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# Preparation of oligoaniline derivative/polyvinylpyrrolidone nanofibers containing silver nanoparticles

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ABSTRACT

Oligoaniline derivative/polyvinylpyrrolidone nanofibers containing silver nanoparticles have been successfully prepared by electrospinning technique. Silver nanoparticles were prepared through reduction of $Ag^+$ by oligoaniline derivative, and the process of redox was monitored by UV–vis spectra. The morphology of Ag-polymer blends nanocomposites and the distribution of Ag nanoparticles were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrochemical analysis of nanocomposites was checked by cyclic voltammetry (CV) in the 0.5 M $H_2SO_4$. In addition, the presence of Ag nanoparticles was indicated by X-ray diffractometer (XRD).



## 1. Introduction

Polyaniline is one of the most frequently investigated conducting polymers because of its potential for advanced applications such as secondary batteries, electrochromic devices, electrostatic discharge protection, biosensor, electrochemical capacitors and chemical sensors [1] due to its good environmental stability, ease of preparation and reversible acid/base doping/dedoping chemistry [2]. In addition, PANI exists in various oxidation states ranging from a reduced leucoemeraldine form to the fully oxidized pernigraniline form. The ability of PANI to exist in a range of intrinsic redox states makes it a unique and interesting class of polymeric materials [3]. The ill-defined structure and limited processability of PANI makes design and chemical manipulation of its nanoscale derivatives more challenging [4]. Oligoanilines with well-defined chain lengths are model compounds for the electronic, optical, magnetic and structure properties of PANI [5]. Thus the novel properties lead oligoanilines to many potential application, for instance, as electroactive materials in fabricating electroluminescent, chemically and electrochemically tunable gas-separation membranes, rechargeable batteries, electroactuator devices, anticorrosion and antistatic coatings, biosensor and so on.

In recent years, the electrospining technique has been proven to be a versatile and effective method for fabricating nanofibers with exceptionally long length, uniform diameter, diverse composition and high surface to volume ratio [6], which can be applied in membrane technology [7], optical sensors and biosensors [8], superhydrophobic surfaces [9], tissue engineering [10], and drug delivery [11]. Since Yang et al. first prepared polyacrylonitrile (PAN)/silver nanocomposite by electrospinning [12], fabrication of nanocomposite fibers with functional nanoparticles in the polymer has attracted the increasing attention. Although nanofibers from pure PANI or blends were well documented [13], oligoanilines nanofibers and oligoaniline nanofibers containing silver nanoparticles have been rarely reported.

Herein, we report the preparation and characterization of oligoaniline derivative/polyvinylpyrrolidone nanofibers containing silver nanoparticles. It is known that PVP is used to immobilize the Ag nanoparticles, and oligoaniline derivative is used as a reducing agent for $Ag^+$ in the PVP solution. The possible formation mechanism of Ag nanoparticles appears to involve a redox reaction between $Ag^+$ and oligoaniline derivative based on the data of UV–vis spectra. Furthermore, the nanocomposite was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), cyclic voltammetry (CV) and X-ray diffractometer (XRD).

## 2. Experimental

### 2.1. Materials

Polyvinylpyrrolidone (PVP, $M_w$ = 1 300 000) was purchased from Aldrich Co. Silver nitrate ($AgNO_3$, 99.8%) were supplied by Beijing Chemicals Co. (China). *N*,*N*′-Dimethylacetamide (DMAc, 99%) was

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obtained from Tianjin Chemicals Co. (China). All reagents were used without further purification.

### 2.2. Preparation of oligoaniline derivative

Suitable preparations for oligoaniline derivative (OD) has been reported in the literature [14].

### 2.3. Preparation of OD/PVP nanofibers

In a typical procedure, 0.2 g PVP was mixed with 1.5 g DMAc in a conical flask by magnetic stirring. After PVP dissolved completely, 0.3 g oligoaniline derivative was added into the above solution, followed by magnetic stirring for about 5 h. The solution was then loaded into a plastic syringe equipped with a 14 cm long copper needle. The needle was connected to a high-voltage supply that is capable of generating DC voltages up to 30 kV. In our experiment, a voltage of 12 kV was applied for electrospinning. A piece of flat aluminium foil was placed 16 cm from the tip of the needle to collect the OD/PVP nanofibers. The electrospinning was conducted in the air.

### 2.4. Preparation of OD/PVP nanofibers containing Ag nanoparticles

0.0787 g $AgNO_3$ in 0.2 mL $H_2O$ was added to the above solution (0.2 g PVP + 0.3 g oligoaniline derivative + 1.5 g DMAc) with strongly magnetic stirring for 0.5 h. Then the solution was loaded into a plastic syringe and electrospun at same condition.

