Rapid microwave synthesis of polyaniline–C$_{60}$ nanocomposites

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ABSTRACT

Nanocomposites of C$_{60}$ with the conducting polymer polyaniline (PANI) are obtained rapidly using enhanced microwave irradiation. Nanoparticles of C$_{60}$ embedded in PANI nanofibres, as well as a coating of larger C$_{60}$ clusters with PANI, are confirmed by SEM and TEM. An interaction between the C$_{60}$ and PANI is indicated by both UV–vis and FTIR studies. The remarkable yield of 45% is obtained after only 10 min in the presence of 10% of C$_{60}$.

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1. Introduction

The conducting polymer polyaniline (PANI) has shown great potential for use in organic electronics owing to its tuneable electronic properties [1]. With appropriate doping its properties can be reversibly changed from semi-conducting to conducting [1] while still retaining the manufacturing benefits of a polymer. Studies of PANI composites with the fullerene carbon molecule C$_{60}$ have mainly focused on the nature of the interaction between PANI and C$_{60}$ in the composite material and as yet have yielded less potential applications [2–7]. The formation of a partial charge-transfer complex between the electron donating imine groups of PANI and the electron withdrawing C$_{60}$ has been suggested [8–10], and quantum-mechanical calculations have indicated possible polymerization of aniline on the surface of C$_{60}$ [11]. These composites were formed either through the blending of PANI with C$_{60}$ in solution [8,10] or mechanically [9,12], or by adding C$_{60}$ during polymerization. The latter method of integrating C$_{60}$ into the PANI polymer yields a composite with greater conductivity relative to blended products [9,12].

The application of microwave radiation to dramatically enhance the reaction rate and yield in PANI syntheses has previously been reported [13]. There are at least two key factors which enthused inspired this project: (a) the opportunity for the large-scale production of PANI based compounds and (b) the advantages of enhanced microwave synthesis over the classical microwave and chemical syntheses. Thus, the application of microwave radiation to the MW synthesis of a PANI-C$_{60}$ would be of great interest. The change in reaction kinetics and the interaction of the components could yield a product with enhanced properties, advancing the potential of PANI-C$_{60}$ composites in materials research and development.

To that end, this communication reports on the fast polymerization of aniline in the presence of C$_{60}$ under the influence of microwave radiation.

2. Experimental

2.1. Method

The concentrations and methods used follow those outlined previously for microwave enhanced syntheses [14].

Microwave enhanced synthesis was performed using a single-mode microwave reactor (CEM, model Discover) using a 12 mL vessel with the liquid cooling jacket. A water-bath was used to pass coolant at a controlled temperature of $4\,^{\circ}C \pm 0.01\,^{\circ}C$ through the cooling jacket. This was used to maintain a low bulk reaction

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mixture temperature as lower synthesis temperatures have shown to increase conductivity [15] and molecular weight [16] of the polymer product.

To a mixture containing aniline (0.480 mL/0.490 g) in HCl (1 M, 6 mL) was added commercial C_{60} at 10 wt% relative to aniline (0.049 g). These mixtures were sonicated for a minimum of 1 h to disperse the C_{60}. Ammonium persulfate (APS, 0.4606 g) was dissolved in HCl (1 M, 6 mL) with stirring and was then added to the aniline/C_{60} mixture with continued stirring; this gives final concentrations of 0.44 M aniline, 0.17 M APS. Immediately after the APS solution was added, microwave irradiation (93 W at 2.45 GHz) was applied for the full 10 min reaction time with continued stirring, after which the reactor was shut off and the reaction halted by the addition of ~45 mL of milliQ water.

The product was retrieved by centrifugation (5 min at 4000 rpm) and was washed twice by subsequent addition of milliQ water and centrifugation. The final pellet of the product was dried in a vacuum oven at between 40 and 50 °C. The yield of the product was 0.2417 g (45% of the mass of aniline + C_{60} used in the synthesis).

2.2. Characterization

2.2.1. Electron microscopy

TEM was performed using a Phillips CM12 electron microscope. Samples were dispersed in water with sonication and deposited/dried on a sample grid. SEM measurements were carried out on an FEI (Phillips) XL30 S-FEG electron microscope. The samples for SEM were mounted on aluminum studs using adhesive graphite tape and sputter-coated with platinum.

