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Synthesis of a Conducting Nanocomposite by Intercalative Copolymerisation of Furan and Aniline in Montmorillonite

Herein, we describe the synthesis of polyfuran, polyaniline, and their copolymer nanocomposites by in-situ oxidative polymerisation of corresponding monomers in the presence of montmorillonite, using ammonium persulfate as an oxidant. The obtained nanocomposites were characterised by Fourier-transform infrared spectroscopy, X-ray diffraction analysis, and UV-vis spectroscopy.

1 Introduction

Polyaniline (PANI) is one of the most intensively investigated conductive polymers, finding applications in the fields of sensing, corrosion protection, energy storage, electromagnetic interference shielding, electronic and optical devices, light-emitting diodes, and rechargeable batteries (Li et al., 2009, 2007, 2005, 2004; Huang et al., 2014). Polymers based on polyaniline and heteroaromatic monomers, e.g., polyfuran (PFu), polythiophene, and polypyrrole, have attracted considerable attention due to their unique electrical, electrochemical, structural, mechanical, and optical properties.

This work builds on the recent progress in the field of conducting polymers (Gonzalez-Tejera et al., 2000), focusing on PFu, PANI, and the corresponding copolymer (poly(ANI-co-Fu)). Conventional copolymerisation is a common strategy for modifying polymer properties. The problems associated with the copolymerisation of monomers with different reactivities can be solved by first synthesising the required sections of the desired polymer chain and subsequently electrochemically combining them to obtain the final polymer (Shilabin and Entezami, 2000).

Aniline/furan copolymers are expected to exhibit special properties. Incorporation of polymer networks into inorganic hosts allows the characteristics of parent constituents to be combined as a consequence of their molecular-level interac-

tions (Sen et al., 2008). For instance, montmorillonite clay denoted as Maghnite-H⁺(M-H⁺), a new non-toxic cationic initiator, has been used to catalyse the cationic polymerisation of a number of vinylic and heterocyclic monomers.

Herein, we examined the synthesis of polymer/M-H⁺ nanocomposites by intercalation of furan and/or aniline monomers in the interlayer spaces of M-H⁺, and characterised the produced polymers using various analytical techniques.

2 Experimental

2.1 Reagents

Aniline (Sigma Aldrich, Saint-Quentin Fallavier, France) was vacuum-distilled prior to use. Furan (Sigma Aldrich), 1-methyl-2-pyrrolidinone (NMP; Merck, Darmstadt, Germany), and ammonium persulfate (Merck) were used as received. Aqueous H₂SO₄ was used to prepare modified montmorillonite(M-H⁺). Solutions were prepared using water purified by an ElgaLabwaterPurelab Ultra system (Veolia Water Technologies Company, France). Natural raw montmorillonite clay was sourced from Tlemcen, Algeria.

2.2 Characterisation

X-ray diffraction (XRD) patterns of powdered nanocomposites were acquired using a CCDApex instrument (Bruker, Wissembourg, France) with an X-ray generator (Cu K_α, Ni filter) operated at 40 kV and 40 mA. Elemental contents were semi-quantitatively determined by X-ray fluorescence spectroscopy (PW1480 spectrometer running on Uniquant II software, Philips, Eindhoven, The Netherlands). UV-vis absorption spectra of NMP solutions of homo- and copolymers were recorded on a U-3000 spectrophotometer (Hitachi, Tokyo, Japan). Fourier transform infrared (FTIR) spectra were recorded using a Bruker Alpha spectrometer.

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2.3 M-H⁺ Preparation

Raw Maghnite (20 g) was washed with distilled water to remove impurities and crushed for 20 min in a ceramic ball grinder (Prolabo, France). To obtain proton-intercalated M-H⁺, the crushed sample was treated with 0.25 M H₂SO₄, filtered, and dried at 105 °C overnight. The composition of as-prepared M-H⁺ was determined by X-ray fluorescence spectroscopy (Table 1). Acid treatment enhanced the catalytic activity of Maghnite, decreasing the content of Al₂O₃ and increasing the proportion of SiO₂.

2.4 Synthesis of Polymer/M-H Nanocomposites

Nanocomposites were prepared by in-situ intercalative polymerisation of monomers. In a typical experiment, M-H was treated with aniline and/or furan monomers (22 mmol each), and the mixture was magnetically stirred at room temperature for 30 min. Subsequently, ammonium persulfate (100 ml, 0.1 M) was slowly added. The mixture was allowed to react upon stirring for 24 h, and the solid product was separated by vacuum filtration, sequentially washed with methanol and distilled water to remove traces of oxidant and oligomers (Samrana et al., 2012), and dried at 60 °C, yielding the target nanocomposite.

