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Rapid Formation of Nanosized Polyaniline Membranes on Surface Modified Glass Substrates

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The paper reports a rapid formation of nanosized polyaniline membranes on the surface-modified glass substrates during dispersion polymerization of aniline. Poly(N-vinylpyrrolidone) (PVP) was used to prevent the formation of the large agglomerates of polyaniline and then improve the smoothness of the membranes. Octa decyltrichlorosilane(OTS) changed the surface of the glass substrate from hydrophilic to hydrophobic, accelerating the deposition of polyaniline and enhancing the thickness of the membrane. FT-IR results proved the doped emeraldine oxidation state of the polyaniline membranes. The prepared nanosized membranes had the conductivity exceeding $10^6 \text{ S} \cdot \text{cm}^{-1}$. The high conductivity and the integrity of membranes render them potential applications in microelectronics, photoelectronics and gas separation.

Keywords: polyaniline; membranes; surface; polymerization

1 Introduction

Among the conducting polymers, polyaniline (PANI) is featured by its easy preparation by electric-chemical or chemical methods. Polyaniline can be reversibly doped and de-doped, providing an easy way to control its conductivity by the degree of doping. Polyaniline can be used as light-weight battery electrodes (1), electromagnetic shielding devices, anticorrosion coating (2, 3), gas and ion sensors (4), and gas separation membranes (5). However, polyaniline encounters large difficulties in processing into a required shape due to its rigid molecular structures. Here, the *in-situ* polymerization of aniline onto the proper templates suggests a new route in forming polyaniline. It has been reported the *in-situ* formation of a thin membrane of polyaniline onto the substrates immersed in the reaction mixture during the chemical oxidation of aniline (6–9). The prepared polyaniline membranes have potential applications in optoelectronics, microelectronics, and gas separations. Water-soluble polymers (10–12) or inorganic microparticles (13) have been introduced into the aqueous aniline solution to prevent the formation of macroscopic precipitation of polyaniline. Another important factor for the membrane formation is the surface condition of the substrates,

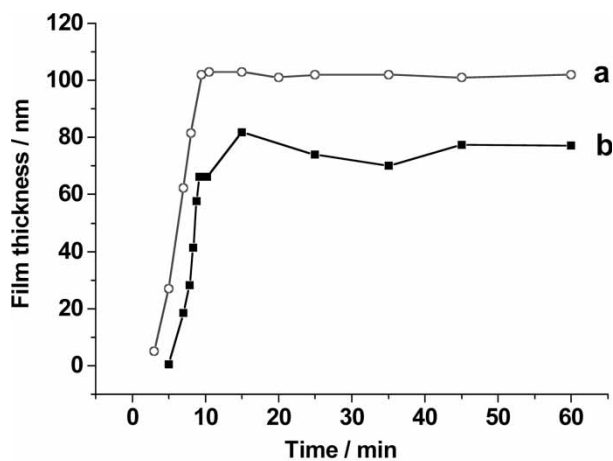
influencing the absorption of polyaniline particles or the active center for molecular growing. However, the surface conditions of the substrates have been unfortunately neglected till now. In this paper, we report the rapid formation of smooth nanosized polyaniline membranes on the octadecyltrichlorosilane modified glass substrates, with water-soluble poly(N-vinylpyrrolidone) introduced into the dispersion polymerization of aniline as the steric stabilizer. The morphology and the spectrometric behaviors of membranes have been investigated as well.

2 Experimental

In a typical surface deposition of polyaniline, 0.2 M aniline was oxidized by ammonium peroxydisulfate under ice bath. 1 wt% of poly(N-vinylpyrrolidone)(PVP) was added as steric stabilizer to prevent the formation of large polyaniline precipitates. The rectangle glass substrates surface-modified by octadecyltrichlorosilane (OTS) were immersed in the reaction mixture. During the polymerization of aniline, a thin polyaniline membrane was formed on the surface of the substrate. For comparison, the unmodified glass substrates or aqueous reaction system without PVP used as a counterpart.

The thickness of the membranes were calculated from the absorption of interferometry at 400 nm, according to the equation $d = 185A_{400}$ (9). The surface morphology of the membranes deposited on the glass substrates was assessed

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a: hydrophobic surface treated with OTS; b: hydrophilic surface

Fig. 1. Membrane thickness as the function of reaction time.

with a scanning electron microscope (JEOL JSM-6700F). The optical spectra of the membranes was recorded using TU-1800PC UV-vis spectrometer. The conductivity of the membranes was measured by a SDY-4 four-probe setup.

3 Results and Discussion

3.1 Formation of Nano-Sized Polyaniline Membranes and their Morphology

During the polymerization of aniline, thin polyaniline membranes formed on the surface of the substrate gradually. Figure 1 showed the change of membrane thickness during the aniline polymerization with 1 wt% PVP as steric stabilizer. The surface conditions of the substrates perform a great role on the formation of polyaniline membranes.

