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ORIGINAL PAPER

Preparation and characterization of Pd/PPy-SDS/foam-Ni and Pd/PPy-CTAB/foam-Ni electrodes with high electroactive surface area

Zhirong Sun · Lin Ma · Xiang Hu

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Abstract Surfactant-doped electrodes, palladium/polymeric pyrrole-sodium dodecyl sulfate/foam-nickel (Pd/PPy-SDS/foam-Ni) electrode and palladium/polymeric pyrrole-cetyl trimethyl ammonium bromide/foam-nickel (Pd/PPy-CTAB/foam-Ni) electrode, were prepared by electrochemical deposition method. The characteristics of the prepared electrodes were investigated. Based on the results of scanning electron microscope, X-ray diffraction, inductively coupled plasma-atomic emission spectrometry, and cyclic voltammetry tests, both of the two surfactants could improve the electrodes' electrocatalytic activity. Results also indicate that Pd/PPy-SDS/foam-Ni electrode has higher catalytic potential capability than Pd/PPy-CTAB/foam-Ni electrode.

Keywords Pd/PPy-SDS/foam-Ni electrode · Pd/PPy-CTAB/foam-Ni electrode · Electrodeposition · Dechlorination

Introduction

Chlorinated organic compounds, which often accumulate in fatty issues and show carcinogenic and mutagenic activity [1], are difficult to be dealt with. Because of the toxic nature, chlorinated organic compounds with high initial concentration are not suitable to be degraded by conventional biological methods. Incineration process involves high costs, harmful byproducts, and adverse public reaction [2]. New technologies for the degradation of chlorinated compounds are highly desirable.

Electrochemically reductive process is emerging as a promising method for the degradation of chlorinated compounds. The process of electrochemical reduction involves electrocatalytic hydrogenolysis [3] and electrocatalytic hydrogenation [4]. The former involves the reductive cleavage of σ bonds, whereas the latter involves the addition of hydrogen to π bonds. As in the electrochemically reductive dechlorination, the electrocatalytic hydrogenolysis is the major reaction for the cleavage of C–Cl bonds. Palladium (Pd) is considered as the most ideal catalyst for dechlorination due to its unique function in absorption and adsorption of hydrogen [5, 6]. However, it is not adapted to large-scale application because of its high cost. A sound way to limit the amount of Pd is to electrodeposit it to a less expensive substrate material such as foam-nickel (Ni) [7] or glassy carbon. High dispersity and large surface area of Pd particles are desirable for the electrochemically reductive dechlorination process.

Since the discovery of electric conductivity polymers [8-11], especially polymeric pyrrole (PPy), the field of electrode material science has been developed rapidly, in virtue of their high electrical conductivity, chemical stability, and satisfactory processability. Conductive polymers can be used as proper host matrices to obtain highly dispersed metallic particles [12]. Metal microparticles dispersed on polymer-modified electrodes have been recognized to have potential applications in electrocatalysis.

In this paper, to get highly dispersed Pd particles and large surface area of electrode, we developed a method for

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the synthesis of thin conductive polymeric film with promising electrocatalytic properties. Surfactants and pyrrole (Py) were utilized as dopants, and foam-Ni was chosen as the substrate material for its porous structure. Pd particles were electrodeposited on the polymeric film to prepare the composite electrode for dechlorination. In order to investigate the effects of surfactants, we chose two kinds of surfactants, the anionic surfactant-sodium dodecyl sulfate (SDS) and the cationic surfactant-cetyl trimethyl ammonium bromide (CTAB). The preparation conditions of the two electrodes were investigated respectively, and their properties were characterized and compared.

Experimental protocols

Chemicals and materials

Experimental chemicals included acetone, Py, SDS, CTAB, sulfuric acid (98%), hydrochloric acid, alumina powder, and Pd chloride powder (chemicals above were all of analytical standard, supplied by Beijing Reagent Co.). The aperture and surface density of foam-Ni were 90 PPI (point per inch) and 400 ± 30 gm^{-2}, respectively. Electrodepositing process was conducted with constant electrode surface area ($2.0\times2.0\times0.15$ cm; total geometrical surface area was 8.9 cm^2). Solutions were all prepared with Millipore-Q water.

Experimental methods

Substrate pretreatment

The substrate of foam-Ni plate was pretreated first. It was placed in 0.5 mol L^{-1} sulfuric acid solution for 1 min to remove the surface oxides. Then, it was placed under ultrasonic conditions in acetone for 10 min to degrease and in Millipore-Q water for 10 min to clean further. Finally, it was rinsed thoroughly with Millipore-Q water and dried at room temperature for later use.

Electrode preparation

Prior to electropolymerization, the solution was deoxygenated by N_2 for 5 min. Foam-Ni plate was used as the anode, and the platinum foil was used as cathode. PPy-SDS film and PPy-CTAB film were formed, respectively, on the surface of foam-Ni substrate by electrodepositing in a 50-mL mixed solution containing 0.5 mol L^{-1} sulfuric acid, 0.04 mol L^{-1} distilled Py, and SDS or CTAB. Pd/PPy-SDS/foam-Ni electrode and Pd/PPy-CTAB/foam-Ni electrode were prepared by electrodeposition in Pd chloride solution with concentration of 22.5 mmol L^{-1}. In this process, the platinum foil was used as anode, and the foam-Ni supporting electrode with polymeric film was used as cathode. Electrodepositing current density and electrodepositing time of Pd particles on these two kinds of supporting electrodes were studied, respectively.

