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ORIGINAL CONTRIBUTION

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Electrochemical polymerization of aniline in SDS admicelles

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Abstract The electrochemical polymerization of aniline was studied in sodium dodecyl sulfate (SDS) admicelles. The results demonstrate that electrochemical polymerization of aniline can be catalyzed by admicelles. The catalytic efficiency in SDS solutions increased slowly with SDS concentration when the SDS concentration was very low, but increased rapidly when SDS admicelles formed on the electrode surface. The catalytic efficiency decreased with the addition of *n*-pentanol. The polyaniline films formed in SDS admicelles were nanometer films and the size of particles in the films increased with SDS concentration, but decreased with the addition of *n*-pentanol. Therefore, *n*-$C_5H_{11}OH$ can be used to regulate the electrochemical polymerization of aniline in SDS admicelles.

Keywords Electrochemical polymerization · Catalysis · Admicelle · Aniline

Introduction

Micelles are the aggregations formed by surfactant's molecules in solution. However, surfactants adsorbed at the solid/liquid interface also can form aggregates that are much like micelles, called admicelles. These admicelles can be used to solubilize some organic molecules in the same manner as micelles, which is called adsolubilization [1]. In recent years, catalytic effects of micelles on some organic and electrochemical reactions have been of great interest [2, 3, 4, 5, 6, 7, 8], but few references are available on the catalytic effects of admicelles.

Due to the commercial availability of the monomer, its easy synthesis, various structures, well-behaved electrochemical properties, good environmental stability, high conductivity and multiple redox and protonation states, polyaniline has been widely used in storage batteries, catalysis, electrochromic devices, light emitting diodes, non-linear optics and in a variety of sensors including chemical and biosensors [9, 10, 11, 12, 13, 14, 15, 16]. Since Leheby prepared polyaniline in 1862, electrochemical polymerization of aniline has been carried out almost entirely in aqueous acidic media [17, 18]. The most widely used laboratory-scale synthesis of electrically conducting polymer films is potentiostatic, galvanostatic and potential cycling [19]. The conducting properties of polymer films greatly depend on the methods of synthesis and different parameters such as electrolytes, synthesis temperature, deposition time, solvent, pH of electrolyte, etc. [20, 21, 22]. Thus, in order to improve the conducting properties of polymer films suitable for a particular application, it is necessary to critically control and optimize various synthesis parameters. In the present paper, polymerization of aniline is performed by cyclic voltammetry in sodium dodecyl sulfate (SDS) admicelles and the effects of the compositions of the admicelles on electrochemical polymerization of aniline are discussed in detail.

Materials and methods

Materials

SDS (Sigma, 98%) was recrystallized twice in ethanol. The surface tension of the recrystallized product had no surface tension minimum around the critical micelle concentration (*cmc*) by the platinum ring method. Aniline (Sigma, 99%) was distilled under reduced pressure before use. Sulfuric acid (MOS grade, 99.99%), *n*-pentanol (n-$C_5H_{11}OH$, Aldrich, 99+%), nitric acid (Sigma, 99.5+%), and twice-distilled and deionized water were also used.

Methods

Determination of voltammetric properties of aniline A 0.05 μm platinum foil electrode was polished with fine diamond paste before use. Then the electrode was washed with nitric acid and twice-distilled water after ultrasonic. A three-electrode system was employed using a platinum foil electrode as the working electrode and a saturated calomel electrode (SCE) as reference electrode. The voltammetric properties of 0.10 mol L^{-1} sulfuric acid were determined by a CHI660A potentiostat (Shanghai Chenhua, China) at a 0.10 V s^{-1} scan rate until a steady voltammogram was acquired. Then the platinum foil electrode was taken out and washed with twice-distilled water.

This platinum foil electrode was used as the working electrode to carry out electrochemical polymerization of aniline in SDS micelles or SDS/n-$C_5H_{11}OH$/ $H_2SO_{4(aq)}$ mixed micelles. The reference electrode was kept in close proximity to the working electrode to minimize the electrolytic ohmic drop.

