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Synthesis and Electrochemical Behavior of Polyaniline/$H_2Ti_4O_9$ Lamellar Nanocomposite

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A novel polyaniline (PANI)/$H_2Ti_4O_9$ lamellar nanocomposite has been synthesized by in situ polymerization using aniline intercalation compound (ANI)/$H_2Ti_4O_9$ as the intermediate. According to the experimental results, the ANI within the interlayer spacing of the layered $H_2Ti_4O_9$ material may be oriented in a single-layer arrangement, with the benzene rings perpendicular to the layer sheets. After polymerization, a monolayer of PANI chains within the confined galleries was produced. The PANI/$H_2Ti_4O_9$ nanocomposite has been studied by electrochemical methods, which revealed good redox activity.

Nanocomposites based on conducting polymers have been widely investigated during recent years due to their potential uses in nanometer electronic devices and other optoelectronic devices.[1,2] Among the many conducting polymers, polyaniline (PANI) is the most promising in this context by virtue of its attractive electrical properties. Lamellar hybrid materials comprising a conducting organic polymer, such as PANI, interleaved within the layers of an inorganic oxide lattice represent intriguing candidates for advanced practical applications. Such lamellar nanocomposites have been investigated for potential applications in many fields, such as organic batteries, electrochromic displays, and microelectronic devices.[3–5] During the past decades, there have been many published reports focusing on the preparation methods and the novel properties of nanocomposites consisting of PANI with different layered materials, such as clay minerals, layered metal oxides (LMOs), and metal phosphates.[6–8]

Tetratitanic acid, $H_2Ti_4O_9$, is a layered transition metal oxide with good intercalating ability[9] and similar properties to TiO_2, which can be easily prepared through acid treatment of layered potassium tetratitanate $K_2Ti_4O_9$. The idealized representation of the crystal structure of $H_2Ti_4O_9$ consists of protons and $[Ti_4O_9]^{2-}$ layers that are built-up from a structure unit of four TiO_6 octahedra arranged in a line and interconnected by sharing edges and corners.[10]

In the present study, aniline (ANI) has been allowed to intercalate into the interlayer spacing of $H_2Ti_4O_9$ and then in situ polymerized to form a novel PANI/$H_2Ti_4O_9$ lamellar nanocomposite. To the best of our knowledge, this is the first time that such a nanocomposite has been prepared. The electrochemical characteristics of a glassy carbon electrode modified with the PANI/$H_2Ti_4O_9$ nanocomposite have been investigated by cyclic voltammetry. The results demonstrate that the PANI/$H_2Ti_4O_9$, nanocomposite, modified electrode has good redox activity, and the electrochemical reactions at the PANI/$H_2Ti_4O_9$ nanocomposite film were typical of surface-controlled processes.

The layered material $K_2Ti_4O_9$ was prepared by calcination of a mixture of powdered K_2CO_3 and TiO_2 (anatase, high-purity grade) in a molar ratio of 1:3.5 at 800 °C for 20 h, followed by a further 20 h after grinding, according to a literature procedure.[9] The protonated form $H_2Ti_4O_9$ was obtained by treatment of $K_2Ti_4O_9$ with $1\,mol\,dm^{-3}$ HCl under vigorous stirring for 3×24 h at room temperature (100 mL of aq. HCl per gram of potassium tetratitanate). Aniline was intercalated into the interlayers of $H_2Ti_4O_9$ as follows: $H_2Ti_4O_9$ (1 g) was dispersed in distilled water (20 mL); the dispersion was cooled in an ice bath, and then aniline (2 mL) was added dropwise. The reaction mixture was maintained under vigorous stirring for two weeks at room temperature. The dispersion was then centrifuged and the solid was washed several times with distilled water and methanol and dried at 60 °C under vacuum overnight to obtain the ANI/$H_2Ti_4O_9$ intercalation compound as a white powder. A 0.5-g portion of sample of the ANI/$H_2Ti_4O_9$ intercalation compound was added to 5 mL of an aqueous solution prepared by mixing $(NH_4)_2S_2O_8$ ($1\,mol\,dm^{-3}$) and HCl ($0.1\,mol\,dm^{-3}$), and the mixture was vigorously stirred at room temperature for one week. A color change from white through blue to dark was observed during the polymerization. The precipitate was collected by centrifugation, washed with distilled water, and then dried overnight at 60 °C under vacuum to obtain PANI/$H_2Ti_4O_9$ nanocomposite.

Figure 1 shows the XRD patterns of $K_2Ti_4O_9$, $H_2Ti_4O_9$, ANI/$H_2Ti_4O_9$, and PANI/$H_2Ti_4O_9$ nanocomposite. The layered compound, $K_2Ti_4O_9$, was identified by powder X-ray diffraction analysis (Figure 1a).[10] Since $K_2Ti_4O_9$ is known to be unreactive toward aniline, the protonation of $K_2Ti_4O_9$ to give tetratitanic acid was carried out by addition of 1 M aq. HCl so that aniline

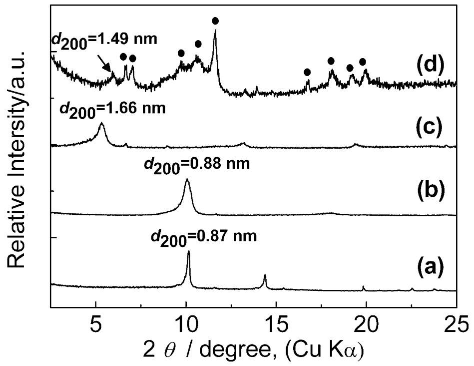

Figure 1. The X-ray diffraction patterns of (a) $K_2Ti_4O_9$, (b) $H_2Ti_4O_9$, (c) ANI/$H_2Ti_4O_9$, (d) PANI/$H_2Ti_4O_9$ (dark points denote the peaks of PANI).

