Influence of the Preparation Conditions on the Morphology of Polyaniline Electrodeposited by the Pulse Galvanostatic Method

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ABSTRACT: The pulse galvanostatic method (PGM) and galvanostatic method (GM) were used to electrodeposit polyaniline (PANI) in H_2SO_4 solutions. Scanning electron microscopy studies showed that PANI prepared with GM had a granular morphology similar to other researchers' results, whereas nanofibular PANI was prepared with PGM. Furthermore, the relationship between the synthetic conditions and morphology of PANI electrodeposited by PGM was investigated. Under some preparation conditions (i.e., mean current density of PGM = 1–4 mA cm^{-2}, ratio of the on-pulse period to the off-pulse period = 0.25–10, temperature = 10–30°C, and experimental frequency = 10–1000 Hz), nanofibular PANI was obtained, whereas flake PANI or granular PANI was prepared under other conditions. Nanosize PANI could result from the highly polarized current of the pulse current signal. The appropriate pulse peak current during the on-pulse period not only produced high electrochemical polarization but also did not lead to overoxidation of PANI; meanwhile, the monomer at the electrode/solution interface could be sufficiently supplied during the off-pulse period. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1389–1394, 2004

Key words: conducting polymers; fibers; morphology

INTRODUCTION

Nanotubes and nanofibers of organic materials have attracted much attention because of their potential applications as molecular wires, drug-delivery systems, electronic and electrooptic devices, and so forth.[1,2]

Chemical[3] and electrochemical[4–10] methods have been extensively applied to the synthesis of polyaniline (PANI) in a medium of a protonic acid of small molecular size, such as HCl, HNO_3, or H_2SO_4; this produces granular PANI. However, PANI prepared by cyclic voltammetry (CV) or a potentiostatic method in $HClO_4$ or HBF_4 solutions has a fibular morphology with a diameter of 0.6–3.3 μm.[6,7] Recently, a method termed *template synthesis* has been successfully developed for the synthesis of fibular conductive PANI.[11–14] Harsh conditions and expensive apparatus are needed for this method. Wan and coworkers[15–17] used another method termed *in situ doping polymerization* in the presence of a special organic sulfonic acid as a dopant to synthesize microtubes of PANI and polypyrrole. In comparison with the template method, *in situ* doping polymerization is simple because one can leave out the microporous membrane, which is used as a template, and the molecular anchor, which is used to bind the polymer to the wall of the microporous membrane. However, the diameter of the fiber is greater than 0.5 μm. In this study, a PANI nanofiber with a diameter of about 100 nm and a length of 10 μm was prepared with the pulse galvanostatic method (PGM). Furthermore, the relationship between the preparation conditions and the morphology of PANI was investigated in detail.

EXPERIMENTAL

Aniline was distilled under reduced pressure. The other chemicals were analytical-grade. Sulfuric acid was used as the preparation background electrolyte, and all the reagents were dissolved in double-distilled water. All reagents were purchased from Shanghai Reagent Company, Shanghai, China.

A three-compartment electrochemical cell contained a platinum wire as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode, and a stainless steel disk (0.95 cm^2) as a working electrode. All the potentials were related to that of the SCE. Before use, the working electrode was mechanically polished and washed with double-distilled water in an ultrasonic bath for 15 min. The electrolyte used to

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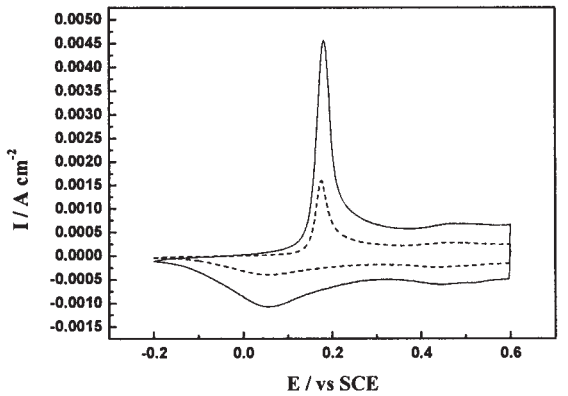

Figure 1 CV for 0.5*M* H_2SO_4 solutions of PANI films prepared by (—) PGM and (- - -) GM. For PGM, the mean current density was 2 mA cm^{-2}, the time was 400 s, t_{on}/t_{off} was 1:3, the frequency was 10 Hz, and the temperature was 20°C. For GM, the current density was 2 mA cm^{-2}, the time was 400 s, and the temperature was 20°C. The scanning rate was 5 mV s^{-1}.

