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Green synthesis of polyaniline/clay/iron ternary nanocomposite by the one step solid state intercalation method

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ABSTRACT

The incorporation of two or more active components into clay layered structure with uniform distribution is expected to facilitate wider applications of the material. In this study, nanocomposite composed of clay, polyaniline and iron nanoparticles was synthesized by a facile and environmentally friendly strategy for the first time. Local smectite clay from Tunisia was exchanged with Fe^{3+} then it was subjected to fine grinding with anilinium chloride using mortar grinder and the mixture has been allowed for ageing at ambient air until the change of color to dark green. Both interlayer Fe^{3+} cations and atmospheric oxygen act as oxidant for aniline polymerization. In addition, the presence of interlayer Fe^{3+} and Fe^{2+} cations (the result of the reduction of Fe^{3+}) at the same time favors the formation of iron nanoparticles phase. Electrical and dielectric properties have studied using spectroscopy impedance. The ac conduction shows a regime of constant dc conductivity at low frequencies and a crossover to a frequency-dependent regime of the type $A\omega^S$ at high frequencies. The material shows high dielectric constant, resulting from the presence of iron nanoparticles, indicating its improved ability to store electric energy and to be used as capacitor.

1. Introduction

Conducting polymers such as polyaniline (PANI) have increasing scientific and technological interest in the synthesis of a broad variety of promising new materials due to their unique electrical, optical and optoelectrical properties as well as the ease of preparation and environmental stability [1]. On the other hand, Smectite clays are layered minerals composed of lamella of octahedral alumina sheet sandwiched between two tetrahedral silica sheets. These thin layers of aluminum silicate are organized in a parallel fashion to form stacks with a regular van der Waals gap in between them called interlayer spacing or gallery. Substituting ions of lower charge for those of higher charge in the octahedral layer (e.g., Mg^{2+} replacing Al^{3+}) produces surface negative charge for the clay. The variability of the *c*-axis dimension permits the intercalation of a large variety of inorganic and organic interlayer cations by the cation exchange process [2]. For these reasons, smectite clays are interesting inorganic-host-layered materials used to prepare functional materials [3]. The formation of polyaniline nanocomposites with smectite clays provides new synergistic properties that cannot be attained from individual materials such as thermal stability and mechanical strength [4]. The synthesis of polyaniline–clay nanocomposites is currently carried out by intercalation of the monomer in the clay interlayer in aqueous or aqueous–organic medium and the in situ polymerization is achieved by introducing an appropriate oxidant [4]. This method presents the disadvantages of being pollutant and it requires a step of separation to collect the nanocomposite. Recently, we have studied the possibility of the preparation of polyaniline clay nanocomposite using persulfate of ammonium as oxidant by a green synthesis method based on solid solid reaction [5]. However, the use of persulfate of ammonium present several disadvantages: (i) this oxidant is stoichiometrically consumed in the reaction and the reaction requires a large amount of chemicals for the mass production [6], (ii) the reaction generates large amount of acidic by-products resulting in difficult separation of polyaniline from the reaction mixtures [6] and (iii) the removal of these by-products from neat PANI represents about one half of the PANI cost [7]. Therefore, the use of others oxidants that can reduce contamination of formed PANI with byproducts and the cost is of importance. Some of the studies investigated the polymerization of aniline using iron (III) chloride and ozone as the oxidant [8]. This reaction is an environmentally benign since small amounts of iron (III) is required and the by-product is only water. Due to these factors, we have the motivation to prepare polyaniline clay nanocomposite by solid reaction using Fe^{3+} intercalated in the clay

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layer as oxidant for polymerization. Nevertheless, it was found, to our surprise, that the grinding of Fe^{3+} exchanged clay with anilinium chloride and the ageing of the product for 10 days at ambient air favors the formation of a novel nanoparticle iron/polyaniline/clay ternary nanocomposite. To the best of our knowledge it is the first time that such an investigation is reported. Firstly, we have characterized the nanocomposites by XRD, UV–vis, SEM and FTIR spectroscopy in order to reveal the structure of the obtained material and to elucidate the mechanism of the formation of this ternary structure. Secondly, we have studied its electrical and dielectric properties.

2. Experimental section

2.1. Material and reagents

Smectite clay was obtained from Zaghouan region in North-eastern Tunisia. The clay was dispersed in water and the $<2\ \mu m$ fraction was separated by gravity sedimentation and centrifugation. The presence of montmorillonite (MMT) was confirmed by the d_{001} spacing of the sample after air drying, calcination at 600 °C for 2 h and ethylene glycol treatment. By means of lithium test it was found that it constituted essentially of montmorillonite. The cation-exchange capacity (CEC) of the clay sample is 100 Meq per 100 g dry clay. The sample has a BET specific surface area of 80 m^2/g. The clay was exchanged with Fe^{3+} by dispersing 10 g of purified clay in 100 mL 1 M $FeC1_3$ solution (sigma Aldrich). The process is repeated three times to ensure the complete exchange of interlayer cations. The removal of excess chloride has been achieved by centrifugation and dialysis.

