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Enhanced thermoelectric performance and ammonia sensing properties of sulfonated polyaniline/graphene thin films

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ABSTRACT

Highly conducting nanocomposite film of polyaniline (Pani) with graphene (GN) was prepared by incorporating GN nanoplatelets in Pani matrix, followed by sulfonating it with fuming sulfuric acid. Sheet-like GN nanoplatelets were distributed uniformly in a Pani matrix, leading to high electrical conductivity due to π–π interaction between sulfonated Pani (*s*-Pani) and GN. Studies of the thermo-electrical behavior and ammonia-sensing behavior on GN@*s*-Pani showed high DC electrical conductivity retention under ageing conditions as well as excellent reproducible sensing response towards ammonia vapor in contrast to acid-protonated Pani.

1. Introduction

Recently, composites of polyaniline (Pani) with carbonaceous materials, such as CNT and graphene (GN), have attracted considerable attention for their potential applications in future technologies [1]. Among the different derivatives of Pani, sulfonated-Pani (*s*-Pani) has attracted considerable interest because it possesses distinct properties, such as high stability, good electrochemical properties, etc., which makes them suitable for applications in sensors, fuel cells, etc. [2,3]. *s*-Pani contains an ionizable sulfonic group that plays the role of an inner dopant ion. Therefore, no anion exchange occurs during the redox process and the material is considerably more stable than acid doped Pani [4]. On the other hand, due to the electron withdrawing nature of sulfonic group, the conductivity of *s*-Pani is lower than acid-protonated Pani. To achieve the beneficial properties of *s*-Pani, suitable fillers can be incorporated, which bestows electrical conductivity and can also give rise to Pani with hitherto unreported properties.

Among the different allotropes of carbon, GN is a rising star owing to its good combination of mechanical strength and conductivity, which is in contrast to the insulating properties of diamond, charcoal, etc. [5]. Owing to the exceptional properties of both *s*-Pani and GN, it is expected that composite of *s*-Pani and GN will give materials with unique properties. A large number of reports on the synthesis of *s*-Pani by different routes have been published [6,7], but there are few reports on the sulfonation of as-prepared Pani film by solution casting method, and its electrical/electrochemical properties. In this study, GN@*s*-Pani film was prepared, and their gas sensing properties and electrical stability under ageing conditions were examined.

2. Experimental section

The synthesis of an emeraldine base (EB) of GN@*s*-Pani film is reported elsewhere [8]. The EB film was sulfonated by stirring in 200 mL of 30% H_2SO_4 for 2 h, followed by washing with water and methanol, and drying at 80 °C [9]. For isothermal and cyclic ageing studies, the film was annealed at 150 °C in order to remove moisture and other volatile impurities. The sulfonated film (GN@*s*-Pani) was checked for electro-neutrality and ammonia vapor sensing. The details of the experimental setup is reported elsewhere [10].

The stability of GN@*s*-Pani was examined in terms of DC electrical conductivity retention under isothermal and cyclic ageing conditions using a standard 4-in-line probe device. In isothermal ageing, the film was heated to 50, 70, 90, 110 and 130 °C, and the electrical conductivity was measured at 10 min intervals. In cyclic ageing experiments, the DC electrical conductivity was measured five times from 40–150 °C.

3. Results and discussion

Scanning electron microscopy (SEM) of the Pani films revealed a uniform morphology without morphological defects on the

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surface (Fig. 1a), whereas in the case of GN@Pani, the GN sheets were imbedded and distributed on the surface (Fig. 1b). The cross-sectional SEM image of the fractured films showed a significant difference in the morphological features. Pani showed a compact structure (Fig. 1c), whereas in GN@Pani, the GN sheets can be observed clearly from the fractured view side (Fig. 1d). A uniform distribution on the surface and inside the matrix may contribute to a better translation of the nano-physical properties of both Pani and GN into the resulting GN@Pani film.

X-ray diffraction (XRD) of emeraldine base GN@*s*-Pani film (Fig. 1e) showed a single broad amorphous peak for Pani at $2\theta = 19.5^\circ$, due to the periodicity parallel to the polymer chain [11], as well as a sharp peak at $2\theta = 26.5^\circ$ that was assigned to graphite, which is indicative of the presence of GN in the composite with a typical *d*-spacing of 0.33 nm [11]. The XRD pattern of GN@*s*-Pani showed an increase in the intensity of the Pani peak, which might be due to the sulfonic group entering the Pani lattice and filling the vacant side leading to a more ordered arrangement [12]. The broadening and slight shift in the peak of Pani after sulfonation was related to steric hindrance induced after the incorporation of sulfonic group in the Pani lattice.

The diffuse reflectance spectra (DRS) of GN@Pani revealed three absorption peaks at 280 nm, 326 nm and 550 nm, which were assigned to the excitation of nitrogen in the benzenoid segments (π–π^*, polaron–π^* and n–π^* transition respectively) (Fig. 1f). In the case of GN@*s*-Pani composite, the absorption peaks shifted to 287 nm, 383 nm and 633 nm, indicating the delocalization of charge through the GN@*s*-Pani chain.