Analysis

Electrochemical characterization of Pd/PPy-SDS/foam-Ni electrode and Pd/PPy-CTAB/foam-Ni electrode was conducted by cyclic voltammetry (CV) using a Model CHI 660C Potentiostat/Galvanostat. A platinum foil was used as the counter electrode, and an Hg/Hg_2SO_4-saturated K_2SO_4 electrode was used as the reference electrode. The morphology of the electrode's surface was studied by scanning electron microscope technique (SEM, JEOL JSM 6500F, Japan). Nitrogen adsorption isotherms were measured at 77 K in the range of relative pressures from 10^{-6} to 0.995 using Micromeritics ASAP 2020. Prior to adsorption measurements, the samples were outgassed under vacuum at 373 K for 3 h in the port of the adsorption analyzer. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The crystalline feature of Pd particles dispersed on the surface of the electrode was determined by X-ray diffraction (XRD) using a D8 Discover with Gadds diffractometer with Cu-Kα radiation, operating at 40 kV and 50 mA (Bruker/AXS, Germany). The loading level of Pd particles was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, RIS Intrepid ER/S, Thermo Elemental, USA).

Results and discussion

Electrode preparation

According to the theory of electrochemically reductive dechlorination [13], adequate adsorption of hydrogen atoms on an electrode is the key step of the dechlorination reaction. Higher hydrogen adsorption/desorption peak current in the voltammograms indicates larger quantity of adsorbed/desorbed hydrogen atom on the electrode [14, 15]. Consequently, electrodes with higher hydrogen adsorption peak current will be more effective for electrochemically reductive dechlorination of chlorinated organic compounds.

Preparation of PPy-SDS film and PPy-CTAB film on foam-Ni substrate

It has been demonstrated that surfactants are effective for chemical and electrochemical polymerization of PPy [16-19]. Comparing with the solution that only contains Py, the surface property of surfactant-Py system can be changed in a large scale. Surfactants can accelerate the reaction of

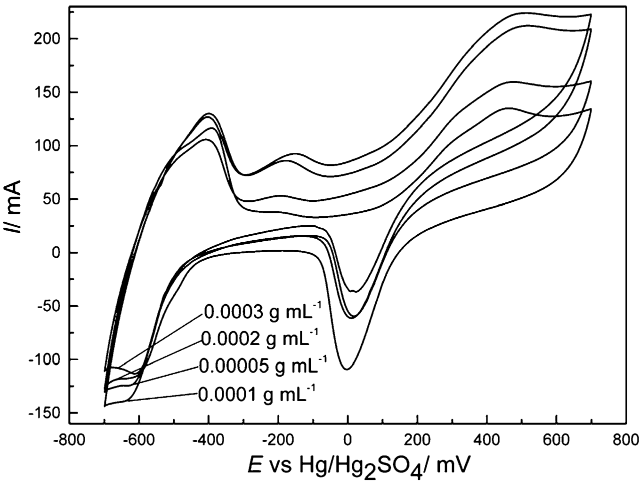

Fig. 1 Cyclic voltammetry curves of Pd/PPy-SDS/foam-Ni electrodes prepared at different SDS concentrations. PPy-SDS electrodepositing current density, 0.562 mA cm^{-2}; electrodepositing time, 3 min; Pd electrodepositing current density, 1.011 mA cm^{-2}; electrodepositing time, 35 min. Voltage range, −700∼700 mV; electrolyte, 0.5 mol L^{-1} H_2SO_4 solution; scanning rate, 50 mV s^{-1}

polymerization and make the polymeric film extend well. Py can also affect the surfactant's physicochemical property, such as surface tension, viscosity, conductivity, and critical micelle concentration (CMC). Hence, the solution that contains both Py and surfactant combines their advantages and has some special properties which are different from that with only surfactant or Py. On a general basis, the driving forces for surfactants associated with polymer are electrostatic, dipolar, and hydrophobic in nature. Electrostatic force and hydrophobic force are the main driving forces [20]. Neutral polymers are known to interact with both anionic and cationic surfactants, but their binding modes are different. The anionic surfactants are found to exhibit stronger interaction with polymers than cationic surfactants with similar chain length [20].

The concentration of the surfactant plays an important role in the electropolymerization process [18]. Generally, the surfactant exists as single molecule below CMC and does not react with Py. Once the concentration reaches CMC, the surfactant begins to congregate on Py and react with it. However, the interaction between surfactant and Py will reach the maximum if the surfactants' concentration increases to some extent. To get the appropriate concentration of SDS or CTAB, a series of experiments were conducted. Pd catalysts were also electrodeposited on the prepared PPy-SDS and PPy-CTAB films under the fixed current density of 1.011 mA/cm^2 and the fixed electrodepositing time of 35 min. The deposited Pd particles were used as the catalysts for producing larger amount of hydrogen atoms from H_2O (producing Pd-H species) and causing higher peak current in CV measurements. Because the deposition conditions of Pd catalysts in all experiments in Figs. 1 and 2 were the same, the differences of hydrogen adsorption peak current in CV curves were believed to be contributed by PPy-SDS and PPy-CTAB film deposition conditions.

