

## Preparation and Characterization of Polydopamine-coated Silver Core/Shell Nanocables

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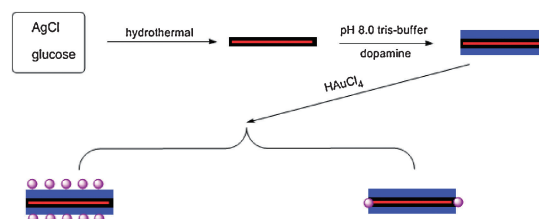
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This paper describes for the first time a simple method to synthesize polydopamine-coated Ag nanocable with well-defined core-shell structure. The morphology, structure, and composition of the products were characterized by transmission electron microscopy (TEM), X-ray power diffraction (XRD), X-ray photoelectron spectrometry (XPS), and Fourier transform infrared (FT-IR) spectroscopy.

In recent years, there has been considerable interest in fabricating coaxial nanocables.<sup>1</sup> In comparison with naked wire, the nanocables are expected to have better and broader application in nanotechnology. Currently, there are several methodologies for the fabrication of coaxial nanocables by high-temperature approaches including laser ablation,<sup>2</sup> high-temperature route,<sup>3</sup> or carbonthermal reduction method.<sup>4</sup> However, it is not economical, which can lead to high cost and low yield. In view on this, the synthesis of nanocable at low temperature has aroused great interest in recent years.<sup>5</sup> For example, Fu et al.<sup>6</sup> have developed a method to synthesize hybrid coaxial silver/organic-inorganic nanocables involving two steps at room temperature. Herein, we demonstrate a novel method for the synthesis of Ag@polydopamine (Pdopa) nanocables with well-defined core-shell structure.

It has been reported that the self-polymerization of dopamine could form stable coating on the surface of inorganic and organic materials in a facile approach in comparison to the other coating techniques.<sup>7a</sup> The Pdopa coatings have the following attractive features: (1) Pdopa coatings can serve as a versatile platform for secondary surface-mediated reactions, leading to tailoring of coatings for diverse uses. Additionally, it offers selectivity of reaction with amine or imidazole functional groups of a variety of biomacromolecules such as proteins and DNA by adjusting the pH of solution;<sup>7b</sup> (2) the electrochemical behavior of Pdopa could accelerate the electron transfer between an electrode and enzymes, showing a good candidates for biosensors;<sup>8</sup> (3) the good hydrophilic and biocompatible properties of Pdopa might be considered as an ideal candidate for biological applications;<sup>9</sup> and (4) the Pdopa remains stable even in harsh environments such as strong acid solution, so it can protect the silver nanowire from etching in acid solution or corrosion in air.

The preparation is described in Scheme 1. First, the Ag nanowire was synthesized according to the literature.<sup>10</sup> Compared to Wang's results, we obtained the uniform Ag@C nanocable, not pure Ag nanowire (Figures 1a and 1b and Figure S1<sup>15</sup>). The transmission electron microscopy (TEM) images of Ag@C show that the composite is composed of a smooth core about 100–200 nm in diameter and a surrounding sheath about 15 nm in thickness. The contrast between the dark inner core and light sheath layer along the axis direction can be easily observed (Figure 1b). Subsequently, the Ag@C nanocable reacted with



Scheme 1. The synthetic procedure of Ag@Pdopa@Au nanocables.

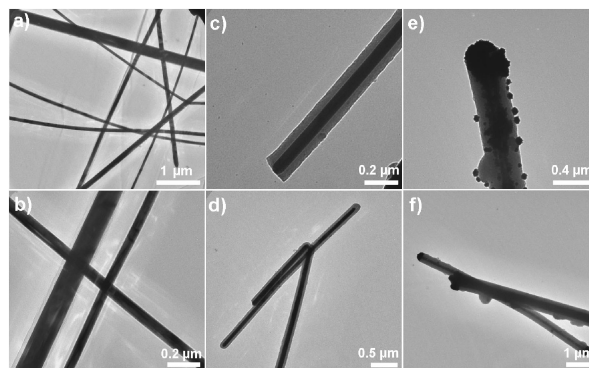
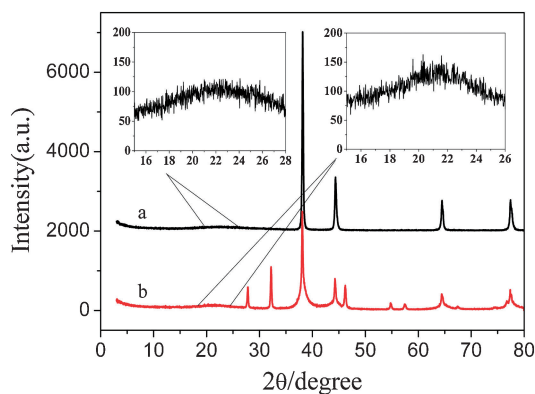


Figure 1. TEM images of Ag@C (a, b), Ag@Pdopa (c, d), and Ag@Pdopa@Au nanocables (e, f) at different magnification.

dopamine in pH 8.0 tris-buffer to obtain Ag@Pdopa nanocable. From the TEM images (Figures 1c and 1d), clearly, all Ag nanowires (dark) are wrapped by Pdopa shell (gray). The interface of Ag and Pdopa is clearly observed, and the thickness of the Pdopa layer is about 50–70 nm. However, we cannot observe the trilayer coating on the Ag nanowire, which may be mainly attributed to the similar density between carbon and Pdopa layer. In addition, the shell thickness gradually increases from 30–40 nm (Figure S2<sup>15</sup>) to 50–70 nm (Figure 1e) with the increase of reaction time from 6 and 24 h. This coating rate can be finely tuned by changing the pH and temperature of reaction medium.<sup>11</sup> The dopamine self-polymerization takes place preferentially under magnetic stirring and continuously deposited on the surface of Ag nanowires rather than in solution, thereby leading to the formation of well-defined Ag@Pdopa nanocable, which is due to the high affinity between the carbon and Pdopa.