2.2. Protocol of preparation of the nanocomposite

0.5 g of Fe^{3+} exchanged montmorillonite (Fe-MMT) was grinded with anilinium chloride (AnCl) (Aldrich) for 120 mn using Retsch mortar, and the molar ratio of aniline to interlayer exchanged iron cation has been varied from 1 to 6. Then, the mixture has been left at ambient air until the color changed to dark green before characterization. Hereafter, Samples are denoted PANI/Fe (n) where n represent the proportion of aniline to Fe^{3+} cation.

2.3. Instruments

The structure was examined by X-ray diffraction using a Panalytical diffractometer X-ray diffractometer using Cu radiation. The IR spectra were collected with a Nicolet spectrophotometer model 560 spectrophotometer using a scanning range from 400 to 4000 cm^{-1}. Samples were prepared as KBr pellet. The electronic structure of the nanocomposites was determined from UV–vis absorption spectra in dimethylformamide (DFM) solutions on a PERKIN ELMER (model LAMBDA 20) spectrophotometer. The SEM images were obtained by a JSM-5400 scanning electron microscope (JEOL). A fine gold coat has been deposited on the samples under vacuum in a JFC-1100 sputter coater (JEOL). The electrical and dielectric conductivity of different samples were prepared as pellet form under a pressure of 5 Mg/cm^2 and coated on both sides with silver paint using a Hewlett Packard model 4192A impedance analyzer.

3. Results and discussions

3.1. Characterization of the nanocomposites

Fig.1 presents digital photos of anilinium chloride, Fe-MMT and their grinded mixture just after synthesis and after ageing period of 10 days at ambient air. As shown, the grinding of Fe-MMT with AnCl turns the color of mixture to green brown which gradually darkens with ageing time to become dark green after 10 days. It is well known that the conductive emeraldine form of polyaniline is dark green and this color has been considered by the majority of authors as indication of the end of the reaction of polymerization

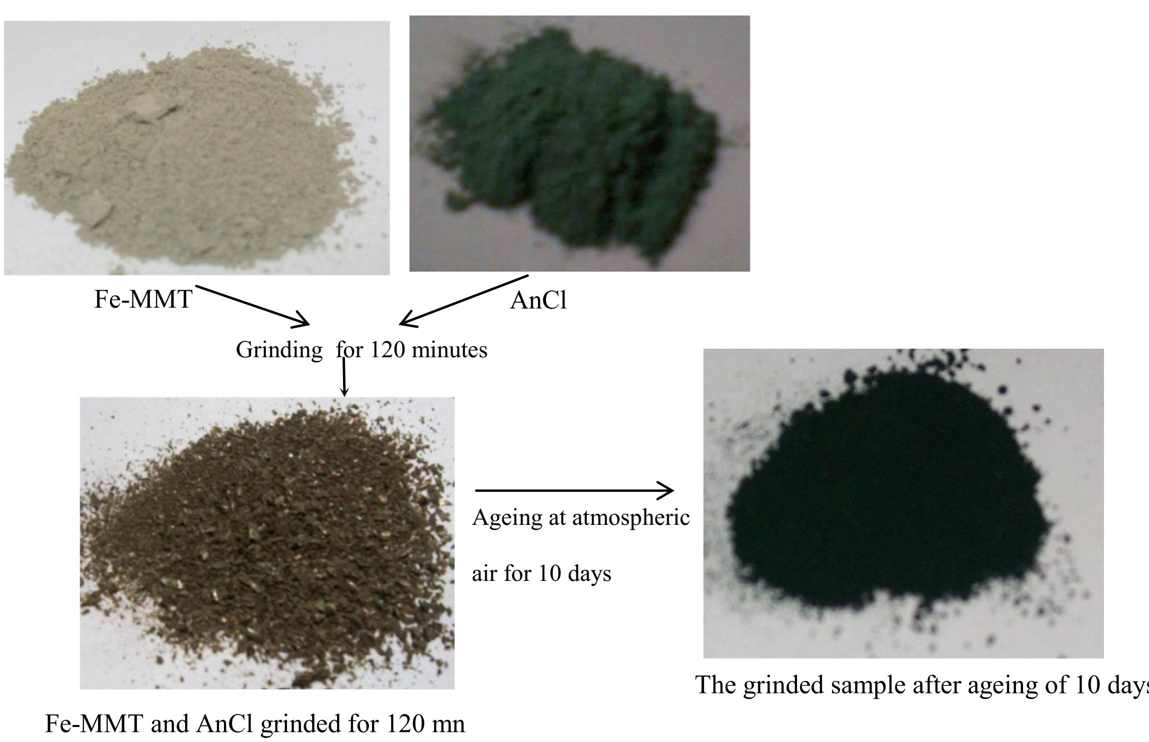

Fig. 1. Digital photos of Fe-exchanged montmorillonite, AnCl and their grinded mixture just after grinding and after 10 days of ageing.