The fixed electrodepositing current density and time for the preparation of PPy-SDS and PPy-CTAB films were 0.562 mA cm^{-2} and 3 min, respectively. Pd/PPy-SDS/foam-Ni electrodes were prepared under different concentrations of SDS (0.00005, 0.0001, 0.0002, and 0.0003 gmL^{-1}, respectively), and Pd/PPy-CTAB/foam-Ni electrodes were prepared under different concentrations of CTAB (0.0001, 0.0002, 0.0003, 0.0004, and 0.0005 gmL^{-1}, respectively). The CV curves of the two kinds of electrodes were shown in Figs. 1 and 2, respectively. The two figures indicate that with the increase of the surfactant concentration, the effects of the two surfactants on the electrodes almost have the same tendency. The value of hydrogen adsorption peak current increases first, and then decreases after reaching a maximal value. The maximal hydrogen adsorption peak values were obtained with SDS concentration of 0.0001 gmL^{-1} and CTAB concentration of 0.0003 gmL^{-1}, respectively. When the surfactant concentration is low, the polymeric film grows slowly. Then, the film is relatively thin, and the force between the film and Pd particles is not strong. As a result, Pd particles will come off easily during electrodepositing or rinsing. This will result in a low value of the hydrogen adsorption peak current. With the surfactant concentration increasing, the polymeric film becomes thicker, and Pd particles could disperse uniformly on the whole film for their acting forces are being strengthened. So, the electrocatalytic capability of the electrode can be enhanced. However, when the concentration exceeds a certain value,

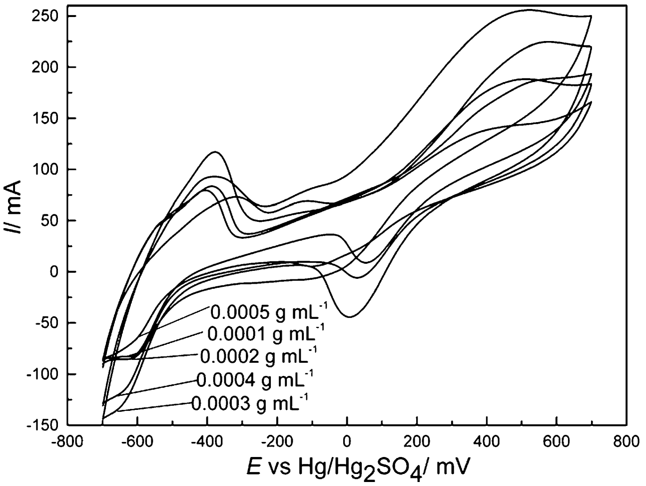

Fig. 2 Cyclic voltammetry curves of Pd/PPy-CTAB/foam-Ni electrodes prepared at different CTAB concentrations. PPy-CTAB electrodepositing current density, 0.562 mA cm^{-2}; electrodepositing time, 3 min; Pd electrodepositing current density, 1.011 mA cm^{-2}; electrodepositing time, 35 min. Voltage range, −700∼700 mV; electrolyte, 0.5 mol L^{-1} H_2SO_4 solution; scanning rate, 50 mV s^{-1}

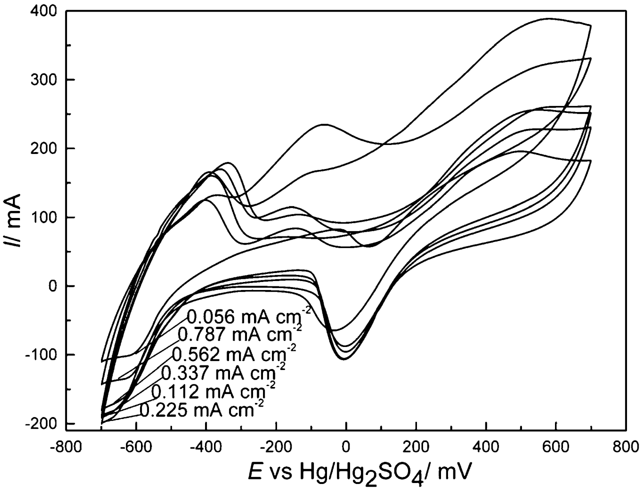

Fig. 3 Cyclic voltammetry curves of Pd/PPy-SDS/foam-Ni electrodes prepared at different electrodepositing current densities. Voltage range, −700~700 mV; electrolyte, 0.5 mol L^{-1} H_2SO_4 solution; scanning rate, 50 mV s^{-1}

the number of nucleation sites on the surface of the polymeric film will reduce. Then, Pd particles will congregate, and the value of the hydrogen adsorption peak current will decrease. Therefore, SDS concentration of 0.0001 gmL^{-1} and CTAB concentration of 0.0003 gmL^{-1} were the proper concentrations and were selected as the preparation constants for PPy-SDS film and PPy-CTAB film on foam-Ni substrate, respectively.

Preparation of Pd/PPy-SDS/foam-Ni and Pd/PPy-CTAB/foam-Ni electrodes

On the basis of the selected electrodepositing conditions of PPy-SDS and PPy-CTAB films, electrodepositing conditions of Pd particles were studied further. Generally, high dispersity and large surface area of Pd particles are desirable for the dechlorination process. In addition, according to the dechlorination mechanism proposed by Cheng [21] and Tsyganok [22], a speculation can be made that both foam-Ni surface and the dispersed Pd particles are required for the dechlorination. The electrodepositing current density and time are two critical factors affecting the configuration of Pd particles on the electrode and influence the catalytic performance of electrode. When the electrodepositing current density is low, the Pd particles may be electrodeposited insufficiently. When the electrodepositing current density is very high, the Pd particles may be electrodeposited too thick to reduce the surface of foam-Ni substrate. Both of the two situations will result in low hydrogen adsorption peak value and may go against the efficiency of the dechlorination reaction. The electrodepositing time may have the same effect on the value of hydrogen adsorption peak.

