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Electrochemical and scanning electron microscopic studies of the influence of anatase TiO_2 nanoparticles on the electropolymerization of aniline

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A hybrid material of polyaniline (PAn)/anatase TiO_2 nanoparticle was prepared by the potential cycling method within dispersed anatase TiO_2 nanoparticles in solution.

Nanostructure materials have received much attention because of their new properties, which differ from those in bulk materials.[1–3]

Titanium dioxide TiO_2, as a semiconductor, shows high photocatalytic activity and is widely used as a catalyst, a catalyst carrier *etc*.[4,5] The performance of titanium dioxide in its various applications depends on its crystalline phase state, dimensions and morphology.[6]

Polyaniline (PAn) is a promising conducting polymer.[7] The incorporation of inorganic components into a conductive polymer led to unique composites, exhibiting enhanced conductivity and special mechanical,[8] electronic,[9] electrochemical,[10] optical[11] and magnetic[12] properties. Such new hybrid polymer/inorganic composites cover a great range of applications including electrochromic devices, light-emitting diodes, *etc*. For example, the PAn/TiO_2 composites were prepared by the *in situ* deposition and oxidative polymerization of aniline hydrochloride using $(NH_4)_2S_2O_8$ as an oxidant. They demonstrated a suitable conductivity (1–10 S cm^{-1}).[13] The PAn/V_2O_5 can serve as a cathode for lithium secondary batteries.[14] Hexanoic acid doped PAn nanocomposites containing TiO_2 nanoparticles were prepared by the template free method.[15]

In this study, the PAn films were developed on a platinum electrode using the electropolymerization of aniline. For the preparation of anatase TiO_2 nanoparticles, a 2 M $(NH_4)_2SO_4$ solution was mixed with 1 M $TiCl_4$ solution to a total volume of 40 ml. Then, the mixture was heated at 80–85 °C and kept at this temperature for 1 h. Dilute ammonium hydroxide (2 M) was added dropwise to the solution under high-speed stirring to pH 6.5–7.0. The precipitated titanium hydroxide was filtered, repeatedly washed with distilled water and ethanol and dried at 60–70 °C. After being calcined at 400 °C for 2 h, the sample was slowly cooled to room temperature. The electrochemical equipment was described previously.[16] Electropolymerization was applied to a solution containing 0.030 M aniline in 0.1 M H_2SO_4 by potential cycling between 0 and 1.1 with a scan rate of 50 mV s^{-1}.

The scanning electron microscopy (SEM) images were recorded using a ZEISS DSM 960 instrument, and the transmission electron microscopy (TEM) studies were performed on a ZEISS CEM 902A instrument. Furthermore, the powder X-ray diffraction (XRD) patterns were recorded on a Siemens D 5000 diffractometer with CuKα radiation.

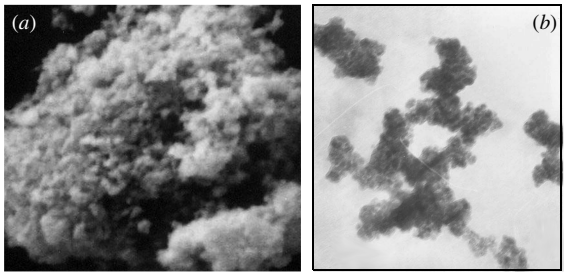

Figure 1 (*a*) SEM and (*b*) TEM images of anatase TiO_2 nanoparticles.