deposit the PANI films was an aqueous 0.5*M* H_2SO_4 solution including 0.2*M* aniline. PANI films were prepared with an SMD-30 pulse galvanostat (Handan Instrument Factory, China). The depositing capacity was controlled and was equal to 800 mC cm^{-2}. The electrochemical properties of the PANI films were investigated by CV in an aqueous 0.5*M* H_2SO_4 solution. All the electrochemical experiments were performed with a CHI660A electrochemical workstation (Shanghai Chenhua Instrument Factory, Shanghai, China). The surface morphology of the PANI films was observed with scanning electron microscopy (SEM; JSM-5600LV, JEOL Co., Japan).

RESULTS AND DISCUSSION

Figure 1 shows the electrochemical properties of the PANI films obtained by PGM and the galvanostatic method (GM). There is a higher anodic current peak in the CV of the PANI film prepared with PGM. The corresponding SEM images are given in Figure 2. Figure 2(a,b) shows the morphology of the PANI films prepared with GM and PGM, respectively. A granular morphology can be observed in Figure 2(a), whereas a nanofibular morphology can be seen in Figure 2(b). Figures 1 and 2 show that the morphology has a great deal of influence on the electroactivity of PANI films. In comparison with the granular film, the nanofibular film had a larger specific surface area. With the surface area the same, the real area used for the electrochemical reaction was larger for the nanofibular film than for the granular film. Meanwhile, the charge-transfer rate in fibular PANI was significantly higher than that in granular or flake PANI.[13] There is no doubt that a nanofibular morphology is beneficial for ion diffusion and migration in the conducting polymer. Therefore, nanofibular PANI has higher electroactivity than granular PANI.

Figure 3 shows CV for background solutions of PANI films. For the synthesis, the mean current density was 2 mA cm^{-2}, the pulse frequency was 10 Hz, the reaction temperature was 20°C, the electrodeposition time was 400 s, and the ratio of the on-pulse period to the off-pulse period (t_{on}/t_{off}) was 0.1 ms/99.9 ms, 50 ms/50 ms, 98 ms/2 ms, or 99.9 ms/0.1 ms. The electroactivity of the PANI films varied with t_{on}/t_{off}, and a maximum value of the anodic peak current can be observed at t_{on}/t_{off} = 50 ms/50 ms [Fig. 3(b)]. For interpretation, the corresponding SEM images are given in Figure 4. Figures 3 and 4 show that the variation of the electroactivity of the PANI films re-