Determination of electrochemical catalytic efficiency The electrochemical rate can normally be evaluated by the electrochemical reaction current. The magnitude of the polymerization rate of aniline can be represented by the polymerization current. At a given scan rate, the electrochemical catalytic efficiency is commonly defined as follows [23]:

$$\eta = \frac{i_a}{i_d} \quad (1)$$

where η is the catalytic efficiency, i_a and i_d are usually the anodic peak current with and without catalyst, respectively. In the present paper, i_a is the anodic peak current in SDS admicelles or SDS/n-$C_5H_{11}OH$ mixed admicelles with 0.10 mol L^{-1} sulfuric acid as solvent, and i_d is the anodic peak current in the 0.10 mol L^{-1} sulfuric acid solution.

Properties of polyaniline electrode The voltammetric properties of the polyaniline electrode were determined in 0.10 mol L^{-1} sulfuric acid by a CHI660A potentiostat with a polyaniline electrode (obtained from the experiment in the Determination of voltammetric properties of aniline section) as working electrode and SCE as reference electrode. The properties of the polyaniline electrode were evaluated according to its voltammetric properties and morphology. The morphology of polyaniline films and the size of particles in the films were observed using a scanning electron microscope (SEM) (TECNAI12 SEM, Philip Apparatus).

All of these experiments were carried out at 40 ± 0.1 °C. The samples were placed in a thermostat at 40 ± 0.1 °C for at least 4 h for phase equilibrium before the experiments.

Results and discussion

There were three couples of typical redox peak in the voltammogram for electrochemical polymerization of aniline in SDS micelles with 0.10 mol L^{-1} sulfuric acid as solvent (Fig. 1). The polymerization current of aniline increased with the number of scan cycles (Fig. 1) and was greater in SDS solution than in 0.10 mol L^{-1} sulfuric acid solution (Fig. 2).

The catalytic efficiency in SDS solution increased slowly with SDS concentration when the SDS concentration was very low, but the catalytic efficiency increased rapidly when SDS admicelles formed on the electrode surface (Fig. 3). However, the catalytic efficiency decreased with increasing n-$C_5H_{11}OH$ content or [$PhNH_2/H_2SO_4$(aq)] content (Fig. 4 and Fig. 5). The color of polyaniline films became darker and darker with the increasing SDS content and also varied from yellow to dark green with the potential from −0.2 V to 1.0 V.

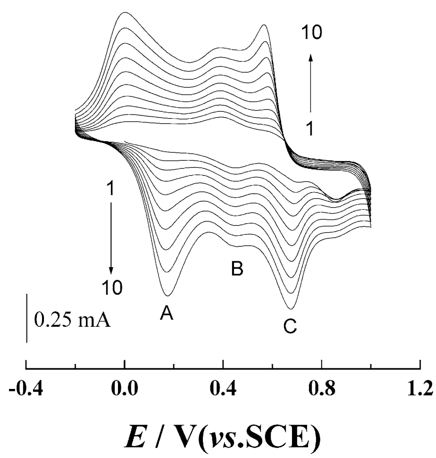

Fig. 1 Cyclic voltammogram for electrochemical polymerization of aniline. [$PhNH_2$] = 0.10 mol L^{-1}, [H_2SO_4] = 0.10 mol L^{-1}, v = 100 mV s^{-1}. *1* → 10 Scan cycles from the first one to the tenth

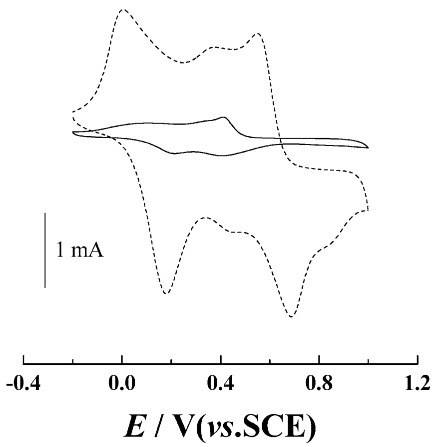

Fig. 2 Cyclic voltammogram for electrochemical polymerization of aniline. $[PhNH_2] = 0.10$ mol L^{-1}, $[H_2SO_4] = 0.10$ mol L^{-1}, $v =$ 100 mV×s^{-1}. *Solid line* In 0.10 mol L^{-1} H_2SO_4 solution, *dotted line* in SDS/0.10 mol L^{-1} H_2SO_4 micelle system.

