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ARTICLE TYPE

Large slabs and allihn condenser type structures of polyaniline by an innovative one-pot approach

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We here describe a water-free synthesis of polyaniline nanostructures as a new chemical oxidative polymerization technique. Large slabs and allihn condenser type structures of polyaniline were obtained in absence and presence of para-toluenesulfonic acid.

Polyaniline has been known for more than 150 years,¹ but the considerable interest has aroused when Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa discovery that a polymer can be made conductive almost like a metal.² The research has mainly focused on understanding chemical structure and electronic conduction mechanisms, designing polymerization techniques, and developing chemical or physical modification methods for attempting to make polyaniline processable.³ A green route to conducting polyaniline by copper and gold catalysis has been investigated.^{4,5} Several methods have been proposed for the production of various types of nano- and micro-scale structures of polyaniline, however, chemical and electrochemical processes are the well known methods for the synthesis of polyaniline.⁶⁻⁹ Recently, polyaniline has caught again attention of researchers because new synthesis process is introduced, such as aqueous/organic interface polymerization method.¹⁰ Generally, for all synthesis procedures an aqueous medium is required to polymerize aniline. Herein, we report on a successful water-free procedure for the synthesis of polyaniline, assisted by pure organic phase and oxidant. Polyaniline consists of three oxidation states including leucoemeraldine, emeraldine, and pernigraniline base forms. The emeraldine base form of polyaniline can be doped to form emeraldine salt by wide variety of doping agents such as HCl, H₂SO₄, HNO₃, *para*-toluenesulfonic acid (PTSA), and camphorsulfonic acid, and conversely, the emeraldine salt form can be dedoped back by base.⁷

Our synthesis procedure is based on the chemical oxidative polymerization of aniline in the absence of common mineral acids (HCl, H₂SO₄, HNO₃) and water, but in the organic phase of tetrahydrofuran (THF) with an oxidant of ammonium persulfate powder [(NH₄)₂S₂O₈ (APS)], unlike traditional (homogeneous aqueous solution of aniline and oxidant in acid medium) and interfacial (biphasic aqueous/organic system) polymerization conditions. In our synthesis, aniline (0.1 mL) was dissolved in 30 mL THF, while the oxidant APS 1g and dopant PTSA 1g were added in powders form. The reaction was carried out at *ca.* 30°C (room temperature) in a conical flask of 125 mL volume. The reaction vessel was air tied by aluminium foil and wrapped with

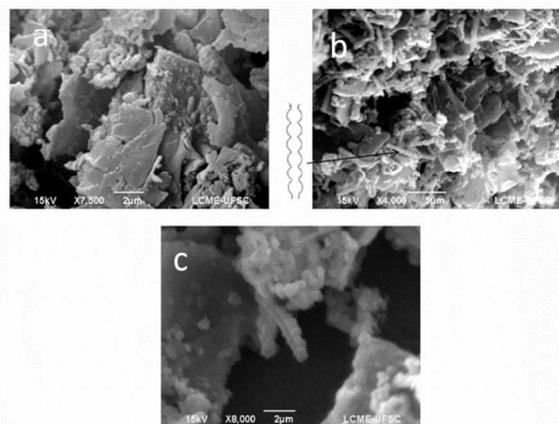
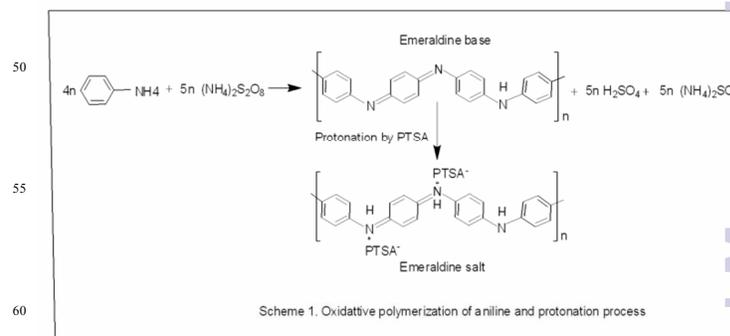


Fig. 1 SEM images of a) as synthesized polyaniline (slabs), b) and c) polyaniline-PTSA (allihn condensers with slabs) at different magnifications.

paraffin cover-lid. The mixture was stirred vigorously to ensure sufficient mixing of powders in the organic solvent. For comparison, polyaniline was also synthesized in the absence of dopant (PTSA) *via* similar procedure above. The reaction proceeds by a colorless induction period of few seconds. The color change pattern of the solution without dopant from milky-white to light yellow to yellowish brown and then to a dark red-orange was observed, from $t = 0$ to 36 h. Polymerization of aniline can be observed when the characteristic blue or green color of solution become visible. After $t = 72$ h, the light blue color precipitate (emeraldine base) was appeared. The color change pattern of the solution with dopant from milky-white to yellow to blue was observed, from $t = 0$ to 1 h. The entire organic

phase was filled with dark-green color (emeraldine salt), only after $t = 5$ h. This indicates that the polymerization of aniline is probably not associated with aqueous phase, and aqueous/organic biphasic, as well as organic phase, but seems to be rather affected by dopant PTSA in organic phase in respect of polymerization time. In the chemical reaction, aniline is oxidized by APS and protonated by PTSA,¹¹ the proposed reactions as follows (Scheme 1).