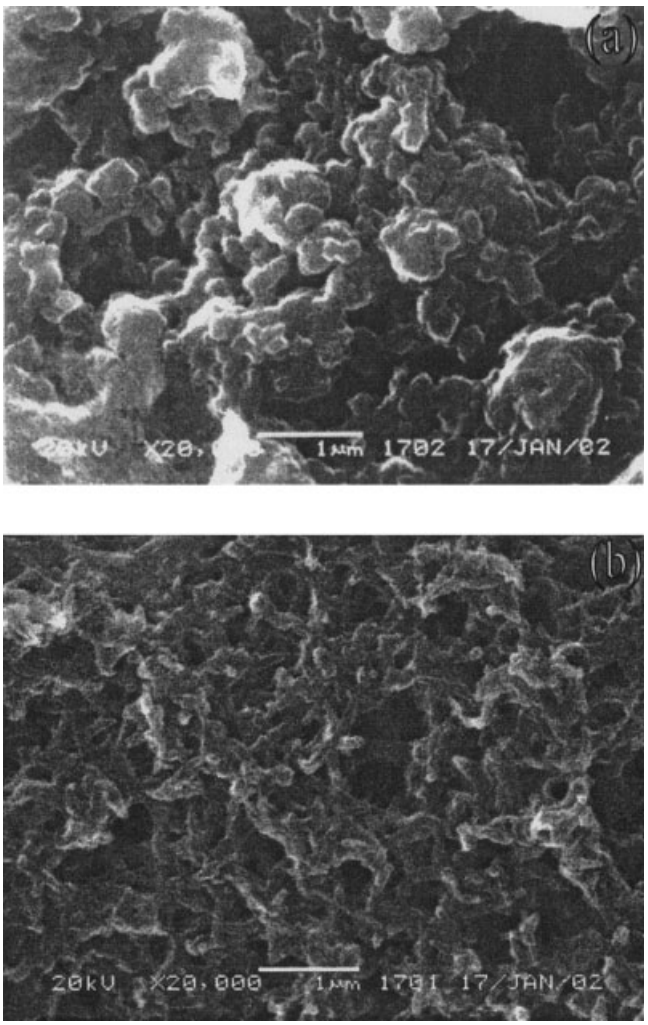

Figure 2 SEM images of PANI films prepared by (a) GM and (b) PGM in 0.2*M* aniline and 0.5*M* H_2SO_4 aqueous solutions. For GM, the current density was 2 mA cm^{-2}, the time was 400 s, and the temperature was 20°C. For PGM, the mean current density was 2 mA cm^{-2}, the time was 400 s, t_{on}/t_{off} was 1:3, the frequency was 10 Hz, and the temperature was 20°C.

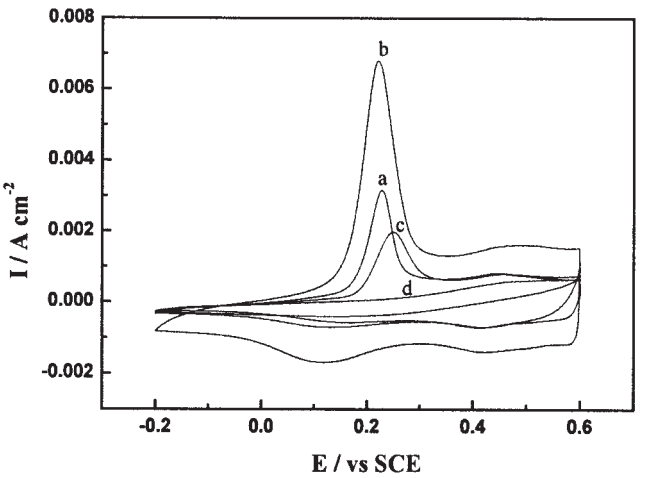

Figure 3 CV for 0.5*M* H_2SO_4 solutions of PANI films prepared by PGM. The mean current density was 2 mA cm^{-2}, the time was 400 s, the frequency was 10 Hz, the temperature was 20°C, and the scanning rate was 10 mV s^{-1}. t_{on}/t_{off} was (a) 1:999, (b) 1:1, (c) 49:1, and (d) 999:1.

sulted from various morphologies. The film with high-quality nanofibular morphology [Fig. 4(b)] had the best electroactivity [Fig. 3(b)]; the electroactivity of the film with a short-fiber morphology decreased [Figs. 4(a) and 3(a)]. In comparison with the short-fiber film, the film with a transitional morphology between nanofibers and flakes [Fig. 4(c)] showed lower electroactivity [Fig. 3(c)], whereas the flake film [Fig. 4(d)] showed the lowest electroactivity [Fig. 3(d)]. These results show that the variation of synthetic conditions can affect the morphology and corresponding electroactivity of PANI films. The effect of t_{on}/t_{off} on the morphology of PANI may have resulted from the variation of the pulse peak current used for electrodeposition. For PGM, when the mean current density was kept constant at 2 mA cm^{-2}, the pulse peak current increased with a reduction of t_{on}/t_{off}. When t_{on}/t_{off} was 90.9 ms/9.1 ms, the pulse peak current density was 2.2 mA cm^{-2}, whereas at t_{on}/t_{off} = 0.1 ms/99.9 ms, the pulse peak current density was 2000 mA cm^{-2}. The higher pulse peak current led to a higher polarized overpotential. According to the kinetics of the electrocrystallization reactions, the first step of PANI deposition is the formation of PANI nuclei, which can grow stably. The critical size of PANI nuclei decreases as the polarized overpotential increases. Therefore, the size of PANI films that grow on the basis of PANI nuclei may be smaller at higher overpotentials, and nanosize PANI films may form. Meanwhile, during t_{off}, the electrochemical reaction

