon dioxide was observed. The electrochemical polymerization of aniline in the C/W emulsion resulted in the formation of polyaniline films with a fine uneven texture, similar to the electrochemical polymerization of pyrrole. On the other hand, PEDOT films prepared by the electrochemical polymerization in the C/W emulsion were rough and irregular. It seems that water-soluble monomers are suitable for the electrochemical polymerization in the C/W emulsion to form a fine uneven texture.

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