The dark-green precipitate was filtered and washed with deionized water, methanol, and finally with ether, and then dried in vacuum for 24 h. The polyaniline precipitate obtained by chemical oxidative polymerization of aniline in THF in the absence of dopant is composed of thick and large irregular slabs while in presence of dopant PTSA, allihn condenser type structure of polyaniline was formed along with slabs under identical conditions, as shown in Fig. 1.

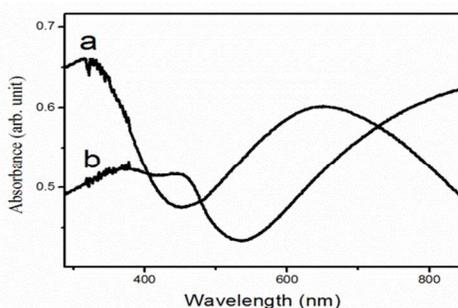


Fig. 2 UV/vis spectra of a) as synthesized polyaniline (without PTSA) and b) polyaniline-PTSA.

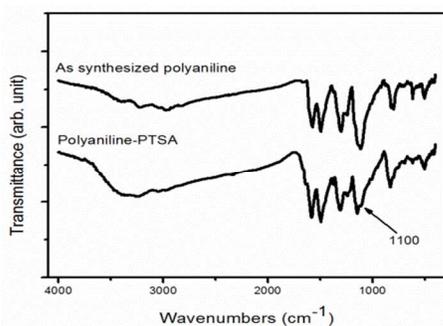


Fig. 3 FTIR spectra of as synthesized polyaniline and polyaniline-PTSA.

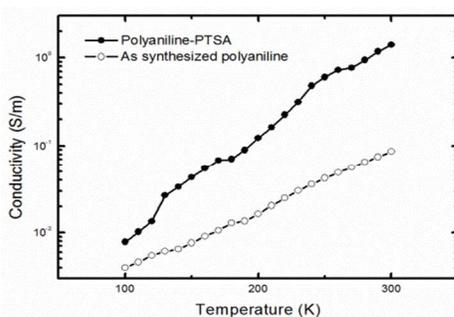


Fig. 4 Temperature dependence conductivity of as synthesized polyaniline and polyaniline-PTSA.

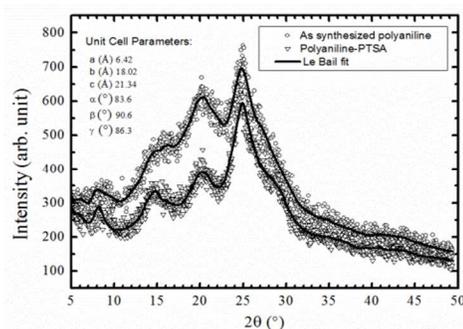


Fig. 5 XRD pattern of as synthesized polyaniline and polyaniline-PTSA.

The role of PTSA in formation of allihn condenser shape polyaniline is not clear, but it appears to be a specific mode of nucleation and dopant-micelle interactions in organic phase system that can guide the growth of polyaniline into an allihn condenser shape morphology.

Fig. 2 presents the UV/vis spectra of polyaniline with PTSA and without PTSA in isopropyl alcohol. The two strong absorption bands at approximately 322 nm and 650 nm are attributed to the emeraldine base (Fig. 2 a). The PTSA doped polyaniline (Fig. 2 b) present the characteristic absorption bands of emeraldine salt (ca. 340 nm, 450 nm, and 850 with a long tail to the IR). The UV/vis absorption patterns of polyaniline nanostructures obtained are consistent with previously reported results.^{10,12} Produced H_2SO_4 during oxidative polymerization of aniline by APS is not competing with PTSA for PANI doping. Therefore, PTSA is acting as both template and dopant.

The Fourier transform infrared (FT-IR) spectrum of PTSA doped polyaniline shows main characteristics bands: 1589, 1490, 1290, 1128, and 792 cm^{-1} . Compared to as synthesized polyaniline and PTSA doped polyaniline, the additional band at 1100 cm^{-1} is correlated with sulfonic group resulting from *para*-toluenesulfonic acid^{13,14} as shown in Fig. 3. The electrical conductivities of pressed pellet of polyaniline-PTSA and as synthesized polyaniline are about 1.4 S/m, and 0.087 S/m, respectively. This is comparable to conductivity reported for conventional polyaniline powders and polyaniline nanotubes synthesized using surfactants.¹⁵⁻¹⁹ Fig. 4 shows the conductivity behavior of polyaniline-PTSA and as synthesized polyaniline as a function of temperature through four-probe measurements. In Fig. 5 all observed XRD peaks are from polyaniline phase and are consistent with earlier reported results.^{18,19} The ratio between peak and background intensities gives the crystallinity of the material, which is 44% for doped and 41% for undoped polyaniline. The Le Bail fit of XRD patterns²⁰ was carried out with GSAS software,²¹ and initial parameters taken from data of polyaniline tetramer.²² As synthesized and doped polyaniline presented a triclinic structure and same unit cell parameters (Fig. 6) leading to the conclusion that the doping process do not distort the crystalline structure.

In summary, a water-free process was introduced for the synthesis of polyaniline nanostructures for the first time. New type morphologies such as large slabs and allihn condenser of polyaniline were observed. By this method aniline can be polymerized homogeneously in the network of polymer-gels; those become cross linked or coagulated in presence of water.

This is a simple method and can be extended to other conducting polymers, such as polypyrrole and polythiophene.

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Notes and references

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