3 Results and Discussion

3.1 XRD Analysis

Figure 1 shows the XRD patterns of M-H⁺, PFu/M-H⁺, poly(ANI-co-Fu)/M-H⁺, and PANI/M-H⁺ nanocomposites, revealing M-H⁺ interlayer spacing changes. Thus, the peak of pristine M-H at $2\theta = 7.12^\circ$ was shifted to 5.05° and 6.02° for PANI/M-H⁺ and PFu/M-H⁺, respectively, being shifted to 5.30° in the case of poly(ANI-co-Fu)/M-H⁺ and indicating increased interplanar distance in M-H⁺ crystals (Table 2). The corresponding d-spacings (d_{001}) were calculated using Bragg's equation, $d = 2\pi/q$, where q is the magnitude of the scattering vector defined as $q = (4\pi/\lambda)\sin(\theta)$, λ is the X-ray wavelength, and 2θ is the scattering angle (Lee et al., 2000).

3.2 UV-Vis Analysis

UV-vis spectra of PANI/M-H⁺, PFu/M-H⁺, and poly(ANI-co-Fu)/M-H⁺ were recorded in NMP, with that of PANI showing maxima (λ_{\max}) at 360 and 600 nm (Fig. 2). In this spectrum, the first absorption band corresponds to the $\pi \rightarrow \pi^*$ transition of the polymer backbone benzene rings, whereas the second one is ascribed to the excitation of the quinone ring (N=Q=N) system due to charge transfer from adjacent benzene rings, with each side contributing half an electron on average (Anunziata., 2005). The spectrum of poly(ANI-co-Fu)/M-H showed

Compositions wt%	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃
Raw Maghnite	69.39	14.67	1.16	0.30	1.07	0.50	1.48	0.16	0.91
M-H ⁺	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34

Table 1. Elemental compositions (wt%) of acid-treated raw Maghnite (M-H⁺)

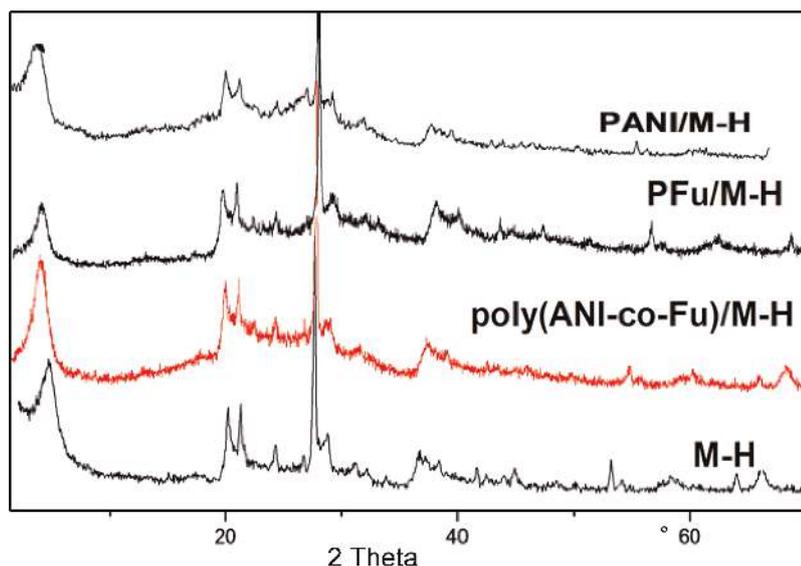
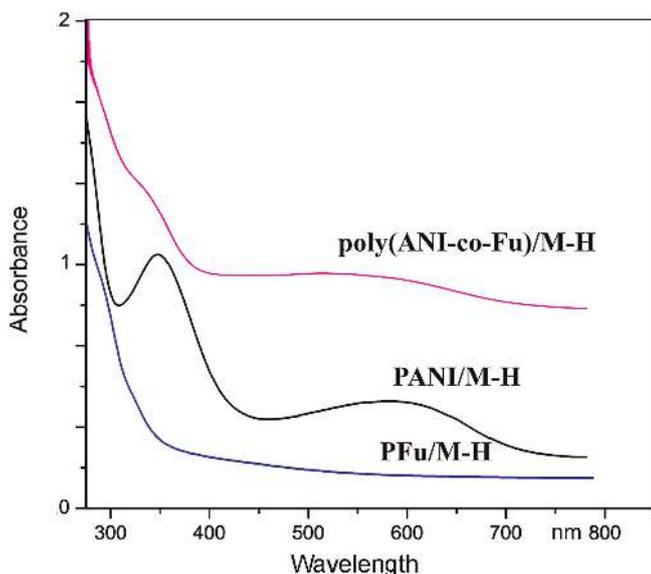