Anatase has a well-known crystal structure.[17] Figure 1(*a*) exhibits the SEM image of a TiO_2 nanoparticle. The TEM image is demonstrated in Figure 1(*b*). In Figure 2(*a*), the cyclic voltammograms (CVs) are displayed which were concurrently recorded after frequency changes during consecutive potential cycles in a 0.1 M H_2SO_4 solution, containing 0.030 M aniline, on a platinum substrate electrode. This way consists of the conventional synthesis with the CV shapes being well-defined.[18] Figure 2(*b*) shows the cyclic voltammograms simultaneously recorded with frequency changes during consecutive potential cycles in a 0.1 M H_2SO_4 in the presence of TiO_2 nanoparticles, dispersed in the electrolyte solution and containing 0.030 M aniline. The addition of anatase nanoparticles

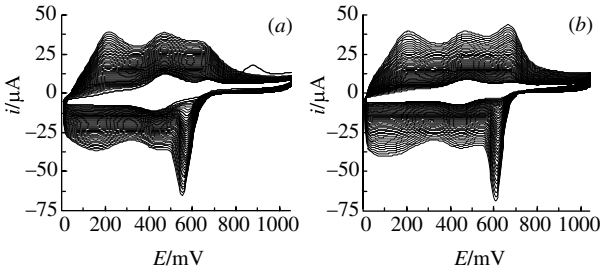

Figure 2 Cyclic voltammograms recorded during the potentiodynamic growth of a PAn film in a solution containing 0.030 M aniline and 0.1 M H_2SO_4 (*a*) without and (*b*) with TiO_2 nanoparticles dispersed in the electrolyte solution at a scan rate of 50 mV s^{-1}.

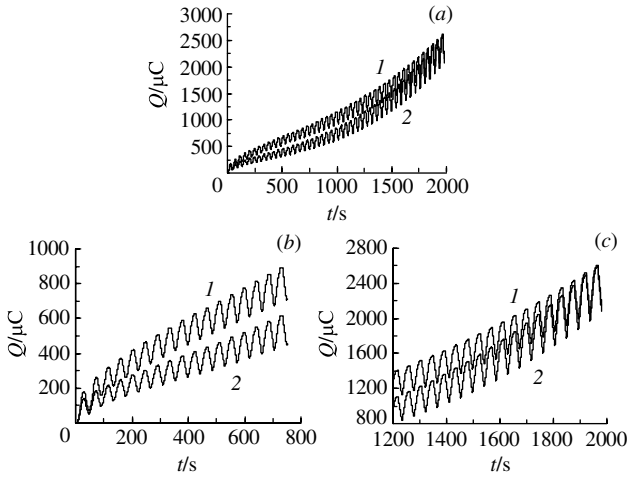

Figure 3 (*a*), (*b*) and (*c*) Charge passed through the electrochemical cell *vs.* time for the electropolymerization of aniline under the same experimental conditions as in (*1*) Figure 2(*a*) and (*2*) Figure 2(*b*).

to the electrolyte solution affects the electropolymerization process. For this purpose, 30 mg of TiO_2 was dispersed in 20 ml of electrolyte solution and then sonicated to obtain a uniform dispersion. Although the general well-defined CV shape is expected, a stronger oxidation peak appears at 600–700 mV. This indicates that the TiO_2 nanoparticle existence results in a severe oxidation process, which plays an important role in the subsequent electropolymerization and polymer growth.

According to Figure 3, the polymer growth investigation in the course of electropolymerization demands the comparison of the charge passed through the electrochemical cell against the time of electropolymerization for Figures 2(*a*),(*b*). The increase of the polymerization rate is approximately constant for the Pt substrate in a conventional solution [Figure 3(*a*), curve *1*]. Nonetheless, the electropolymerization of aniline on an initial polymer film, formed in the presence of TiO_2 nanoparticles, is more difficult because the amount of polymer deposited during the first cycles decreases. This is concluded from Figure 3(*a*),(*b*), curve *2* in contrast to curve *1*. Since the subsequent polymerization on the initial polymer layer is related to the initial polymer