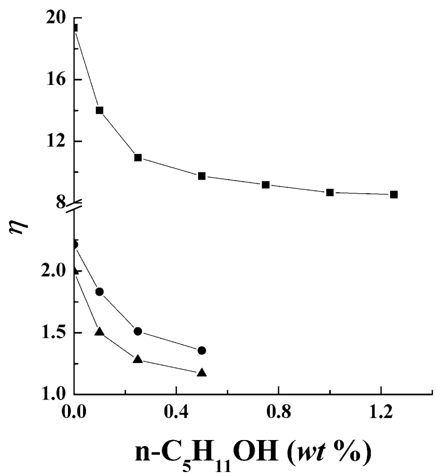

Fig. 4 Variety of the catalytic efficiency with the content of *n*-$C_5H_{11}OH$. Concentration of SDS: *triangle* 0.005 mol L^{-1}, *circle* 0.01 mol L^{-1}, *square* 0.05 mol L^{-1}

The SEM results show that the particles in the polyaniline films formed in SDS admicelles were nanometer ones, and that the size of particles in the films increased with SDS concentration (Fig. 6 and Fig. 7), but decreased with the increasing *n*-$C_5H_{11}OH$ content (Fig. 8).

Electrochemical polymerization of aniline

Figure 1 illustrates the cyclic voltammograms of the reaction at a potential scan rate of 100 mV×s^{-1}. The overall voltammetric feature of Fig. 3 is quite similar to the results of Borole [18] obtained in various supporting electrolytes. In the three couples of typical redox peaks of the voltammogram (Fig. 1), peak A (at about 0.20 V) corresponds to the formation of cationic radical, peak B (at about 0.45 V) to the formation of $C_6H_4N^+H_2^-$, and peak C (at about 0.70 V) to the structure of di-imine [24, 25]. The increase in polymerization current with the number of scan cycles in Fig. 1 indicates that the reaction of electrochemical polymerization of aniline is an autocatalytic reaction [26]. The polymerization of aniline includes two steps: formation and growing of films. In the first step, aniline is first oxidized at a certain potential to form radicals, and then the radicals react with aniline monomer to produce dimer, trimer, etc. In the second step, polymer is deposited on the platinum foil

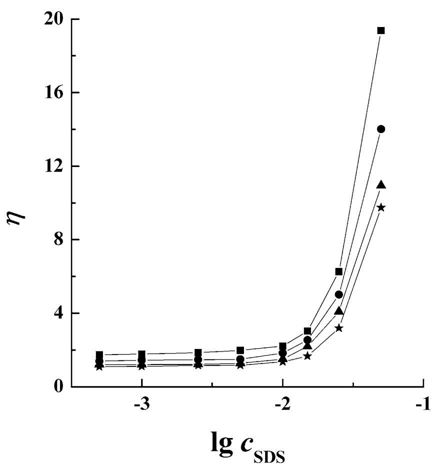

Fig. 3 Variety of the catalytic efficiency with the logarithm of SDS concentration. Content of *n*-$C_5H_{11}OH$: *square* 0%, *circle* 0.10%, *triangle* 0.25%, *star* 0.50%

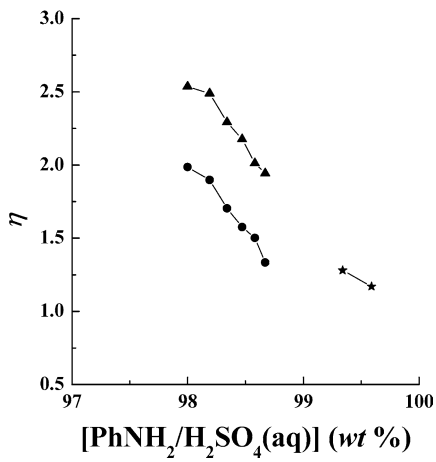

Fig. 5 Variety of the catalytic efficiency with the content of $[PhNH_2/H_2SO_{4(aq)}]$. Weight ratios of SDS/*n*-$C_5H_{11}OH$: *circle* 98/2, *triangle* 99/1, *star* 72/28