Due to the metal-binding ability of catechols<sup>12</sup> present in the Pdopa layer, the Ag@Pdopa@Au nanocable has been synthesized via Ag nanowires as chemical template in the presence of HAuCl<sub>4</sub> solution. After mildly stirring at room temperature for 12 h, then separating by centrifugation, and washing, it can be seen that there are many Au nanoparticles adhered to the Ag@Pdopa. In view on the reduction capacity of Ag, the reduction between the Ag and HAuCl<sub>4</sub> was also observed (Figure 1f),



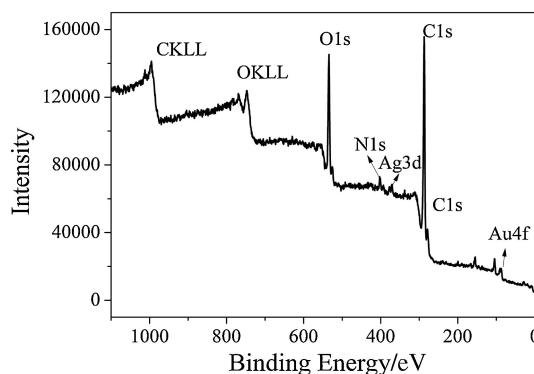
**Figure 2.** XRD patterns of (a) Ag@C and (b) Ag@Pdopa@Au.

and the elaborate spherical shapes of Au particles (20–30 nm) on Pdopa layers are clear. Due to the difference of reduction capacity between Ag and Pdopa, the  $\text{HAuCl}_4$  is preferentially reacted with Ag via replacement reaction between  $\text{Au}^{3+}$  and Ag, so the number of deposited Au nanoparticle is not many.

The XRD patterns of the Ag nanowire and Ag@Pdopa@Au are shown in Figure 2. The weak reflection centered at a  $2\theta$  value of  $22^\circ$  was characteristic of the thin, amorphous carbon layer. The diffraction peaks at  $38.1$ ,  $44.2$ ,  $64.5$ , and  $77.3^\circ$ , which represent the reflections from (111), (200), (220), and (311) planes of Ag were in good agreement with the reported data,<sup>13</sup> showing clearly the existence of Ag in the Ag nanowire and Ag@Pdopa@Au composites. In comparison with the Ag@C nanowire, the increase of signal intensity of reflection centered at  $22^\circ$  for Ag@Pdopa@Au is attributed to the successfully coated polydopamine. Due to the coating layer of Pdopa, the intensity of Ag signal is greatly decreased compared to the uncoated. In addition, the peaks at  $38$ ,  $43$ , and  $65^\circ$ , representing the Bragg reflections from (111), (200), and (220) planes of Au were also observed (JCPDS card No. 04-0784). This indicated that Au exists in the Ag@Pdopa@Au composites. It must be mentioned that the other peaks in Figure 2b can be attributed to the by-product of which the Ag nanowire, polydopamine was reacted with  $\text{HAuCl}_4$ .

The bands appearing at  $1614$  and  $3420\text{ cm}^{-1}$  in the typical FT-IR spectrum of Ag@Pdopa@Au (Figure S3<sup>15</sup>) are due to the aromatic ring stretching and the catechol –OH groups mode in Pdopa layer, respectively.<sup>11</sup> In addition, the band at  $1720\text{ cm}^{-1}$  correspond to the stretching vibration of the OH group of COOH, which indicates the carbonization of glucose in the resulting composites. Further evidence for the surface composition of the Ag@Pdopa@Au nanocables was obtained from X-ray photoelectron spectra (XPS) (Figure 3). It is clear that the elemental contents of the surface are C, O, N, and Au. The two very strong peaks at  $284.64$  and  $532.54\text{ eV}$  correspond to the C 1s and O 1s binding energies. The binding energies at  $368.3$  and  $373.45\text{ eV}$  are attributed to the Ag  $3d_{2/3}$  and Ag  $3d_{5/2}$ .<sup>10</sup> These XPS results confirm that the nanocables are composed of inner silver nanowires and outer carbonaceous and Pdopa layers. In addition, there were two peaks located at the binding energies of  $84.2$  and  $87.8\text{ eV}$ , which was consistent with the emission of 4f photoelectrons from  $\text{Au}^0$ , thereby suggesting the successful formation of Au NPs on the surface Ag@Pdopa.<sup>14</sup>

In conclusion, we have demonstrated a facile method of preparing well-defined core/shell structure polydopamine-coat-



**Figure 3.** XPS spectroscopy of the resulting Ag@Pdopa@Au composite.

ed Ag@Pdopa nanocable through the self-polymerization of dopamine at room temperature. This coating thickness can be finely tuned by controlling the reaction time. The resulting Pdopa coating is a versatile platform for reducing Au to form Ag@Pdopa@Au nanocomposite. Therefore, this easy approach can promote the practical applications of Ag nanowire. Most importantly, this method could be applied to all kinds of other metal nanowire; further work is underway.

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