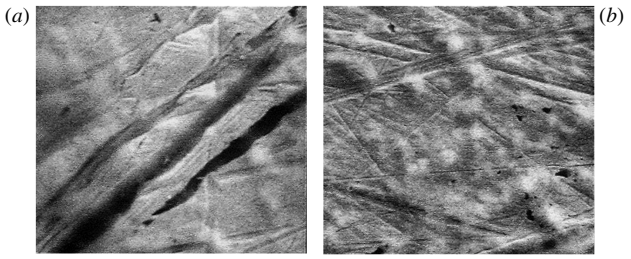

Figure 4 SEM images of PAn growth under the conditions applied in (*a*) Figure 2(*a*) and (*b*) Figure 2(*b*).

growth, it can be concluded that electropolymerization on the initial layers of the polymer growth in the presence of TiO_2 nanoparticles is easier because the amount of deposited polymer increases during the last cycles, as follows from Figure 3(*a*),(*c*), curve *2* in contrast to curve *1*. According to the SEM images of polyaniline films deposited onto the platinum substrate [Figure 4(*a*)], the polymer film has cracks. This failure is accompanied by a polymer breakdown. These empty holes can be observed in Figure 4(*a*). Figure 4(*b*) illustrates the SEM image of a PAn film deposited on the Pt substrate in the presence of TiO_2 nanoparticles.

Thus, the reported results indicated that TiO_2 nanoparticles can affect the electropolymerization process. TiO_2 acts as an incorporating agent. The presence of TiO_2 results in the stable polymer film formation without any film breakdown or cracks. However, it is simple to control the composite structure using various metal oxide nanomaterials. This approach can be productively employed for practical purposes.

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References

1 S. Iigima and T. Lchihashi, *Nature*, 1993, **363**, 603.
2 P. M. Ajayan, O. Stephan, P. Redlich and C. Colliex, *Nature*, 1995, **375**, 564.
3 A. Bayandori Moghaddam, M. R. Ganjali, R. Dinarvand, P. Norouzi, A. A. Saboury and A. A. Moosavi-Movahedi, *Biophys. Chem*., 2007, **128**, 30.
4 A. Fujishima and K. Honda, *Nature*, 1972, **37**, 238.
5 A. Fujishima, *Science*, 2003, **301**, 1673a.
6 A. Narayanasamy, V. A. Maroni and R. W. Siegel, *J. Mater. Res*., 1989, **4**, 1246.
7 B. A. Deore, I. Yu and M. S. Freund, *J. Am. Chem. Soc*., 2004, **126**, 52.
8 M. S. Cho, H. J. Choi and W. S. Ahn, *Langmuir*, 2004, **20**, 202.
9 H. Yoshikawa, T. Hino and N. Kuramoto, *Synth. Met*., 2006, **156**, 1187.
10 Y. K. Zhou, B. L. He, W. J. Zhou, J. Huang, X. H. Li, B. Wu and H. L. Li, *Electrochim. Acta*, 2004, **49**, 257.
11 S. Kuwabata, N. Takahashi, S. Hirao and H. Yoneyama, *Chem. Mater.*, 1993, **5**, 437.
12 H. L. Frisch, H. Song, J. Ma, M. Rafailovich, S. Zhu, N. L. Yang and X. J. Yan, *Phys. Chem. B*, 2001, **105**, 11901.
13 S.-J. Su and N. Kuramoto, *Synth. Met*., 2000, **114**, 147.
14 F. Huguenin, M. Ferreira, V. Zucolotto, F. C. Nart, R. M. Torresi and O. N. Oliveira, Jr., *Chem. Mater*., 2004, **16**, 2293.
15 S. W. Phang, M. Tadokoro, J. Watanabe and N. Kuramoto, *Curr. Appl. Phys*., 2008, **8**, 391.
16 A. Bayandori Moghaddam, M. R. Ganjali, P. Norouzi and M. Niasari, *J. Electroanal. Chem*., 2007, **601**, 205.
17 M. Horn, C. F. Schwerdtfeger and E. P. Meagher, *Z. Kristallogr.*, 1972, **136**, 273.
18 D. E. Stilwell and S. M. Park, *J. Electrochem. Soc*., 1988, **135**, 2254.

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