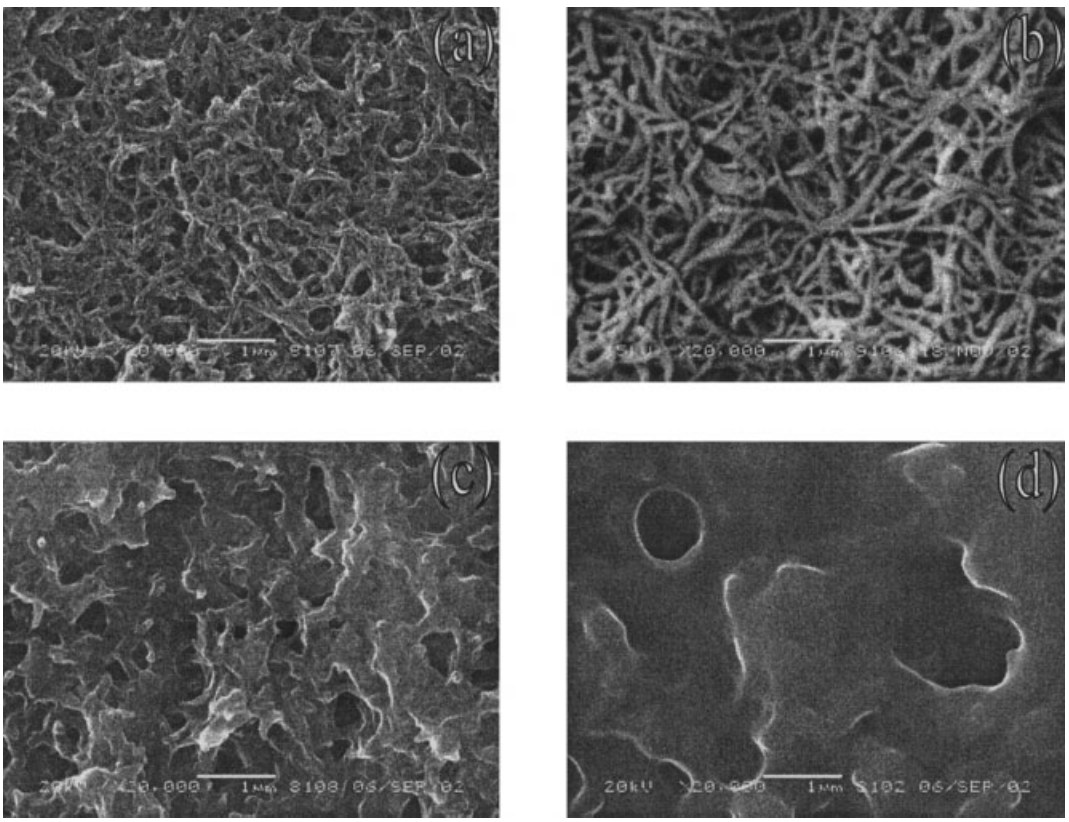

Figure 4 SEM images of PANI films prepared by PGM in 0.2*M* aniline and 0.5*M* H_2SO_4. The mean current density was 2 mA cm^{-2}, the time was 400 s, the frequency was 10 Hz, and the temperature was 20°C. t_{on}/t_{off} was (a) 1:999, (b) 1:1, (c) 49:1, and (d) 999:1.

TABLE I
Effect of t_{on}/t_{off} of PGM on the Morphology of PANI Films

Experiment	$\text{Log}(t_{on}/t_{off})$	Mean Current Density (mA/cm^2)	Pulse Peak Current (mA/cm^2)	Morphology
1	−3	2	2002	Short fiber
2	−2	2	202	Short fiber
3	−1	2	22	Short fiber
4	0	2	4	High-quality nanofiber
5	1	2	2.2	Nanofiber and flake
6	2	2	2.02	Flake
7	3	2	2.002	Flake

Temperature = 20°C; frequency = 10 Hz.

stops, and the aniline monomer consumed during t_{on} can be supplemented again, so the concentration polarization will not occur. Additionally, the PANI nuclei will not grow continuously, and so large PANI crystallization will not occur because of the existence of t_{off} in PGM. However, because PGM is a transient-state electrochemical technique, the potential of the electrode changes quickly during the initial stage of the electrochemical polarization. The pulse current that passes through the electrode/solution interface will be partially consumed by the charge of the electric double layer. Consequently, the formation of PANI nuclei and the growth of PANI will be affected by the charge of the electric double layer. Obviously, the influence of the charge current on PANI prepared by PGM will increase with a reduction of t_{on} when the pulse period is constant. The results show that, when t_{on}/t_{off} was less than 20 ms/80 ms (the pulse peak current density was greater than 10 mA cm^{-2}), short fibular or flake PANI films with low electroactivity appeared because of the charge effect of the electric double layer. On the other hand, the pulse peak current became close to the mean current with an increase in t_{on}/t_{off}; this did not produce high electropolarization and resulted in the surface lack of aniline molecules because of the relatively short t_{off}. As a result, the morphology of the PANI obtained was granular or flake, being similar to that produced by GM. The relationship between t_{on}/t_{off} and the morphology of PANI is shown in detail in Table 1.

