

Large scale, templateless, surfactantless route to rapid synthesis of uniform poly(*o*-phenylenediamine) nanobelts

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We reported the interesting finding that large scale uniform poly(*o*-phenylenediamine) nanobelts with several hundred micrometers in length, several hundred nanometers in width, and several ten nanometers in height can be rapidly yielded from an *o*-phenylenediamine–HAuCl₄ aqueous solution without the additional introduction of other templates or surfactants at room temperature.

In recent years, electrically conducting and intrinsically colored polymers are widely used in diverse applications.¹ Polyaniline (PANI) is one of the most studied conducting polymers due to its chemical stability and relative high conductivity.² Polymers based on aniline derivatives have also been extensively investigated.³ Among them, poly(phenylenediamine) homopolymer is reported to be a highly aromatic polymer containing 2,3-diaminophenazine or quinoraline repeating unit and exhibiting high thermostability.⁴ Poly(*o*-phenylenediamine) (PPD) conducting polymers⁵ have been used as an electrochemical reduction catalyst for dioxygen⁶ and as a sensor for some chemical species.⁷ PPD is usually prepared by electrochemical polymerization of *o*-phenylenediamine (*o*-PD).⁸ On the other hand, chemical oxidation of the monomer of *o*-PD is proved to be an effective preparative method for preparing PPD.⁹

Researches into molecular wire have developed largely since the discovery of carbon nanotubes.¹⁰ Conducting polymers also hold promise as advanced materials in this area due to their long conjugated length and metal-like conductive property.^{2c,11} Zhang *et al.* have fabricated conducting polymer nanowires with soft lithography.¹² Polypyrrole nanotubes have been fabricated by reverse microemulsion polymerization in an apolar solvent.¹³ Wan and co-workers have reported the synthesis of PANI and polypyrrole microtubes with the use of β -naphthalene sulfonic acid to serve as a dopant and surfactant.¹⁴ Carswell *et al.* reported that PANI nanowires could be formed on flat surface under the control of the adsorbed surfactants.¹⁵ Tubes, fibers, or filaments of polypyrrole, poly(3-methylthiophene), polyacetylene, and PANI have been successfully prepared with a template-based method characteristic of synthesizing the desired material within the pores serving as a template.¹⁶ However, a rather tedious post-synthesis process is often required to remove the template used. Additionally, the nanotubes or nanofibers preformed may be destroyed or form undesirable aggregates when released from the template. Therefore, although chemical synthesis of conducting polymers with one-dimensional structure is a very interesting project, seeking a simple but effective synthetic approach is still a main challenge for materials chemists. In this communication, we reported a novel but simple templateless, surfactantless route to the large scale and rapid synthesis of uniform PPD nanobelts by directly mixing HAuCl₄ and *o*-PD aqueous solutions at room temperature without the additional introduction of other templates or surfactants.

HAuCl₄ was purchased from Aldrich and *o*-PD from Beijing Chem. Co. All reagents were used as received without further purification. The water used was purified through a Millipore system. In a typical experiment, 4 mL of 0.072 M *o*-PD aqueous solution was diluted with 10 mL of water and the pH value of the resulting *o*-PD solution is 7.5. After then, 1 mL of 0.024 M HAuCl₄ aqueous solution was rapidly added into this solution under vigorous stir. A quick color change was observed upon the addition

of HAuCl₄. A large amount of precipitates were observed after stored for several hours.

The morphology of the resulting precipitates was characterized with a XL30 ESEM FEG scanning electron microscopy (SEM) at an accelerating voltage of 20 kV. Fig. 1 shows typical SEM images. Lower magnification image [Fig. 1(A)] indicates that the precipitates consist of a large quantity of uniform one-dimensional structures. Higher magnification image [Fig. 1(B)] reveals these structures are transparent nanobelts with several hundred micrometers in length, several hundred nanometers in width, and several ten nanometers in height. It is important to note that all these nanobelts are separated from each other. Also observed in these images are a number of nanoparticles.

The X-ray diffraction (XRD) analysis of the resulting precipitates was carried out on a D/MAX 2500 V/PC X-ray diffractometer using Cu (40 kV, 200 mA) radiation. Fig. 2 shows the XRD pattern obtained. The broad peak centered at $\sim 25^\circ$ can be ascribed to the formation of amorphous PPD polymer and the occurrence of strong diffraction peak at low Bragg angle can be attributed to larger crystalline size.¹⁷ The other four peaks located at 37.82, 43.82, 64.38, and 77.27° are assigned to 111, 200, 220, and 311 faces of an Au crystal, respectively, demonstrating the formation of gold.¹⁸

The chemical composition of the belts and particles obtained was further determined by elemental analysis of the resulting precipitates coated on indium tin oxide (ITO) glass slide using secondary electrons by SEM. The peaks of Au, C, and N are noticed (other peaks originated from ITO glass substrate), as shown in Fig 3. Based on the elemental composition of belts and particles, we can