Firstly, Pd electrodepositing current density was investigated under the fixed Pd electrodepositing time of 35 min. Figure 3 shows the CV curves of Pd/PPy-SDS/foam-Ni electrode under different Pd electrodepositing current densities (0.056, 0.112, 0.225, 0.337, 0.562, and 0.787 mA cm^{-2}, respectively), and Fig. 4 illustrates the CV curves of Pd/PPy-CTAB/foam-Ni electrode under different Pd electrodepositing current densities (0.112, 0.337, 0.562, and 0.787 mA cm^{-2}, respectively). With the electrodepositing current density increasing, the electric potential on the electrode improves. Hence, the driving forces for forming Pd nucleus are strengthened, and the crystallite size of Pd on the polymeric films becomes smaller. However, if the electrodepositing current density becomes too high that concentration polarization occurs, Pd particles will aggregate, and the electrocatalytic capability of the electrode will fall down. The value of hydrogen adsorption peak current becomes lower correspondingly. The maximal hydrogen adsorption peak values were obtained with the electrodepositing current densities of 0.225 and 0.337 mA cm^{-2} for Pd/PPy-SDS/foam-Ni electrode and Pd/PPy-CTAB/foam-Ni electrode, respectively. Therefore, Pd electrodepositing current densities of 0.225 and 0.337 mA cm^{-2} were selected as the preparation constants for Pd/PPy-SDS/foam-Ni electrode and Pd/PPy-CTAB/foam-Ni electrode separately. Comparing the two values, it indicates that the electrodepositing current density for Pd/PPy-SDS/foam-Ni electrode was lower than that for Pd/PPy-CTAB/foam-Ni electrode. Therefore, it may save more electricity to prepare Pd/PPy-SDS/foam-Ni electrode.

Electrodepositing time can affect the number of deposited Pd particles. Only appropriate number of dispersed Pd

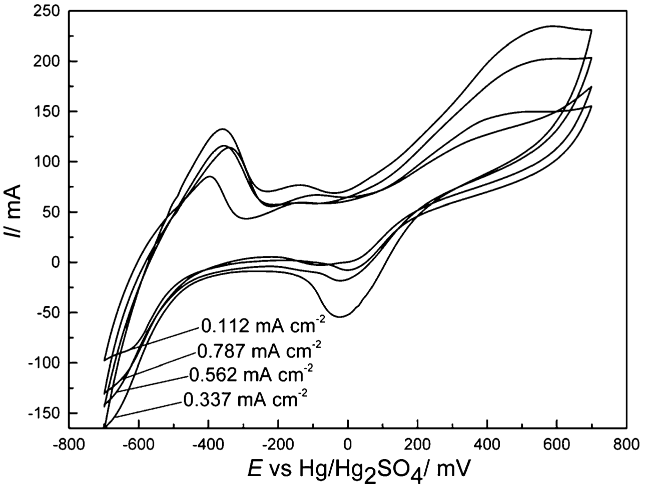

Fig. 4 Cyclic voltammetry curves of Pd/PPy-CTAB/foam-Ni electrodes prepared at different electrodepositing current densities. Voltage range, −700~700 mV; electrolyte, 0.5 mol L^{-1} H_2SO_4 solution; scanning rate, 50 mV s^{-1}

particles and proper uncovered foam-Ni surface can make the electrode have high electrocatalytic capability. Therefore, it is an important parameter for electrode preparation. Under the selected Pd electrodepositing current density, the effect of Pd electrodepositing time on Pd/PPy-SDS/foam-Ni electrode and Pd/PPy-CTAB/foam-Ni electrode was investigated further. Figure 5 shows the CV curves of Pd/PPy-SDS/foam-Ni electrode under different Pd electrodepositing time (20, 30, 35, 40, and 45 min, respectively), and Fig. 6 shows the CV curves of Pd/PPy-CTAB/foam-Ni electrode under different Pd electrodepositing time (30, 40, 45, and 50 min, respectively). The maximal hydrogen adsorption peak values were obtained with the electrodepositing time of 35 min for Pd/PPy-SDS/foam-Ni electrode and 45 min for Pd/PPy-CTAB/foam-Ni electrode. Therefore, Pd electrodepositing times of 35 and 45 min were selected as the preparation constants for Pd/PPy-SDS/foam-Ni electrode and Pd/PPy-CTAB/foam-Ni electrode, respectively.

To confirm the preparation conditions for Pd/PPy-SDS/foam-Ni and Pd/PPy-CTAB/foam-Ni, we also studied the values of the hydrogen adsorption charge in each CV process (results were shown in Table 1).

Table 1 indicates that the maximal hydrogen adsorption charges of 0.43, 0.42, 0.58, 0.46, 0.58, and 0.54 C in each figure (Figs. 1, 2, 3, 4, 5, and 6) were obtained with SDS concentration of 0.0001 gmL^{-1}, CTAB concentration of 0.0003 gmL^{-1}, Pd electrodepositing current density (for Pd/PPy-SDS/foam-Ni electrode preparation) of 0.225 mA cm^{-2}, Pd electrodepositing current density (for Pd/PPy-CTAB/foam-Ni electrode preparation) of 0.337 mA cm^{-2}, Pd electrodepositing time (for Pd/PPy-SDS/foam-Ni electrode preparation) of 35 min, and Pd electrodepositing time (for Pd/PPy-CTSB/foam-Ni electrode preparation) of 45 min.