The mean current density affected the pulse peak current when the value of t_{on}/t_{off} was 50 ms/50 ms. In other words, the mean current density of PGM could be another important factor in producing nanofibular PANI by PGM. The effect of the mean current density of PGM on the morphology of films was investigated, and the results are given in Figure 5. A flake morphology was observed when the mean current density was 6 mA cm^{-2} [Fig. 5(b)], and a transitional morphology between nanofibers and flakes was obtained with a mean current density of 5 mA cm^{-2} [Fig. 5(a)]. These morphologies were remarkably different from the nanofiber morphology prepared at 2 mA cm^{-2} [Fig. 4 (b)]. When t_{on}/t_{off} was kept at 50 ms/50 ms, with an increase in the mean current density, the pulse peak current increased. When the mean current density increased to a certain value (5 mA cm^{-2}), the high pulse peak current density (10 mA cm^{-2}) led to the

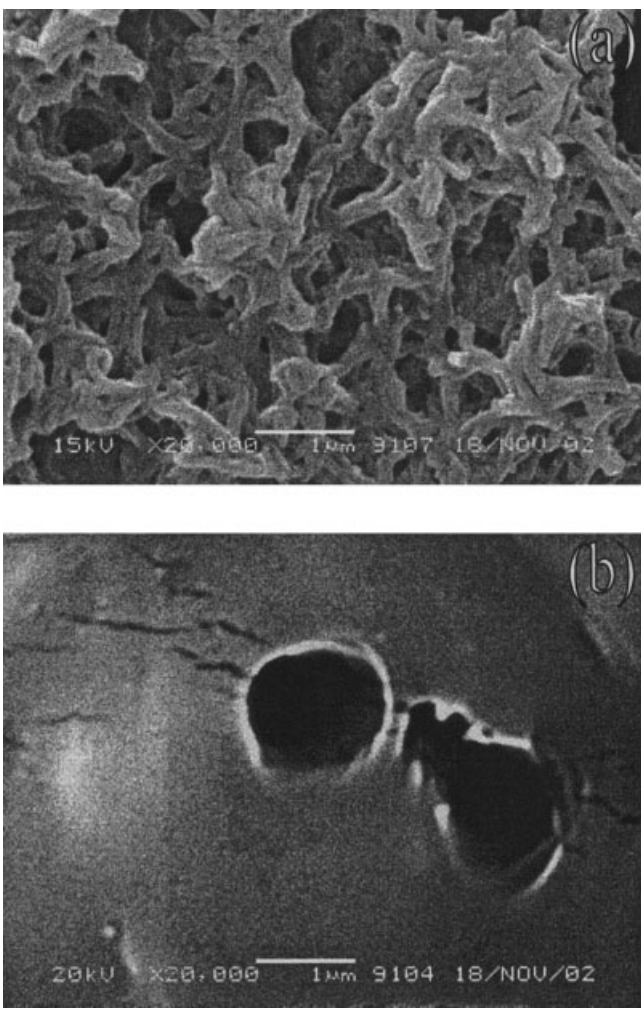

Figure 5 SEM images of PANI prepared by PGM in 0.2*M* and 0.5*M* H_2SO_4 aqueous solutions. t_{on}/t_{off} was 1:1, the frequency was 10 Hz, and the temperature was 20°C. The mean current density was (a) 5 and (b) 6 mA/cm^2.

overoxidation of aniline and hence affected the morphology of PANI.

The effect of the frequency on the morphology of PANI films electrodeposited by PGM was investigated. The results showed that the morphology of the PANI films were not related to the frequency of PGM. When the mean current density and t_{on}/t_{off} were kept at 2 mA cm^{-2} and 1:1, respectively, PANI films were prepared by PGM at 1000 Hz; the corresponding morphology is given in Figure 6. A morphology similar to that of 10 Hz [Fig. 4(b)] can be observed. If t_{on}/t_{off} and the mean current density of PGM were kept constant, the pulse peak current did not vary with the frequency. It could not obviously affect the growth of nanofibular PANI.