Modification by octadecyltrichlorosilane (OTS) changed the surface of glass substrate from hydrophilic to hydrophobic, and then accelerated the formation of polyaniline membranes notably. After 10 min, polymerization of aniline, the membrane would reach its maximum, 130 nm, on the hydrophobic substrate. By comparison, the hydrophilic substrate needed 15 min to form the 80 nm thick membrane.

The morphologies of the membranes prepared under different conditions were compared in Figure 2. Image (a) showed a smooth and whole membrane on hydrophobic substrate after 8-minute polymerization, while counterpart membrane had obvious sizeable flaws, as shown in image (b). Here, the rapid formation on hydrophobic substrate was revealed as well. In both cases, the membranes seemed to be mono-particle layers of polyaniline. A small amount of colloidal particles of polyaniline absorbed on the membranes were glistening bright due to its height under SEM.

Image (c) of Figure 2 showed the large amount of precipitation on the polyaniline membrane without PVP in the aqueous reaction solution, to indicate its effect on preventing the formation of large agglomerates of polyaniline.

3.2 Conductivity and Spectrometric Absorption of the Membrane

FT-IR spectra were used to characterize the structure of PANI membranes prepared, as shown in Figure 3. The membrane prepared with PVP as steric stabilizer had characteristic absorption of C-C stretching of quinoid ring (1479 cm^{-1}) and benzenoid ring (1566 cm^{-1}). The absorption at 1133 cm^{-1} was the contribution of electron-like charge carriers, to prove the doped emeraldine oxidation state. Moreover, the absence of characteristic absorption of PVP at 1668 cm^{-1} in the spectra of PANI membrane suggested the amount of PVP was quite small in the polyaniline membrane, if any.

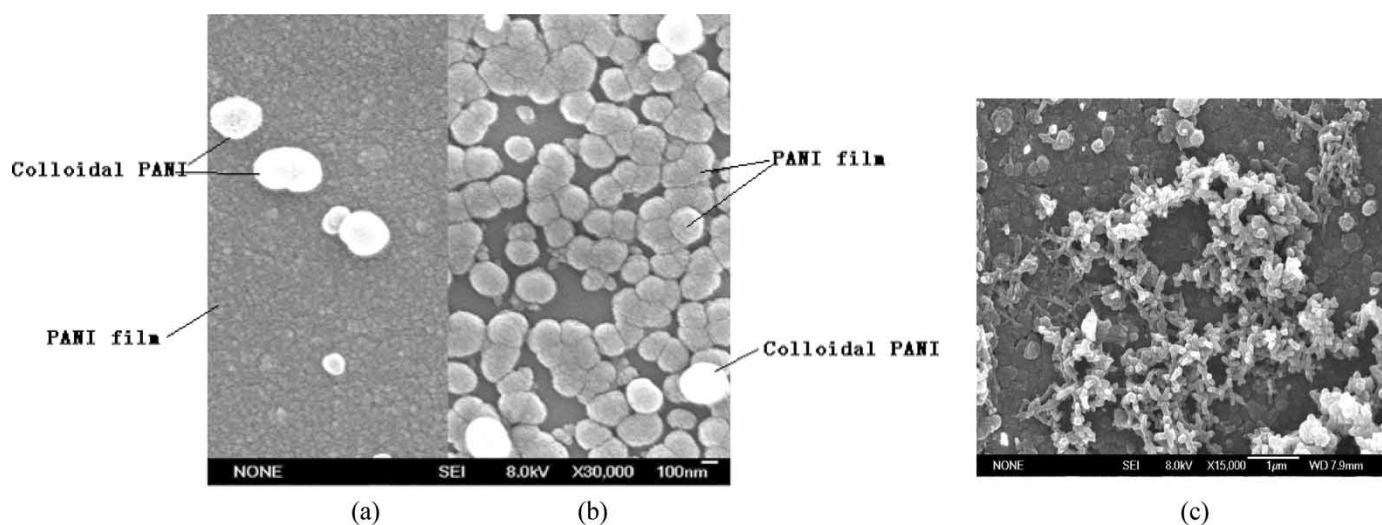


Fig. 2. Surface morphology of polyaniline membrane prepared in the presence of PVP: (a) on hydrophobic surface, (b) on hydrophilic surface; and (c) without PVP.