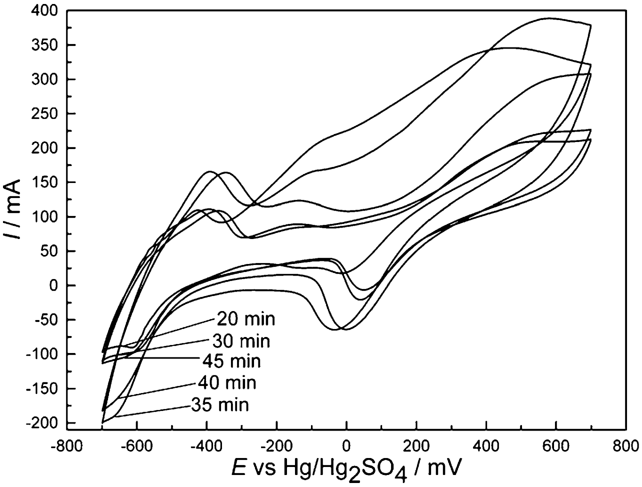

Fig. 5 Cyclic voltammetry curves of Pd/PPy-SDS/foam-Ni electrode prepared at different electrodepositing time. Voltage range, −700~700 mV; electrolyte, 0.5 mol L^{-1} H_2SO_4 solution; scanning rate, 50 mV s^{-1}

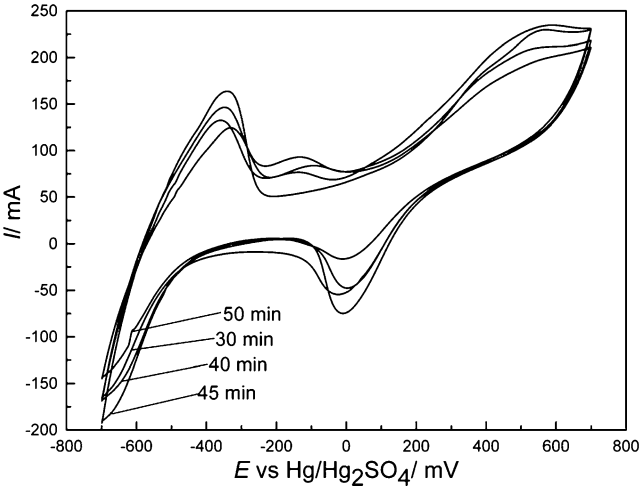

Fig. 6 Cyclic voltammetry curves of Pd/PPy-CTAB/foam-Ni electrode prepared at different electrodepositing time. Voltage range, −700~700 mV; electrolyte, 0.5 mol L^{-1} H_2SO_4 solution; scanning rate, 50 mV s^{-1}

Table 1 Hydrogen adsorption charge in each cyclic voltammetry process

	Parameters	Level	Adsorption charge/C
Fig. 1	SDS concentration/g mL^{-1}	0.00005	0.41
		0.0001	0.43
		0.0002	0.40
		0.0003	0.37
Fig. 2	CTAB concentration/g mL^{-1}	0.0001	0.28
		0.0002	0.31
		0.0003	0.42
		0.0004	0.40
		0.0005	0.25
Fig. 3	Pd electrodepositing current density (Pd/PPy-SDS/foam-Ni electrode)/mA cm^{-2}	0.056	0.33
		0.112	0.56
		0.225	0.58
		0.337	0.56
		0.562	0.55
		0.787	0.44
Fig. 4	Pd electrodepositing current density (Pd/PPy-CTAB/foam-Ni electrode)/mA cm^{-2}	0.112	0.31
		0.337	0.46
		0.562	0.41
		0.787	0.40
Fig. 5	Pd electrodepositing time (Pd/PPy-SDS/foam-Ni electrode)/min	20	0.28
		30	0.33
		35	0.58
		40	0.56
		45	0.49
Fig. 6	Pd electrodepositing time (Pd/PPy-CTAB/foam-Ni electrode)/min	30	0.48
		40	0.49
		45	0.54
		50	0.40

The results were consistent with the hydrogen adsorption peak current values in CV curves in Figs. 1, 2, 3, 4, 5, and 6.

Characterization test

Scanning electron microscope (SEM) test

The morphologies of the surface of Pd/PPy-SDS/foam-Ni and Pd/PPy-CTAB/foam-Ni electrodes were studied by SEM. In order to examine how the two kinds of surfactants influence the deposited configuration of PPy film on foam-Ni substrate, the SEM images of PPy-SDS film, PPy-CTAB film, and PPy film on foam-Ni substrate were measured and analyzed first (shown in Fig. 7a–c). Comparing these three pictures, we can easily find that there are no obvious differences in the microstructures of PPy-CTAB film and PPy film on foam-Ni substrate. PPy-CTAB film and PPy film seem like sheets of thin plate on the surface of the foam-Ni substrate. However, the morphology of PPy-SDS film on foam-Ni substrate is different from the other two films. The surface of the PPy-SDS film is not smooth. There are a lot of small and irregular protuberances. We can see them more clearly from the morphology of magnification of ×10,000, which is shown in Fig. 7d. This morphology greatly increases the specific surface area of the substrate, and it will be easier for Pd particles to be electrodeposited. Therefore, it indicates that the surfactant SDS can greatly modify the substrate's surface and affect the electropolymerization process, while the effect of surfactant CTAB is not obvious on the polymerization process of the PPy film. It has been reported [20] that neutral polymers are known to interact with both anionic and cationic surfactants, but their binding modes are different. The anionic surfactants are found to exhibit stronger interaction with polymers than cationic surfactants with similar chain length.

