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Template-free solid state synthesis of ultra-long hairy polyaniline nanowire supercapacitor

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ABSTRACT

Present investigation deals with the formation of ultra-long hairy polyaniline (PANI) nanowire synthesized via mechanochemical (solid state) polymerization method using ammonium peroxydisulphate (APS) as an oxidant and citric acid as a dopant. Solid state synthesis method is a simple mechanochemical route for synthesis of PANI. Granular nanostructure is observed for undoped PANI, whereas doping with citric acid facilitates the formation of nanowire structure. This is the first ever report of nanowire structure of PANI using mechanochemical route. Undoped PANI granules agglomerate directionally or arbitrarily to form rods or clusters. PANI nanowires agglomerate to form irregular structures. FTIR spectra prove successful formation of PANI. Smaller PANI nanoparticles are joined end-to-end by dopant to form ultra-long hairy nanowire. Citric acid doped PANI nanowire exhibits less thermal degradation and superior supercapacitative performance compared to undoped PANI.

1. Introduction

PANI is an intrinsically conducting polymer (ICP) owing to its conjugated molecular structure. It has potential applications such as supercapacitor [1], gas sensor [2], pH sensor [3], biosensor [4] etc. Apart from its electrical conducting nature, it has been attracting researchers from years because different morphologies (e.g. rod [5], wire [6], sphere [7], tube [8], flower-like [9], fan-like [10], rice-grain-like [11] structures etc.) can be obtained for template-free [12] self-assembled PANI using different synthesis processes like chemical [13], electrochemical [14], mechanochemical (or, solid state) [15], interfacial [16] etc. Literatures are available on different synthesis routes [17] like electrospinning [18], potentiostatic methods [19,20] etc. resulting in PANI nanowire. Different morphologies e.g. granular [21], hollow spherical [22] etc. are reported for citric acid doped PANI. However, nanowire formation is not yet reported for citric acid doping of PANI. Formation of self-assembled wire-like nanostructure is also yet to be reported for PANI synthesized in the solid state method, which requires simple physical mixing of the reagents in solid state for the polymerization. In the present work, synthesis of ultra-long hairy PANI nanowire through mechanochemical route has been reported. Solid state synthesis of PANI without citric acid dopant exhibits small granules and their agglomerated structures, whereas nanowire formation occurs in presence of citric acid. Superior performance regarding thermal and supercapacitative behaviour are exhibited by ultra-long doped PANI nanowire, compared to undoped ones.

2. Experimental

Aniline and sulfuric acid were reacted in room temperature in deionized water medium without stirring where white coloured aniline sulphate (AS) was precipitated. AS and APS were mixed together in presence and absence of citric acid (for undoped and doped PANI) in mortar pestle for 30 min and kept for one day to provide sufficient time for reaction. Synthesized PANI was filtered with deionized water, ethanol and methanol to eliminate unreacted reagents if any and oligomers of PANI followed by drying at 50 °C for 30 min. Synthesized PANI was characterized by FTIR, FESEM and TEM. Thermal degradation was studied by TGA at 20 °C/min heating rate. Electrochemical property was investigated with potentiostat–galvanostat (Autolab) using 1 M H_2SO_4 electrolyte.

3. Results and discussion

TEM micrograph (Fig. 1a) reveals the granular nanostructure (diameter: 10–15 nm and length: 20–100 nm) for undoped PANI and ultra-long hair-like nanowire morphology (dia. 30–70 nm) for the citric acid doped PANI (Fig. 1b) with the most probable