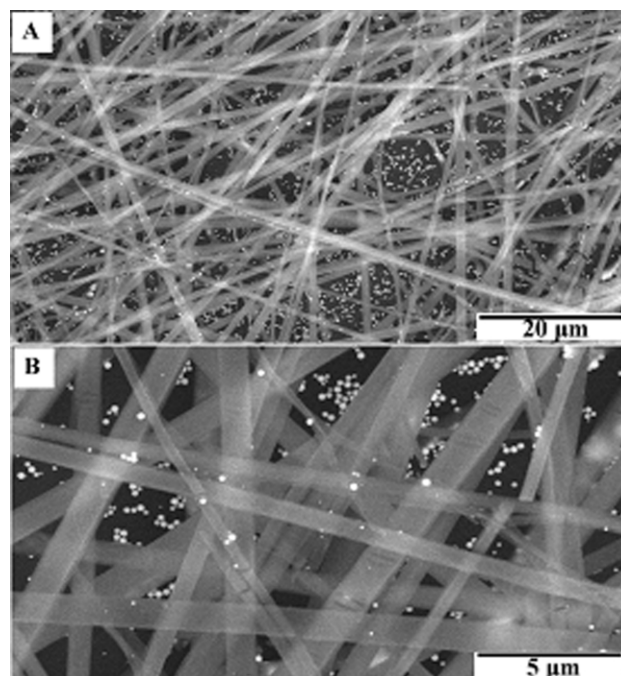
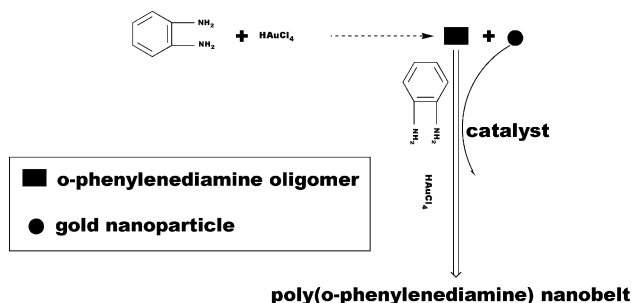


Fig. 1 Typical SEM images of the resulting precipitates.

conclude that the belts are PPD polymers and the particles are gold particles. It also suggests that all the PPD precipitates have the same belt-like morphological structures.

Prasad *et al.* have reported recently that gold nanoparticles can catalyze the polymerization of an alkylsilane $C_{18}H_{35}SiH_3$ with water to form nanowires and filaments.¹⁹ $HAuCl_4$ is a powerful oxidant with high reduction potential and *o*-PD serves as an electron donor for $HAuCl_4$ in this study. We may suggest the spontaneous formation of nanobelts can be attributed to gold nanoparticles-catalyzed oriented growth of PPD polymers. Scheme 1 shows the schematic diagram to illustrate the probable reaction mechanism on the nanobelts spontaneous formation. The reduction of $HAuCl_4$ by *o*-PD leads to the formation of gold nanoparticles with the occurrence of *o*-PD oligomers first, then gold nanoparticles produced serve as active catalysts to catalyze the oriented oxidative polymerization of other *o*-PD monomers by $HAuCl_4$



Scheme 1 Schematic diagram to illustrate the probable reaction mechanism on the nanobelts spontaneous formation.

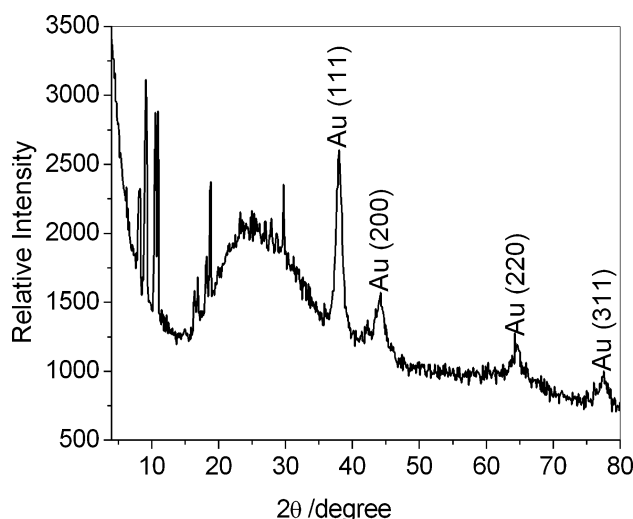


Fig. 2 XRD pattern of the resulting precipitates.

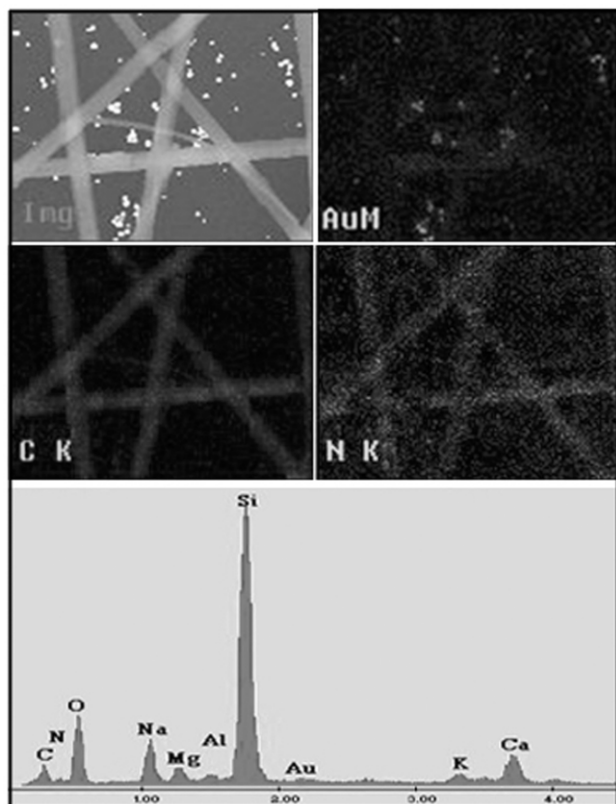


Fig. 3 Elemental analysis of the resulting precipitates using secondary electrons by SEM.

along the oligomers produced, resulting in the formation of PPD nanobelts. It is also worthwhile mentioning that most of these belts are, although several hundred micrometer in length, very straight, suggesting their strong rigidity.

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