Figure 8a–c shows the morphologies of Pd/PPy-SDS/foam-Ni, Pd/PPy-CTAB/foam-Ni, and Pd/PPy/foam-Ni electrodes, respectively. We can see that under the same magnification, the Pd particles on the surface of Pd/PPy-

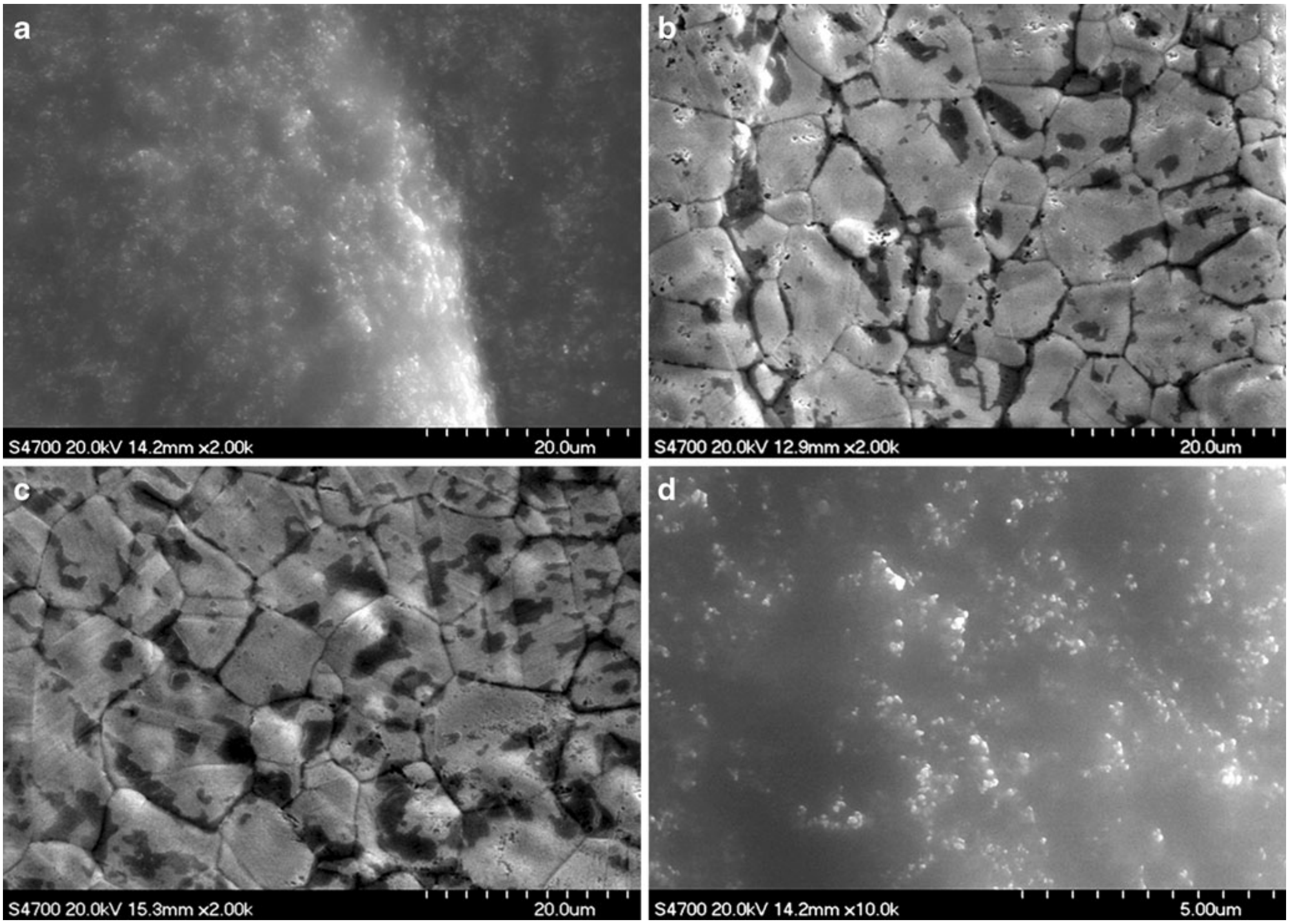

Fig. 7 Scanning electron microscope (SEM) images of PPy-SDS/foam-Ni (**a**), PPy-CTAB/foam-Ni (**b**), and PPy/foam-Ni (**c**) electrodes. **d** SEM image of PPy-SDS/foam-Ni in the magnification of ×10,000