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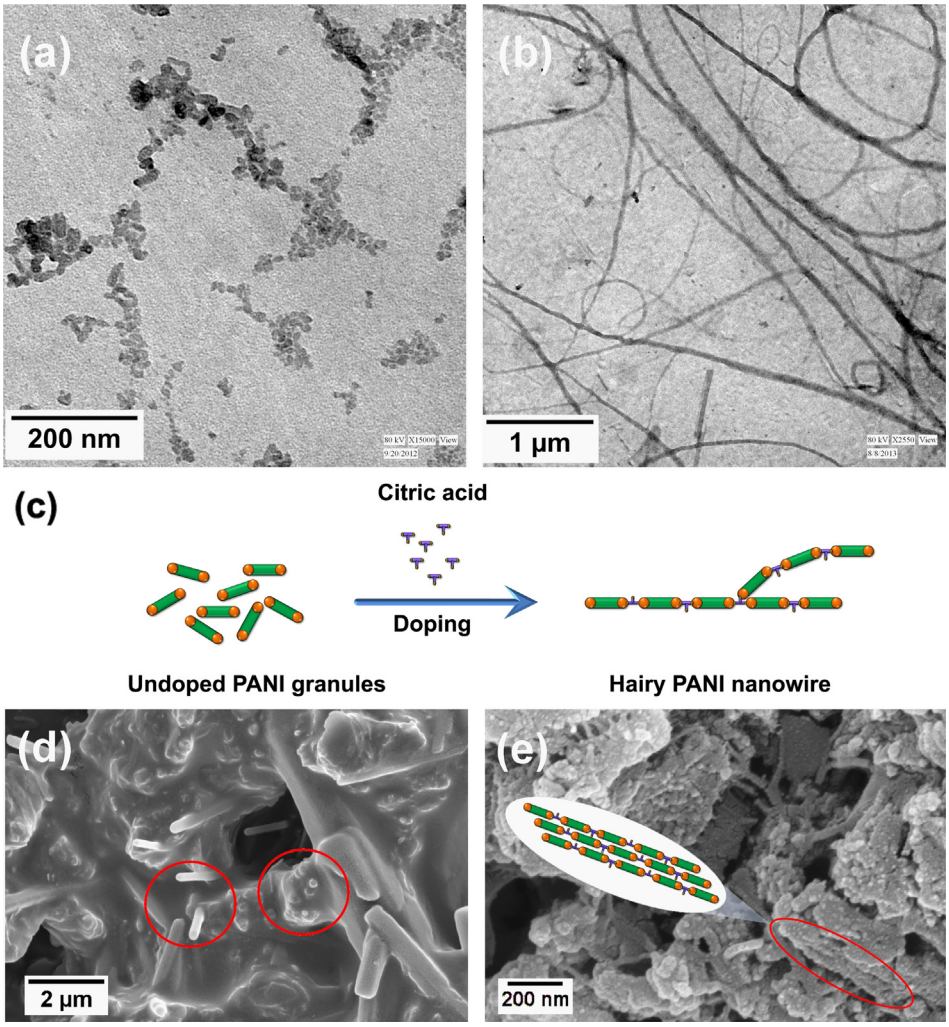

Fig. 1. (a,b) TEM and (d,e) FESEM micrographs of (a,d) undoped and (b,e) citric acid doped PANI. (c) Schematic representation of the mechanism of formation of hairy PANI nanowire.

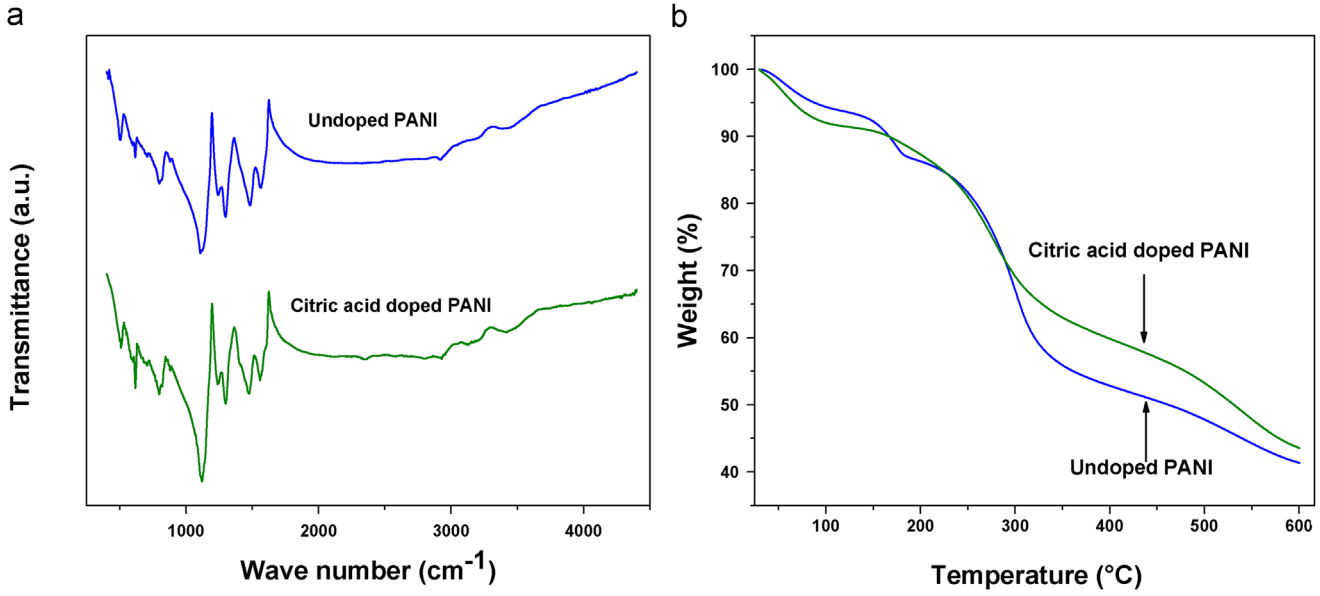

Fig. 2. (a) FTIR and (b) TGA thermograms of synthesized PANI.

diameter of ca. 20 nm (Fig. S1) and 25 nm (Fig. S2) respectively. During the process of solid state synthesis of PANI granular nanoparticles are formed in the absence of dopant. In case of in-situ doping with a tribasic dopant (citric acid) during synthesis, mostly two carboxyl groups attached to two $-CH_2-$ groups in citric acid show affinity towards positively charged polaronic sites in