2.2.2. UV–vis spectroscopy

Dried samples were dissolved in *N*-methyl-2-pyrrolidone (NMP) and spectra of these solutions were recorded on a Shimadzu UV-1700 spectrometer over the range 250–900 nm. There is possibility for NMP to slowly interact with C_{60} through its tertiary amine function, irreversibly changing its visible spectrum over time [12,17]. Therefore, all spectra were taken immediately after the dissolution of the composite samples to minimize the influence of this interaction on product characterization.

2.2.3. FTIR spectroscopy

The samples were dried, and the spectra were obtained using a PerkinElmer Spectrum 100 Series spectrometer (ATR, Diamond/ZnSe crystal, at 4 cm^{-1}).

3. Results and discussion

3.1. Electron microscopy

The TEM of C_{60} and the MW nanocomposite are shown in Fig. 1. The TEMs of C_{60} sample reveal that one part of the sample could not be dispersed into nanoparticles (Fig. 1A) while there are other regions which show relatively well separated C_{60} nanoparticles (Fig. 1B). TEM of the nanocomposite product exhibits C_{60} nanoparticles coated by PANI (Fig. 1C). These nanoparticles are on the scale of 50–100 nm, similar to nanoparticles that were observed in small amounts after sonication of C_{60} (Fig. 1B). This suggests the incorporation of nano-scaled C_{60} clusters during polymerization. These coated nanoparticles could potentially be in or on the PANI fibre-like morphologies seen in Fig. 1C.

SEMs of C_{60} and the MW nanocomposite are represented in Fig. 2. SEMs of the C_{60} sample revealed solid and featureless blocks covered by smaller particles (Fig. 2A and B).

This is in line with TEMs that imply the heterogeneous morphology of C_{60} obtained after sonication (Fig. 1A and B). SEM micrographs of the composite product (Fig. 2C and D) exhibit that the C_{60} is partly coated by nanostructured PANI. This suggests that there exist two processes: (1) the incorporation of C_{60} nanoparticles into PANI structure and (2) a coating of C_{60} clusters with PANI.

3.2. UV–vis spectroscopy

Three characteristic spectral absorption features of pure doped-as-synthesised PANI in the MW syntheses are shown in Fig. 3: a broad band at around 440 nm and a broad tail beyond 700 nm are due to the PANI transitions from polaron band to π^* band and π band to delocalized polaron band, respectively [18]. The low-intensity shoulder at ca 340 nm indicates the presence of a peak due to a transition from π band to π^* band that is probably overlapped with much broader 440 nm band. The sharp peak at 332 nm for the MW composite product originates from C_{60}. The strongest characteristic absorbances observed for pure C_{60} is the symmetry allowed transition at 332 nm, with a weaker allowed transition seen around 410 nm and very broad and weak forbidden transitions seen around 500–600 nm (see inset, Fig. 2) [19].

The differences between the polaron-π^* band and delocalized polaron band are reflected in a greater reduction in the intensities of polaron band transitions in the spectra of the MW composite, which occur at 407, 453 nm (Fig. 3). This indicates a change in the delocalization of polarons in the PANI structure, either through
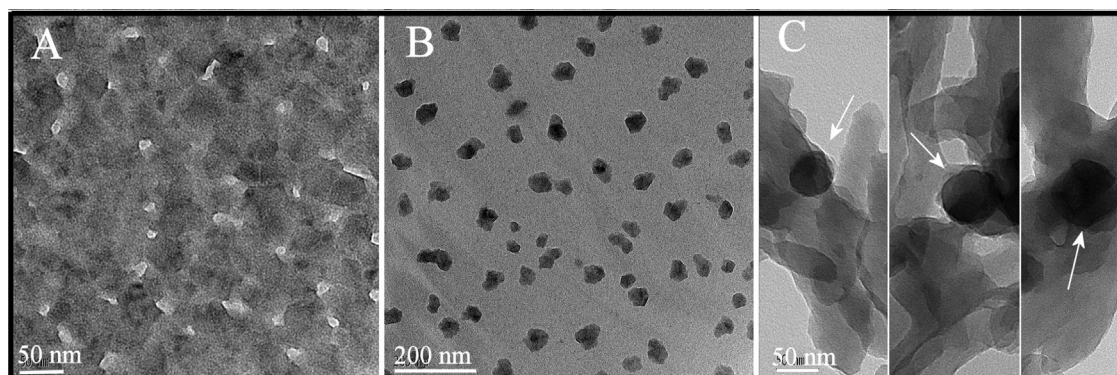

Fig. 1. TEM of the pure C_{60} sample obtained after sonication (A and B) and MW nanocomposite product with 10 wt% C_{60} (C; the C_{60} particles are indicated by arrows).