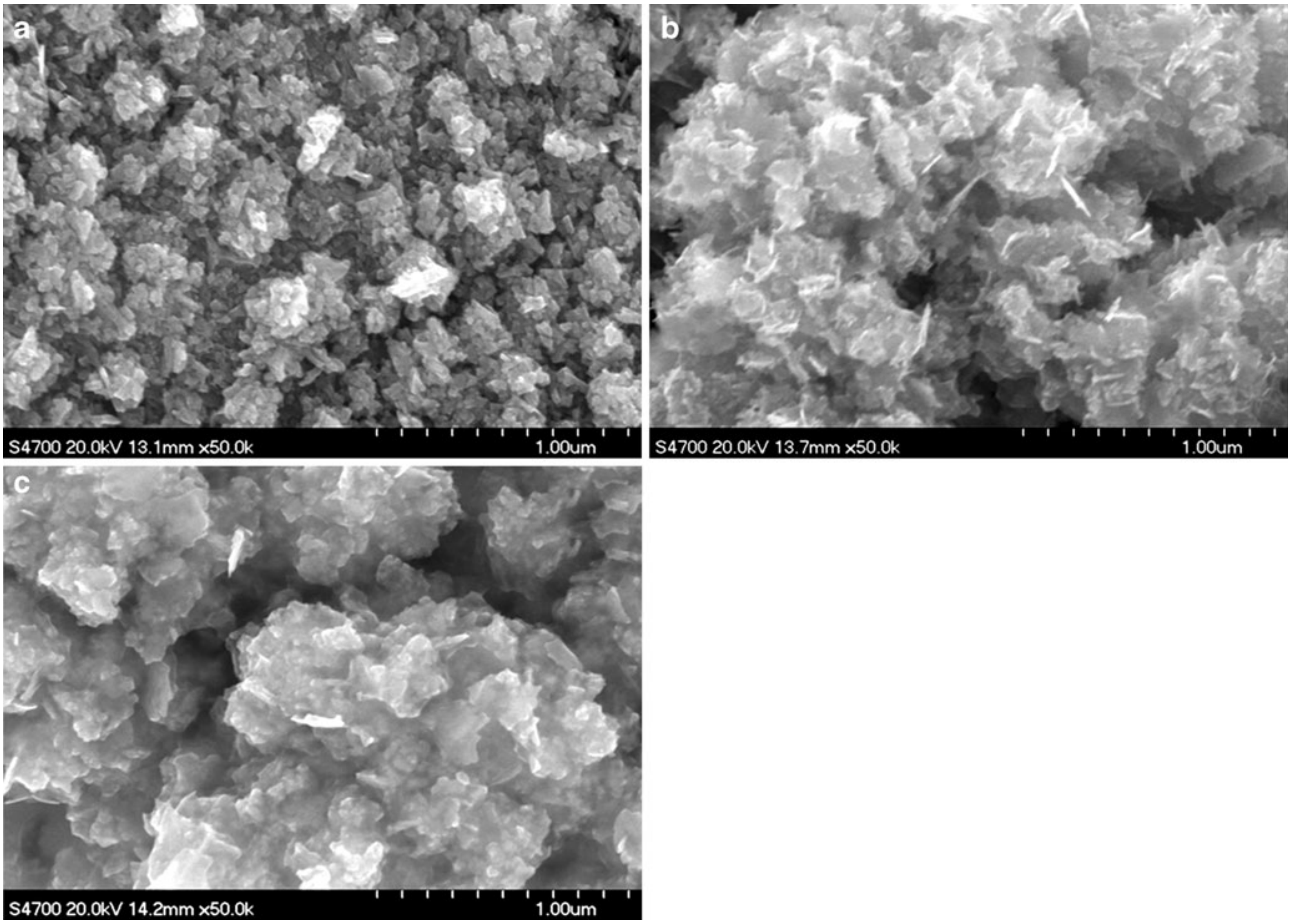

Fig. 8 Scanning electron microscope images of Pd/PPy-SDS/foam-Ni (**a**), Pd/PPy-CTAB/foam-Ni (**b**), and Pd/PPy/foam-Ni (**c**) electrodes

SDS/foam-Ni electrode are the smallest in the three electrodes. They disperse very well and could supply enough catalytic sites for the dechlorination reaction. The Pd particles congregate in some degree on the surface of Pd/PPy-CTAB/foam-Ni and Pd/PPy/foam-Ni electrodes. Comparing with Pd/PPy/foam-Ni electrode, the Pd particles on Pd/PPy-CTAB/foam-Ni electrode disperse a little better and have some kinds of floss. Therefore, the surfactant CTAB can also improve the dispersity of Pd particles on the electrode to some extent.

Brunauer–Emmett–Teller (BET) surface area and X-ray diffraction (XRD) measurements

The BET surface areas of Pd/PPy-SDS/foam-Ni, Pd/PPy-CTAB/foam-Ni, and Pd/PPy/foam-Ni electrodes were calculated from the nitrogen adsorption at 77 K. It is 40.8, 36.2, and 25.2 m^2g^{-1} for Pd/PPy-SDS/foam-Ni, Pd/PPy-CTAB/foam-Ni electrode, and Pd/PPy/foam-Ni electrodes, respectively. It indicates that Pd/PPy-SDS/foam-Ni electrode has the highest BET surface area and may have high electrocatalytic potential capability in electrochemically reductive dechlorination.

To obtain the crystallographic information of Pd/PPy-SDS/foam-Ni electrode and Pd/PPy-CTAB/foam-Ni electrode, XRD measurements were carried out and shown in Fig. 9. The XRD spectrum of Pd/PPy/foam-Ni electrode was also shown in Fig. 9 for comparison. It can be easily observed that the three electrodes almost had the same peak shape. The peaks near 2θ values of 44.5, 51.8, 76.2, and 92.8 originated from the crystal lattice of Ni. The diffraction peaks at 2θ values of 40.1, 46.7, 68.2, 82.2, and 86.7 could be attributed to the (111), (002), (022), (311), and (222) reflection of the crystal lattice of Pd. The results confirmed that Pd particles with the crystal lattice were successfully deposited on the three electrodes. The Pd's crystallite size on Pd/PPy-SDS/foam-Ni electrode is about 16.0 nm, and that on Pd/PPy-CTAB/foam-Ni electrode is about 16.7 nm. On Pd/PPy/foam-Ni electrode, the Pd's crystallite size is about 17.7 nm. Therefore, the Pd's crystallite sizes on the two surfactant-doped electrodes are smaller than that in the absence of surfactant.