Table 1. X-ray diffraction data

Compound	d_{200}/nm	Δd^{a}/nm
$K_2Ti_4O_9$	0.87	
$H_2Ti_4O_9$	0.88	
$ANI/H_2Ti_4O_9$	1.66	0.78
$PANI/H_2Ti_4O_9$	1.49	0.61

[a] Δd means the increase in d_{200} from that of $H_2Ti_4O_9$.

could easily intercalate into the interlayer of $H_2Ti_4O_9$ by neutralization of the acid. Approximately 91% of the potassium ions were removed by this treatment. In previous papers, the d_{200} value corresponding to the average interlayer spacing in tetratitanic acid was reported to be ca. 0.91 nm after complete removal of the interlayer potassium ions.[10,11] However, in the present study, d_{200} is 0.88 nm (Figure 1b). After intercalation with aniline, the (200) diffraction peak of $ANI/H_2Ti_4O_9$ at 5.32° ($d = 1.66$ nm) (Figure 1c) had clearly shifted to a lower 2θ angle compared with that of pristine $H_2Ti_4O_9$, which indicated that aniline molecules had been successfully intercalated into the nano-interlamellar spaces of $H_2Ti_4O_9$. The basal spacing and the Δd values of the product are shown in Table 1. The net expansion of $ANI/H_2Ti_4O_9$, $\Delta d = 0.78$ nm, is similar to the molecule length of ANI itself (ca. 0.7 nm).[7] This implies that ANI is likely to be oriented in a monolayer arrangement, with the benzene rings perpendicular to the layer sheets. The XRD pattern of $PANI/H_2Ti_4O_9$ (Figure 1d) shows a weak (200) diffraction peak at 5.94° ($d = 1.49$ nm) and some new peaks (dark points), which indicate a lower degree of crystallinity due to the polymerization of aniline within the confined interlayers but with retention of the layered structure after polymerization. The new diffraction peaks (dark points) may be assigned to the regularities of the PANI.[12] The net expansion of $PANI/H_2Ti_4O_9$, $\Delta d = 0.61$ nm, indicates that monolayers of the polymer are formed and compares well with the published values of ca. 0.60 nm in $PANI/Ti(PO_4)_2$.[8]

The FT-IR spectrum of $PANI/H_2Ti_4O_9$ further indicates the presence of PANI within the interlayers of $H_2Ti_4O_9$. The characteristic bands of $PANI/H_2Ti_4O_9$ nanocomposite may be summarized as follows: bands at about 1580, 1500, and 1140 cm^{-1}, attributable to stretching of N=Q=N, N–B–N (B and Q as benzenoid and quinonoid units), and a mode of $Q{=}N^{+}H{-}B$ and B–NH–B formed upon protonation, and a band at 1440 cm^{-1}, attributable to stretching of benzene ring.[13]

Figure 2 shows the cyclic voltammograms of a glassy carbon electrode modified with $PANI/H_2Ti_4O_9$ nanocomposite measured at different scan rates. It is clear that the $PANI/H_2Ti_4O_9$ film exhibits very good redox activity in 0.1 M HCl. Two pairs of redox peaks are seen for $PANI/H_2Ti_4O_9$ in 0.1 M HCl solution at different scan rates. The first oxidation wave at around $E_{SCE} = 0.15$ V may be assigned to the leucoemeraldine state to emeraldine salt transition. The second oxidation wave at around $E_{SCE} = 0.30$ V is due to the transition from the emeraldine salt to the pernigraniline state.[14] The inset reveals that the anodic peak currents are surface-controlled redox processes.

In conclusions, a novel $PANI/H_2Ti_4O_9$ lamellar nanocomposite has been synthesized by in situ polymerization using aniline intercalation compound $(ANI)/H_2Ti_4O_9$ as the intermediate. The properties of the $PANI/H_2Ti_4O_9$ nanocomposite have been characterized by means of XRD and FT-IR. The electrochemical behavior of a glassy carbon electrode modified with the $PANI/H_2Ti_4O_9$ nanocomposite has been studied, which revealed very good redox activity with a potential application in chemical sensors.

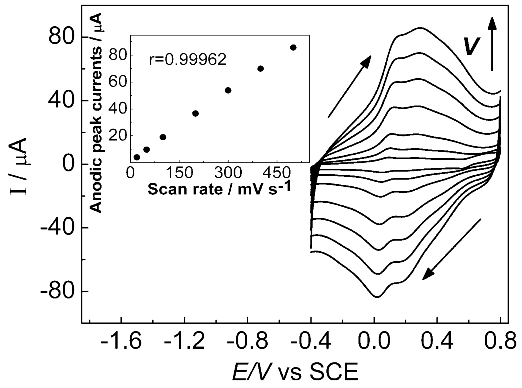

Figure 2. Cyclic voltammograms of a glassy carbon electrode modified with $PANI/H_2Ti_4O_9$ nanocomposite recorded in 0.1 M HCl at a scan rate of 20, 50, 100, 200, 300, 400, and 500 mV s^{-1}, respectively. Inset shows the relationship between anodic current and scan rate.

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