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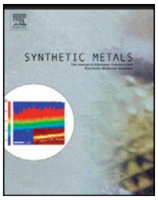

An intercalated polyaniline–titanate nanomaterial

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ABSTRACT

In this paper we report on the synthesis of a nanomaterial consisting of polyaniline sandwiched between the sheets of layered titanate. This was achieved by first intercalating aniline into the titanate, followed by heat treatment in air. The resulting intercalate was characterized by powder X-ray diffraction, thermogravimetric analysis and FTIR spectroscopy.

1. Introduction

Recently, polyaniline nanocomposites based on layered metal compounds have attracted a considerable amount of interest [1–9]. These nanocomposites were shown to possess improved electrical conductivity, due to the presence of the conductive polyaniline. Hence, these materials could potentially be used as electrodes in rechargeable batteries. Polyaniline nanocomposites with layered structures containing metals such as Fe, V, U, Mn, Cd, Sn, Mo and W have been reported in the literature [1–8]. While the inclusion of polyaniline into layered titanium phosphate [9] has been reported, to date there has been no work done on the intercalation of electrically conductive polymers into layered titanate. It is worthy to note that polyaniline–TiO_2 nanocomposites have been synthesized and characterized [10–15]. However, it should also be emphasized that these nanocomposites are not intercalated, but rather consist of TiO_2 nanoparticles, in either the anatase or rutile phase, mixed with the polymer.

As an extension of the research on the intercalation of electrically conductive polymers in our laboratory [16–23], we have turned our attention to layered titanate. We are interested in this layered compound because it contains titanium, one of the strongest metals from the periodic table. A survey of the literature revealed that the synthesis of layered titanate with interlamellar alkali metals has been well established. In fact, Izawa et al. [24] showed that these interlayer alkali metals could be exchanged with protons to yield a protonated phase of TiO_2. They also discovered the acid–base intercalation properties of the latter [25]. Further research revealed that suspensions of single layers could be obtained by reaction of the protonated titanate with tetrabutylammonium hydroxide [26,27].

Further, Sukpiron and Lerner [28] have described the intercalation of poly(ethylene oxide) and poly(vinylpyrrolidinone) between the layers of titanate. These guest polymers exhibit ionic conductivities when complexed with inorganic salts. However, up to date, it is interesting to note that there has been no report on the intercalation of electrically conductive polymers into titanates. By exploiting the acidic properties of the layered host, we were able to first and foremost insert aniline. Heat treatment on the resulting inclusion solid resulted in the formation of an intercalated polyaniline phase.

2. Experimental

2.1. Materials

Anatase TiO_2 and Cs_2CO_3 were purchased from Aldrich and used as received with no further purification. Aniline was also purchased from Aldrich and was vacuum-distilled prior to use. $(NH_4)_2S_2O_8$ was purchased from Fisher and was used as received.

2.2. Instrumentation

Fourier transform infra-red spectroscopy was run on a Bruker Equinox 55 FTIR instrument as pressed KBr pellets.

Powder X-ray diffraction (XRD) was run on a Bruker AXS D8 Advance diffractometer equipped with a graphite monochromator, variable divergence and antiscatter slits, along with a scintillation detector. Cu Kα radiation($\lambda = 1.542$ Å) was used and the data collection was carried out in air, at room temperature, using a scan range of 2–60°. Samples were run as thin films on glass substrates.

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Thermogravimetric analysis (TGA) was performed on a TA 500 instrument using a heating rate of 10 °C/min.

2.3. *Synthesis of protonated titanate*

The synthesis of the protonated titanate was performed as per the literature method [28]. Anatase TiO_2 (4.22 g, 0.0529 mol) was placed in an alumina crucible to which 0.2 equivalent of Cs_2CO_3 was added. The solid mixture was ground to a fine powder and the crucible was capped. The mixture was briefly heated to 800 °C in order to remove CO_2 and then reground. The crucible was then placed back in the furnace at 800 °C for 20 h. The white product was reground and then placed back in the furnace for an additional 20 h. The resulting white material, $Cs_xTi_{2-x/4}\square_{x/4}O_4{\cdot}yH_2O$ where $\square$ is a vacancy, was ground to a fine powder.

The protonated form of the titanate was afforded via ion exchange with 1 M HCl (0.0108 g titanate/mL HCl). The mixture was stirred for 2 days with the HCl being replaced every 24 h. The white protonated titanate, $H_xTi_{2-x/4}\square_{x/4}O_4{\cdot}yH_2O$ where $x \sim 0.7$ and $y \sim 1$, was obtained via filtration under reduced pressure. In this paper we will refer to the protonated titanate simply as $HTiO_2$.

2.4. *Intercalation of aniline into $HTiO_2$*

$HTiO_2$ was placed into an Erlenmeyer flask to which ten equivalents of freshly distilled aniline was added as a 50% (v/v) mixture with H_2O. The resulting mixture was sonicated for 4 h in a Fisher brand solid state ultrasonic FS-9 sonicator operating at 75W/45 kHz. The resulting suspension was cast on a glass slide, resulting in an off white powder.[1]

2.5. *Synthesis of polyaniline–$HTiO_2$ nanocomposite*

The powdered aniline/titanate nanocomposite was placed in an alumina crucible and placed in a furnace at 140 °C for 4 h. This treatment resulted in a dark green–black powder.