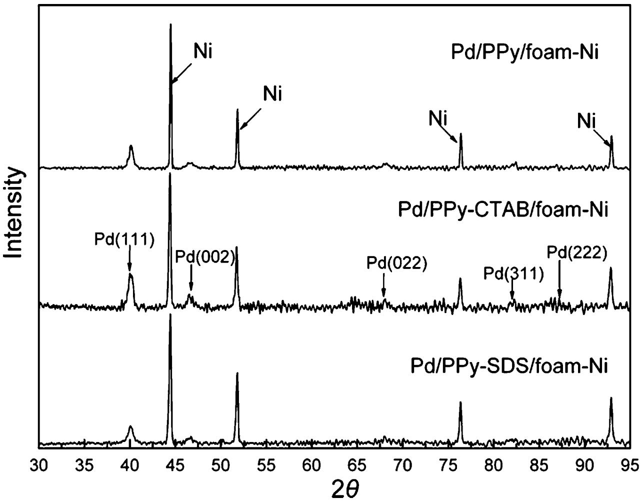

Fig. 9 X-ray diffraction spectrums of Pd/PPy-SDS/foam-Ni electrode, Pd/PPy-CTAB/foam-Ni electrode, and Pd/PPy/foam-Ni electrode

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) test

Under the selected deposition conditions, the loading levels of Pd particles on Pd/PPy-SDS/foam-Ni, Pd/PPy-CTAB/foam-Ni, and Pd/PPy/foam-Ni electrodes were analyzed by ICP-AES. The loading levels of Pd particles on Pd/PPy-SDS/foam-Ni, Pd/PPy-CTAB/foam-Ni, and Pd/PPy/foam-Ni electrodes are 0.91, 1.53, and 2.42 mg cm^{-2}, respectively. It is in accordance with the XRD results that the Pd's crystallite size on Pd/PPy-SDS/foam-Ni electrode is the smallest and that on Pd/PPy/foam-Ni electrode is the biggest. Both of the two surfactants can decrease the loading level of Pd particles, and it will reduce the cost for preparation of these kinds of electrodes.

Electrochemical property comparison

Cyclic voltammetric characterization (shown in Fig. 10) of the freshly prepared Pd/PPy-SDS/foam-Ni, Pd/PPy-CTAB/foam-Ni, and Pd/PPy/foam-Ni electrodes, which were all prepared under their selected conditions, was carried out to investigate the effect of surfactants of SDS and CTAB on the electrochemical behavior. The CV curves with surfactant addition show higher hydrogen adsorption peak current than that in the absence of surfactants. The hydrogen adsorption peak current of Pd/PPy/foam-Ni electrode (150.4 mA) is the lowest in the three electrodes. Pd/PPy-SDS/foam-Ni electrode has the best electrochemical property, and its hydrogen adsorption peak current (193.3 mA) is the highest. Although the hydrogen adsorption peak current of Pd/PPy-CTAB/foam-Ni electrode (179.3 mA) is a little lower than that of Pd/PPy-SDS/foam-Ni electrode, it is higher than that of Pd/PPy/foam-Ni electrode. Furthermore, we also studied the values of the hydrogen adsorption charge in each CV process in Fig. 10. Results indicate that the hydrogen adsorption charges of Pd/PPy-SDS/foam-Ni, Pd/PPy-CTAB/foam-Ni, and Pd/PPy/foam-Ni electrodes were 0.58, 0.54, and 0.48 C, respectively. The results were consistent with hydrogen adsorption peak current in CV curves. Therefore, the addition of CTAB also can improve the electrode's electrochemical property. Meanwhile, based on the results of microscopic characterization, the electrocatalytic activities of the two electrodes are both improved. The enhancement of surface catalytic activity as well as the large surface area achieved with low Pd loading levels makes such a system attractive for application in electrochemically reductive dechlorination.

Conclusions

Pd/PPy-SDS/foam-Ni and Pd/PPy-CTAB/foam-Ni electrodes were prepared by an electrochemical deposition method. SDS concentration of 0.0001 gmL^{-1}, electrodeposition current density of 0.225 mA cm^{-2}, and electrodeposition time of 35 min were selected for Pd/PPy-SDS/foam-Ni electrode's preparation. CTAB concentration of 0.0003 gmL^{-1}, electrodeposition current density of 0.337 mA cm^{-2}, and electrodeposition time of 45 min were selected for Pd/PPy-CTAB/foam-Ni electrode's preparation. Comparing with Pd/PPy/foam-Ni electrode, both the anionic surfactant SDS and cationic surfactant CTAB can modify the PPy film deposition on foam-Ni. Furthermore, it is more economical to get Pd/PPy-SDS/foam-Ni electrode, which also shows higher electrocatalytic activity for electrochemically reductive dechlorination.

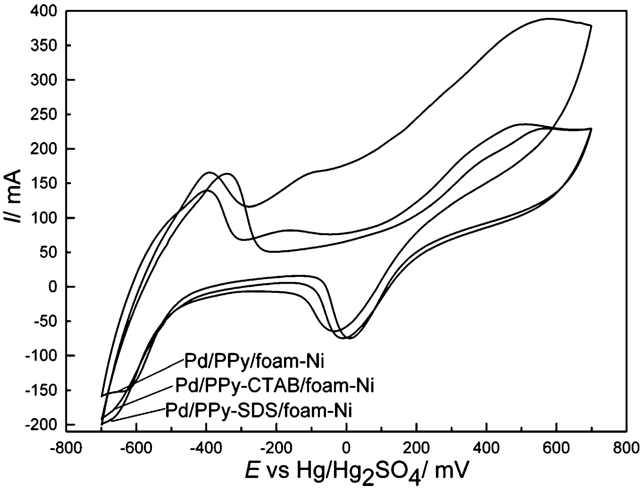

Fig. 10 Cyclic voltammetry curves of Pd/PPy-SDS/foam-Ni, Pd/PPy-CTAB/foam-Ni, and Pd/PPy/foam-Ni electrodes prepared under selected conditions: voltage range, −700~700 mV; electrolyte, 0.5 mol L^{-1} H_2SO_4 solution; scanning rate, 50 mV s^{-1}

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