### 2.5. Instruments

The obtained OD/PVP nanofibers and OD/PVP with Ag nanocomposite images were taken using SEM and TEM. The SEM measurements were performed on a SHIMADZU SSX-550 microscope. TEM experiments were performed on a Hitachi H-8100 electron microscope with an acceleration voltage of 200 kV. XRD patterns were obtained with a Siemens D5005 diffractometer using Cu Kα radiation. UV–vis spectra were performed on UV-2501 PC Spectrometer (SHIMADZU) in DMAc. The CV of the nanocomposite was performed with a CHI 660A Electrochemical Workstation (CH Instruments, USA) in a conventional three-electrode cell, by using thin films cast from DMAc solutions onto a g-c electrode.

## 3. Results and discussion

OD/PVP solution containing Ag nanoparticles in DMAc was prepared by directly reducing $Ag^+$ ions in the solution and then electrospinning the solution into the nanofibers. OD could reduce $Ag^+$ ions into $Ag^0$, which was used as reducing agent. It has been reported that PANI exists in various oxidation states ranging from a reduced leucoemeraldine form to the fully oxidized pernigraniline form, which makes aniline polymers and oligoaniline a unique class of reducing and/or oxidizing agents [15]. In order to study the reducing $Ag^+$ to $Ag^0$ in the OD/PVP solution, UV–vis absorbance spectroscopy was used; specifically, it could be used to track the transition of oxidation states of oligoaniline derivative. From Fig. 1 we can see that there is only one absorption at 320 nm observed in OD/PVP solution which is associated with a $\pi$–$\pi^*$ transition of the conjugated ring system [16]. When $AgNO_3$ solution was added into the OD/PVP solution, the absorption started to undergo a blue shift (from 329 nm to 318 nm) and the UV–vis spectra showed a new absorption at about 615 nm which is assigned to exciton-type transition between the HOMO orbital of the benzoid ring and the LUMO orbital of the quinoid ring. It shows that the oxidation state of OD changed from leucoemeraldine form to emeraldine form after adding $AgNO_3$ solution, which indicated that the $Ag^+$ changes into $Ag^0$, as shown in Fig. 2. Through the monitoring of UV–vis spectra, we can see that the whole process of reduction is not longer than 20 min. Therefore, we consider that the OD plays an important role in reducing of $Ag^+$ and the action of DMAc in reducing would be ignored. However, we cannot find the absorption of the Ag nanoparticles because of less amount of $AgNO_3$ than that of OD.

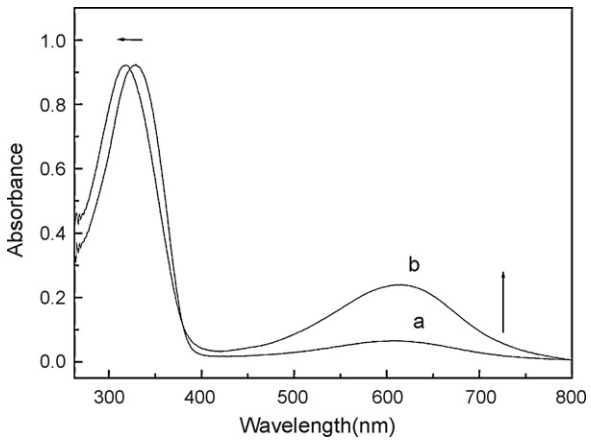


**Fig. 1.** UV–vis absorption spectra of OD/PVP solution (a) and OD/PVP solution after adding $AgNO_3$ (b).

Fig. 3a shows SEM image of the electrospinning OD/PVP nanofibers nanofibers. The obtained nanofibers are smooth and uniform. They are longer than several millimeters, with

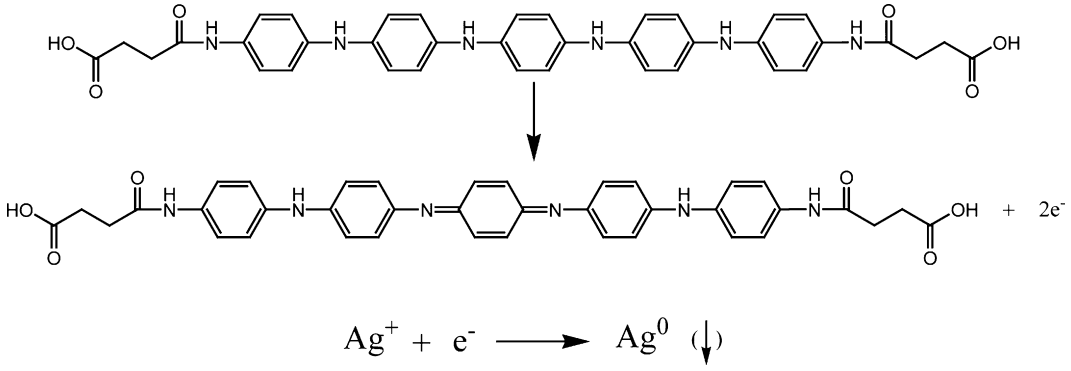


**Fig. 2.** Formation of Ag nanoparticles with OD used as reducing agent.