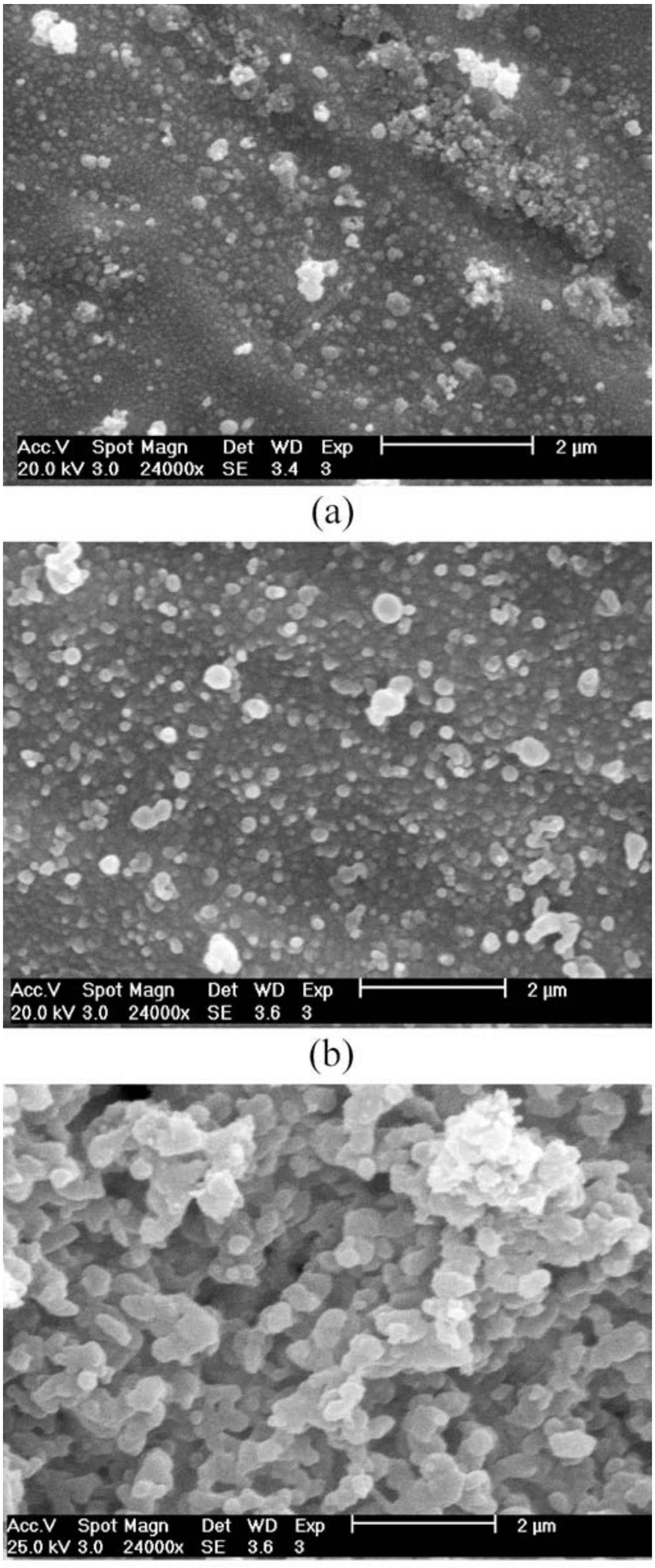

Fig. 6 SEM images of polyaniline films formed in SDS admicelles. Concentration of SDS: **a** 0 mol L^{-1}, **b** 0.005 mol L^{-1}, **c** 0.05 mol L^{-1}