3. Results and discussion

The reaction of TiO_2 and Cs_2CO_3 at elevated temperatures serves a twofold purpose. First and foremost, heating of TiO_2 affords the layered form, and the presence of Cs_2CO_3 results in Cs^+ ions being intercalated between the layers of the TiO_2. Powder X-ray diffraction of the Cs-intercalated phase surprisingly yielded no peaks indicating that the material is amorphous. Ion exchange of the Cs^+ ions with acid is easily accomplished which results in the desired protonated titanate ($HTiO_2$).

The diffraction pattern of $HTiO_2$ (Fig. 1) clearly shows an ordered system with a strong diffraction peak at $2\theta = 9.7°$, corresponding to an interlayer spacing value of 9.1 Å. This value is in good agreement with the literature [28]. The FTIR spectrum of $HTiO_2$ (Fig. 2) reveals a broad band around 3400 cm^{-1} along with a weak peak at 1630 cm^{-1}, both corresponding to intercalated water molecules. A relatively strong absorption between 400 and 1000 cm^{-1} corresponding to Ti–O and Ti═O vibrations are also observed.

Thermo gravimetric analysis on $HTiO_2$ under compressed air (Fig. 3) shows no major features except at relatively low temperatures. The major mass loss of $HTiO_2$ is that of adsorbed water observed from room temperature up to about 120 °C. A further minor weight loss is attributed to intercalated water. It was established by XRD that upon further heating the layered structure breaks down forming an amorphous material. Further heating of the amorphous material leads to the formation of anatase TiO_2. The reformation of anatase was confirmed by running powder X-ray diffraction on the residue of the TGA experiment, which gave a diffraction pattern identical to the anatase starting material. Fig. 4 illustrates the anatase TiO_2 produced after the TGA run on $HTiO_2$.

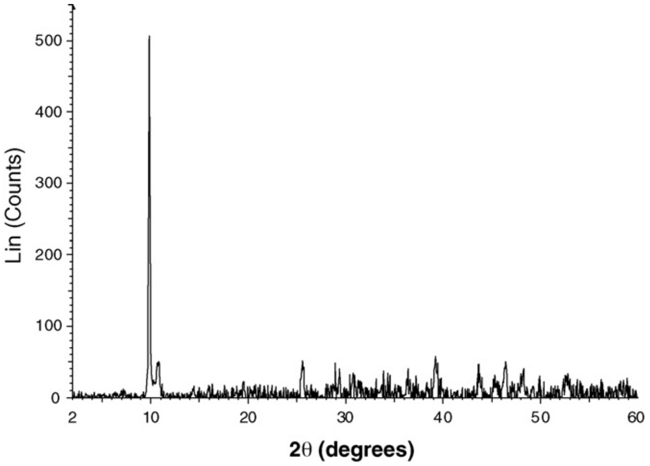

Fig. 1. XRD of $HTiO_2$.

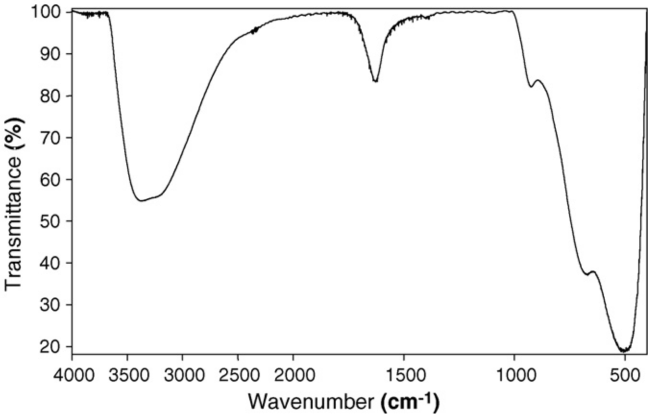

Fig. 2. FTIR spectrum of $HTiO_2$.

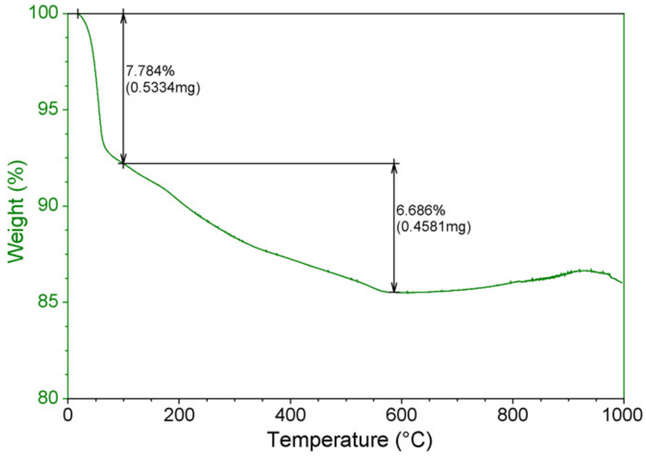

Fig. 3. TGA of $HTiO_2$ in air.

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[1] The casting was done in a fume-hood with air flowing at a face velocity of 100 ft/min. This results in evaporation of most of the adsorbed aniline molecules. However, it is quite conceivable to have remnant aniline molecules adsorbed on the surface of the TiO_2 nanomaterial, and this has, in fact, been confirmed by TGA analysis. In principle, the adsorbed aniline molecules could be washed away with polar solvents; however, this washing procedure usually leads to de-intercalation of the encapsulated aniline through an ion exchange process, and was therefore avoided.