Fig. 1. XRD patterns of M-H, PANI/M-H, PFu/M-H, and poly(ANI-co-Fu)/M-H

Samples	Peak maximum 2 θ max deg	Basal spacing, $d_{(001)}$ Å	Interlayer spacing, Δd Å
M-H	7.12	12.40	//
PANI/M-H	5.05	17.51	5.11
PFu/M-H	6.02	14.66	2.26
Poly(50/50)/M-H	5.30	16.54	4.14

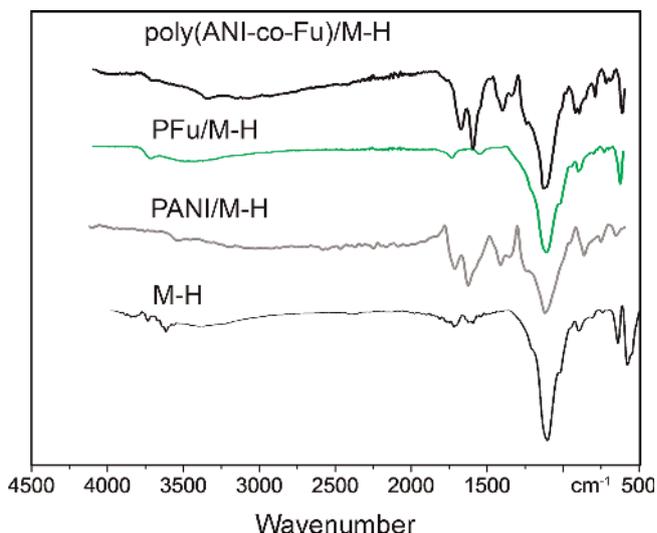
Table 2. XRD characterization of as-prepared nanocomposites

Fig. 2. UV-vis spectra of PANI/M-H⁺, PFu/M-H⁺, and poly(ANI-co-Fu)/M-H⁺

characteristic peaks at 325 and 580 nm, ascribed to the $\pi \rightarrow \pi^*$ transition and the copolymer polaron state, respectively. However, the spectrum of PFu/M-H did not show any absorption bands, indicating that polyfuran is insoluble in NMP.

3.3 FTIR Analysis

FTIR spectroscopy provides further structural insights (Fig. 3). The spectra of PANI/M-H⁺, PFu/M-H⁺, and poly(ANI-co-Fu)/M-H⁺ are almost identical, showing bands typical of similar conducting polymers (Asmat et al., 2017). Based on previous reports, the characteristic bands of pure M-H⁺ were assigned as 3630 cm⁻¹ (M-OH), 3395 cm⁻¹ (Mg-O), and 787 cm⁻¹ (Al-OH). The broad absorption band at 1007 cm⁻¹ involves the Si-O stretching mode of M-H, and that at 1623 cm⁻¹ is ascribed to the H-O-H bending of water (Yahiaoui et al., 2003; 2006; Hachemaoui et al., 2006). The characteristic peaks of polymer/M-H⁺ nanocomposites, i.e., the C=C stretch of benzenoid rings at 1492 cm⁻¹ and that of quinoid rings at 1591, 1301, and 1213 cm⁻¹ are associated with C-N stretching modes (Li et al., 2012; 2008). The FTIR spectrum of polyfuran

Fig. 3. FTIR spectra of M-H⁺, PANI/M-H⁺, PFu/M-H⁺, and poly(ANI-co-Fu)/M-H⁺

shows four characteristic bands of furan units, i.e., the C-H out-of-plane vibration at 717 cm⁻¹, the C-O-C stretching vibration at 1031 cm⁻¹, the C=C stretching vibration at 1624 cm⁻¹, and the aromatic C-H stretch at 3112 cm⁻¹ (Li et al., 2006). Moreover, the band at 791 cm⁻¹ suggests that furan rings in the produced polymer are linked in the "a" position (Wan et al., 1999). The strong peak at 1007 cm⁻¹ and those at 777 and 683 cm⁻¹ represent characteristic M-H vibrations.

4 Conclusion

We have successfully synthesised PANI/M-H, PFu/M-H, and poly(ANI-co-Fu)/M-H⁺ nanocomposites by oxidative polymerisation using ammonium persulfate as an oxidant and montmorillonite (M-H⁺) as a host. Aniline and/or furan were polymerised in-situ and largely incorporated into M-H⁺, as confirmed by XRD, FTIR, and UV-vis data, which reveal the appearance of novel spectral features and support the intercalation of polymer chains into the interlayer spaces of montmorillonite.

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