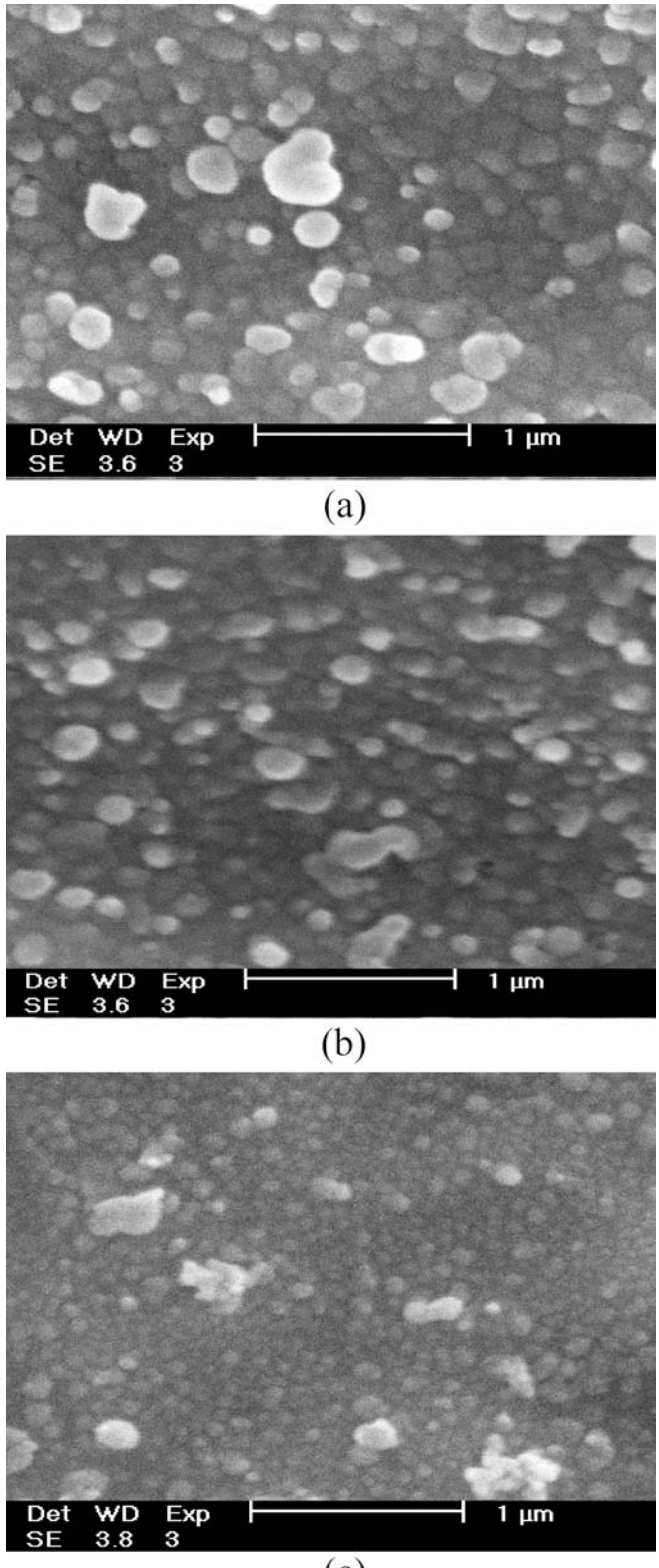

Fig. 7 SEM images of polyaniline films formed in SDS/*n*-$C_5H_{11}OH$ mixed admicelles. Concentration of SDS: **a** 0.0005 mol L^{-1}, **b** 0.005 mol L^{-1}, **c** 0.05 mol L^{-1}. Content of *n*-$C_5H_{11}OH$: 0.25%