The influence of the temperature on the morphology of PANI synthesized by PGM was investigated with SEM. The results showed that a nanofibular morphology could be observed when the reaction temperature was 10–30°C, whereas films with granular morphology could be obtained when the reaction temperature was greater than 40°C. Within the range of 30–40°C, short fibers appeared. A representative granular morphology of films synthesized by PGM at 60°C is given in Figure 7. The electrochemical reaction rate and diffusion rate of the monomer both increased with an increase in the temperature, but the acceleration of the former was much greater. As the temperature increased from 10 to 30°C, the electrochemical reaction rate increased rapidly, and this led to an improvement in the efficiency of the film formation. In this temperature range, the electrochemical reaction could still be the controlling step, and it was beneficial for the formation of nanofibular PANI films. With a further increase in the temperature, the rate of the electrochemical reaction became much higher than the diffusion rate of the monomer; therefore, the diffusion step became the controlling process, and the monomer in the vicinity of the electrode surface was not sufficiently supplemented. This was unfavorable for the growth of nanofibular PANI. When the temperature was greater than 40°C, PANI became unstable, and the granular PANI was obtained.

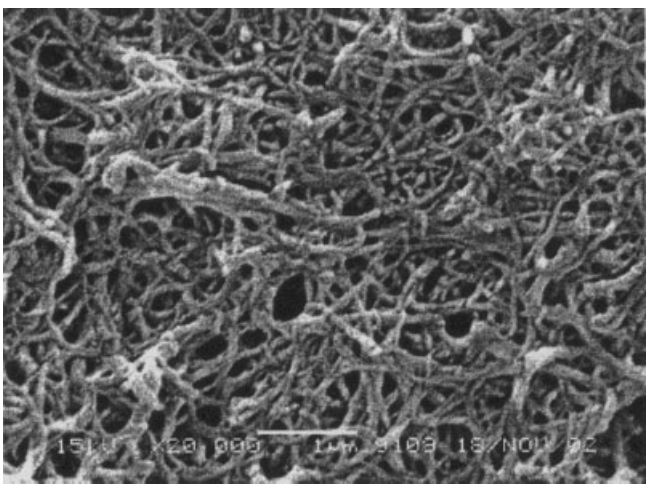

Figure 6 SEM image of PANI prepared by PGM in 0.2*M* aniline and 0.5*M* H_2SO_4 at 1000 Hz. The mean current density was 2 mA cm^{-2}, the time was 400 s, t_{on}/t_{off} was 1:1, and the temperature was 20°C;

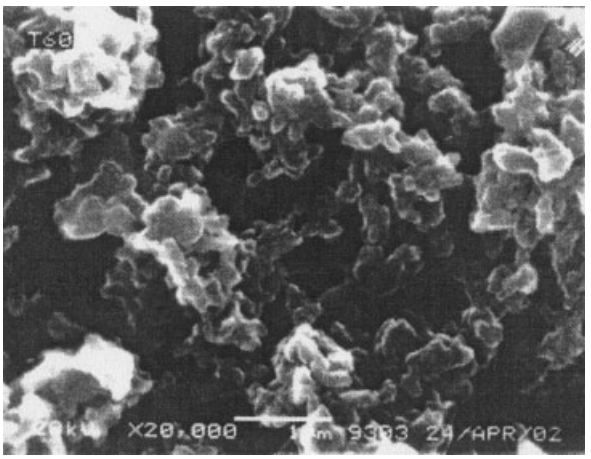

Figure 7 SEM image of PANI prepared by PGM in 0.2*M* and 0.5*M* H_2SO_4 at 60°C. The mean current density was 2 mA cm^{-2}, the time was 400 s, t_{on}/t_{off} was 1:1, and the frequency was 10 Hz.

CONCLUSIONS

Nanofibular PANI was obtained with PGM. The magnitude of the polarized current was a dominant factor in the growth of PANI nanofibers. The effects of the preparation parameters of PGM on the morphology of PANI were investigated. The results showed that the synthetic parameters of PGM, such as t_{on}/t_{off}, the mean current density, and the reaction temperature, had great influence on the morphology of PANI films. Only under certain preparation conditions (mean current density of PGM = 1–4 mA cm^{-2}, t_{on}/t_{off} = 0.25–10, temperature = 10–30°C, and every experimental frequency = 10–1000 Hz) could nanofibular PANI be obtained, whereas flake PANI or granular PANI were prepared under other conditions.

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