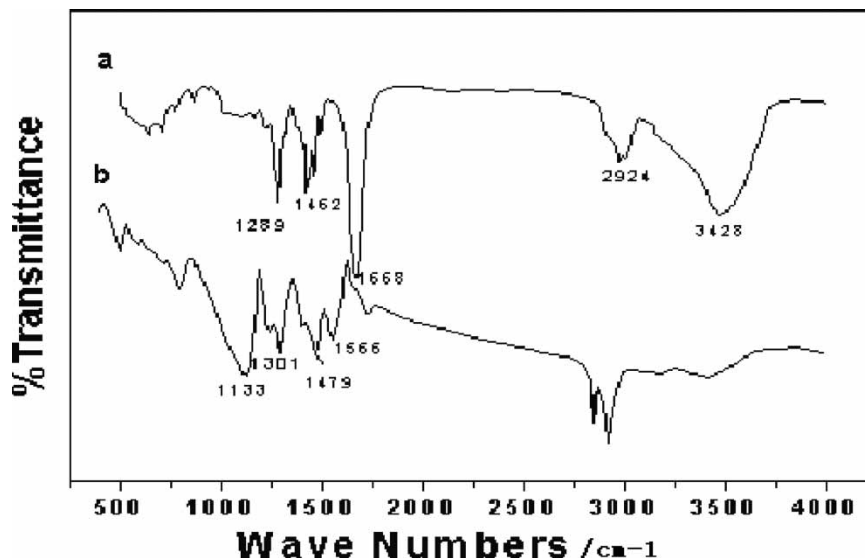


Fig. 3. FT-IR spectra of (a) (n-vinylpyrrolidone) and (b) HCl-doped polyaniline membrane.

The UV absorption of the membranes was shown in Figure 4. The membranes had the shifted UV absorptions in both de-doped and doped states. For the doped cases, the absorption of the excitation of amine in benzenoid segments shifted from about 330 nm of the polyaniline solution to 420 nm of nanosized membrane; The contribution of the polaron (14) of the membrane appeared at about 810 nm, while the corresponding absorption of polyaniline solution appeared at about 950 nm (not shown in the scale of the figure). The UV absorption of polyaniline membrane was

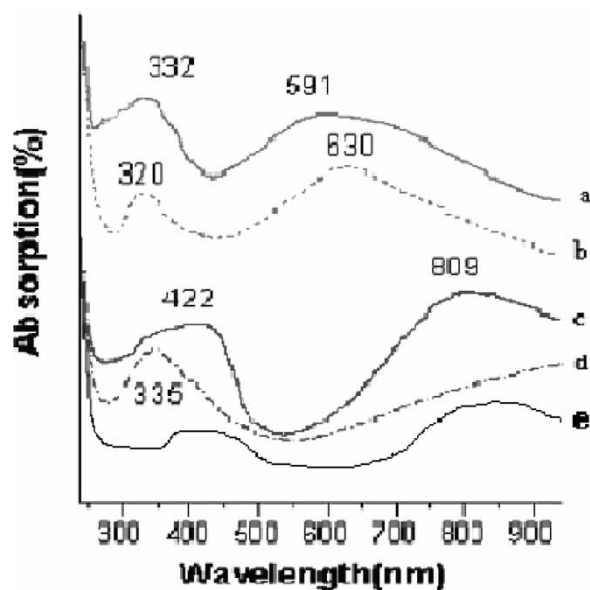


Fig. 4. UV-Vis absorption spectra of *in-situ* polymerized polyaniline membrane; a) dedoped nanosized membrane; b) dedoped polyaniline; c) HCl-doped nanosized membrane; d) HCl-doped polyaniline, and e) Colloidal PANI particals in aqueous media.

quite similar with the colloidal particles formed in the aqueous solution (15), which suggested the deposition of small colloidal polyaniline particles on the surface modified substrates, quite different from the mechanism of *in-situ* polymerization of aniline on the unmodified substrates. The influence of the surface modification on the formation mechanism should be one of the focuses of the future investigation.

The conductivities of the polyaniline membranes were determined by their thickness. When the thickness reach their maximum, the polyaniline membranes had the conductivity of $10\text{--}10^1 \text{ S} \cdot \text{cm}^{-1}$, as indicated by absorption of the free charge carriers in the spectra.

4 Conclusions

The paper reports on the preparation of nanosized PANI membranes on the surface-modified glass during dispersion polymerization of aniline. Their high conductivity and the integrity of membranes suggest a promising future in industrial applications. Some conclusions should be noted as below:

The combination of water-soluble polymer PVP in the surrounding aqueous media and surface modification on the glass substrates by OTS could result in the rapid formation of a smooth and dense polyaniline membrane in nanoscale.

Polyaniline in the membranes had doped emeraldine oxidation state, and provided them the conductivity exceeding $10^2 \text{ S} \cdot \text{cm}^{-1}$.

Polyaniline in the membranes had similar UV absorption with the small colloidal particles formed in the surrounding media. It seemed that the formation mechanism on the surface modified substrates involved in the deposition of the colloidal particle, not merely a surface polymerization of aniline. The formation mechanism will be studied in the future.

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