The initial electrical conductivity at room temperature of as-prepared GN@*s*-Pani was 1.42 S/cm, which is much higher than *s*-Pani (0.2×10^{-2} S/cm). The incorporation of sulfonic group decreases the conductivity of Pani due to the $-M$ effect but GN@*s*-Pani exhibited high electrical conductivity due to the very high electron mobility of GN. The increase in electrical conductivity was attributed to the additional synergistic effect of *s*-Pani and GN

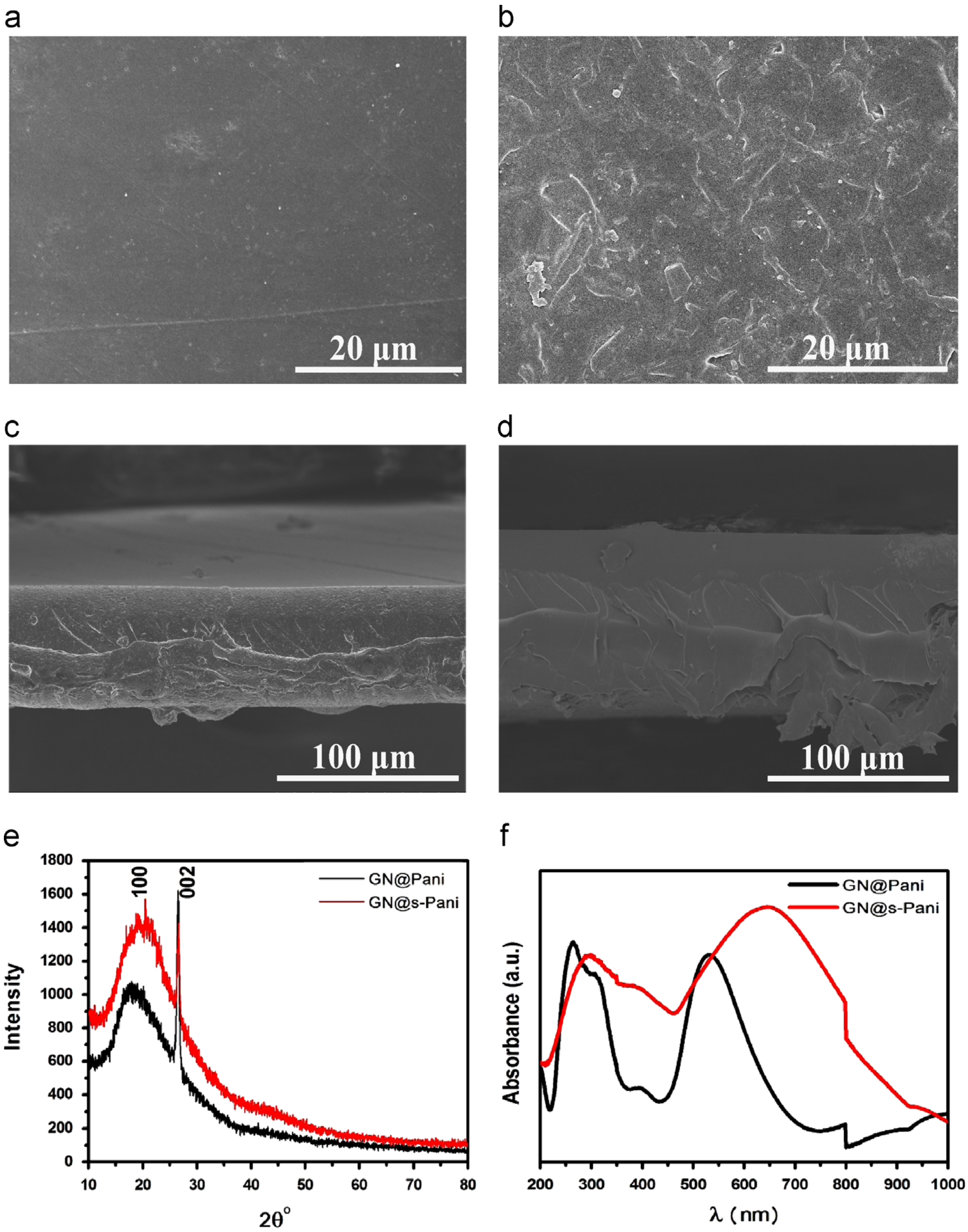

Fig. 1. (a) SEM image of Pani, (b) GN@Pani, (c) side view of fractured Pani film, (d) side view of fractured GN@Pani film, (e) XRD patterns of GN@Pani and GN@*s*-Pani and (f) Diffuse reflectance spectra of GN@Pani and GN@*s*-Pani.