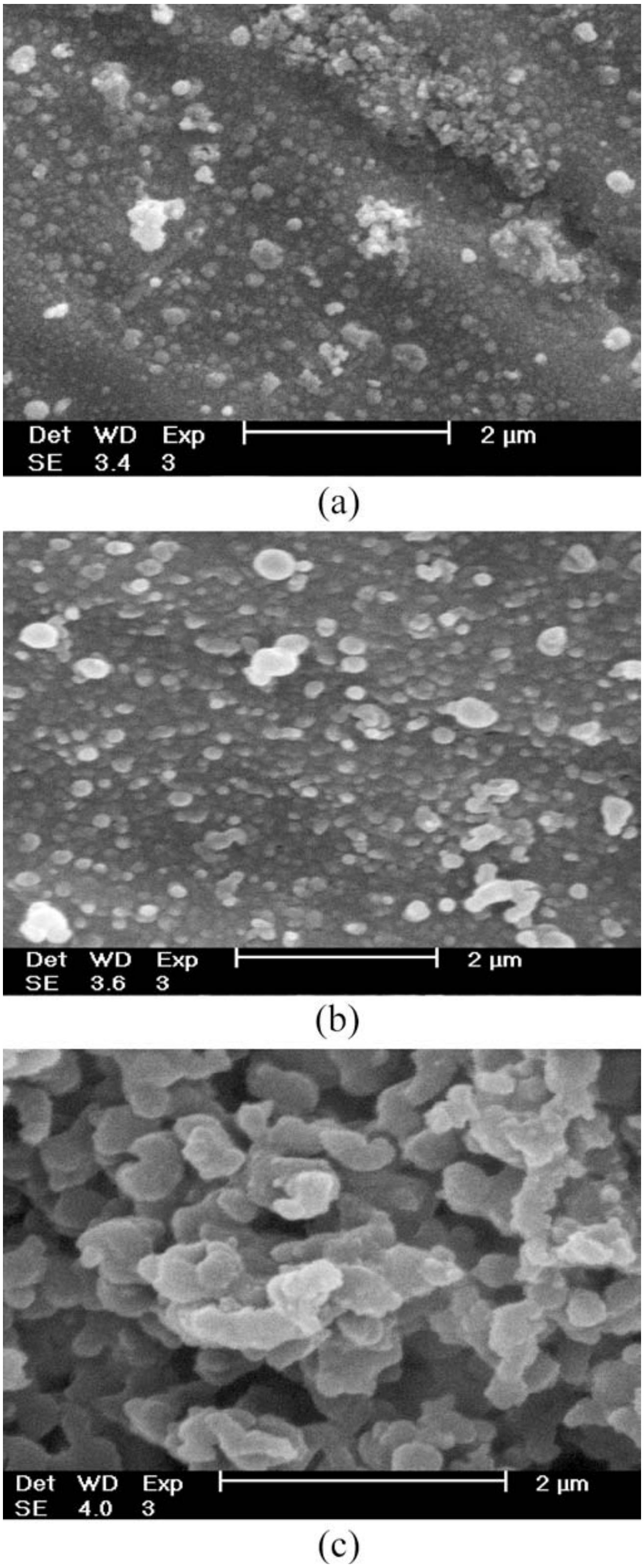

Fig. 8 SEM images of polyaniline films formed in SDS/n-$C_5H_{11}OH$ mixed admicelles. Concentration of SDS is 0.05 mol L^{-1}. Content of n-$C_5H_{11}OH$: **a** 0.25%, **b** 0.50%, **c** 1.25%

electrode to form a lamellar polyaniline film (Fig. 9), which may be related to the template of orderly surfactant aggregations on the electrode surface.

Catalytic properties of SDS admicelles

When SDS concentration is very low, SDS anions are absorbed in an orderly fashion on the surface of the platinum foil electrode, which increases the hydrophobicity of the electrode surface and is beneficial to the stability of aniline cationic radicals. Thus, the catalytic efficiency increases, but very slowly (Fig. 3). Then, admicelles are formed on the electrode surface and the catalytic efficiency starts to increase with the increasing SDS content, because the solubilization of aniline in admicelles is also beneficial to the stability of aniline cationic radicals.

As in micelle solution [27, 28, 29, 30], the apparent rate (R_{app}) of a chemical reaction in admicellar system is usually considered to be the sum of the rates in the continuous aqueous phase (R_w) and in the admicellar "pseudophase" (R_{adm}):

$$R_{app} = R_w + R_{adm} \quad (2)$$

Under normal circumstances, the solubility of organic reactants in water is very small. So the rate of the reaction in the continuous aqueous phase (R_w) can be negligible. Thus,

$$R_{app} \approx R_{adm} = k_{adm}[A]^n_{adm} \quad (3)$$

where k_{adm} is the rate constant, $[A]_{adm}$ is the concentration of aniline and n is the order of the reaction in the admicellar phase. According to the law of mass conservation, the following equation can be derived:

$$[A]V_t = [A]_w V_w + [A]_{adm} V_{adm} \quad (4)$$

where, [A] is the total concentration of aniline in the solution, V_t is the total volume of the solution, V_w and V_{adm} are the volumes of the continuous aqueous and admicellar phases, respectively. Equation 4 can be rearranged to:

$$[A] = \frac{V_w}{V_t}[A]_w + \frac{V_{adm}}{V_t}[A]_{adm} \quad (5)$$

$$[A] = \frac{V_w}{V_t}[A]_w + \phi_{adm}[A]_{adm} \quad (6)$$

where Φ_{adm} ($\phi_{adm} = \frac{V_{adm}}{V_t}$) is the volume fraction of admicelles. Because the solubility of aniline in water is very small, the first term in the right of Eq. 6 can be negligible, and Eq. 6 can be rearranged to:

$$[A]_{adm} \approx \frac{[A]}{\phi_{adm}} \quad (7)$$

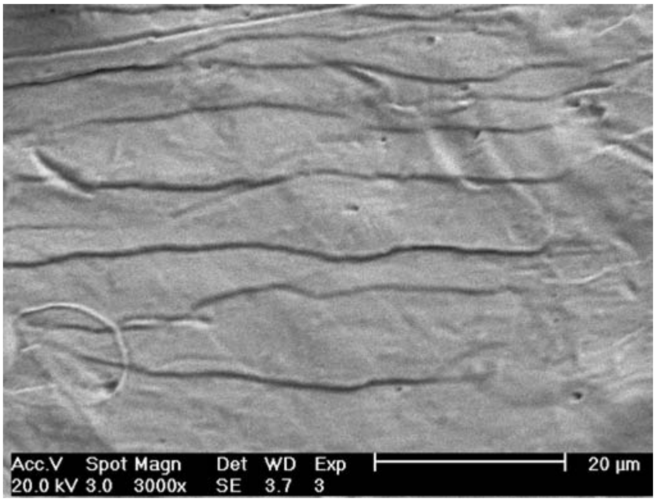

Fig. 9 SEM image of lamellar polyaniline film formed in SDS admicelles. Concentration of SDS: 0.005 mol L^{-1}

So the actual concentration of aniline in admicellar phase $[A]_{adm}$, is approximately $\frac{[A]}{\phi_{adm}}$, and Eq. 3 can be rearranged to:

$$R_{app} \approx k_{adm}[A]^n_{adm} = k_{adm}\left(\frac{[A]}{\phi_{adm}}\right)^n \qquad (8)$$

Therefore, the apparent rate of the polymerization reaction (R_{app}) is proportional to $[A]^n$ or $[A]_{adm}{}^n$. The aggregation number of SDS admicelles increases with SDS content [31, 32]. So the amount of aniline adsolubilized in admicelles increases with SDS content. Therefore, the polymerization rate of aniline (R_{app}) increases (Fig. 3), and the size of particles in polyaniline films becomes larger (Fig. 6 and Fig. 7) with increasing SDS content.

However, the stability of SDS admicelles on the electrode surface decreases with the addition of *n*-pentanol so that the amount of aniline solubilized in admicelles decreases. Thus, electrochemical polymerization rate, catalytic efficiency and the size of particles decrease with the addition of *n*-pentanol (Fig. 4 and Fig. 8). Therefore, *n*-pentanol can be used to regulate the rate of the electrochemical polymerization of aniline in SDS admicelles and the size of polyaniline particles in the films.

The effects of SDS content on the catalytic efficiency in SDS/n-$C_5H_{11}OH$ mixed admicelles are similar to those in SDS admicelles. The polymerization rate of aniline and the size of particles in the polyaniline films increase with the addition of SDS (Fig. 3 and Fig. 7).

Further, the solubilization of aniline in SDS admicelles is decreased by the addition of [$PhNH_2/H_2SO_{4(aq)}$], which make the catalytic efficiency decrease (Fig. 5).

To conclude, the electrochemical polymerization of aniline can be catalyzed by SDS admicelles. The catalytic efficiency in SDS solution increases slowly with SDS concentration when SDS concentration is very low, but increases rapidly when SDS admicelles are formed on the electrode surface. The catalytic efficiency decreases with increasing *n*-pentanol content or [$PhNH_2/H_2SO_{4(aq)}$] content, but increases with SDS content in SDS admicelles. The polyaniline films formed in SDS admicelles were nanometer films and the size of particles in the films increased with SDS concentration, but decreased with increasing *n*-pentanol content. Therefore, n-$C_5H_{11}OH$ can be used to regulate the electrochemical polymerization of aniline in SDS admicelles.

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