

## Synthesis and Characterization of Coaxial Silver/Silica/Polypyrrole Nanocables

Wenqin Wang, Linchao Lu, Wujin Cai, Zhong-Ren Chen

Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, People's Republic of China

Correspondence to: W. Wang (E-mail: wqwang@126.com) or Z.-R. Chen (E-mail: chenzhongren@nbu.edu.cn)

**ABSTRACT:** Double-shelled coaxial nanocables of silver nanocables with SiO<sub>2</sub> and polypyrrole (PPy; Ag/SiO<sub>2</sub>/PPy) were synthesized by a simple method. The thickness of the outer PPy shell could be controlled by the amount of pyrrole monomer. The silver nanocables encapsulated in the interior of the hollow PPy nanotubes were obtained by the removal of the midlayer SiO<sub>2</sub>. By the silver-mirror reaction, flowerlike Ag nanostructures could be formed on the surface of the Ag/SiO<sub>2</sub>/PPy multilayer nanocable. The application of the as-prepared Ag/SiO<sub>2</sub>/PPy–Ag composites in surface-enhanced Raman scattering (SERS) was studied with Rhodamine B (Rh B) as a probe molecule. We found that the composites could be used as SERS substrates and that they exhibited excellent enhancement ability. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2377–2382, 2013

**KEYWORDS:** composites; conducting polymers; morphology

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### INTRODUCTION

Recently, many efforts have been devoted to the fabrication of coaxial nanocables because of their unique structure and many novel properties.<sup>1,2</sup> To date, numerous coaxial nanocables, including metal/semiconductor,<sup>3</sup> metal/metal oxide,<sup>4</sup> and metal/polymer nanocables,<sup>5</sup> have been successfully prepared. Among these nanocables, noble metal/conducting polymer nanocables are a promising material; they have the properties of both metal and conducting polymers. There have been various strategies reported for the synthesis of noble metal/conducting polymer nanocables Shi et al.<sup>6</sup> reported the synthesis of gold–poly(3,4-ethylenedioxythiophene) nanocables at room temperature by a one-step interfacial reaction of 3,4-ethylenedioxythiophene (in an organic phase) and HAuCl<sub>4</sub> (in an aqueous phase). Nadagouda and Varma<sup>7</sup> synthesized silver cables with polypyrrole (PPy) via the direct polymerization of pyrrole in an aqueous solution with AgNO<sub>3</sub> as an oxidizing agent without the use of any surfactant/capping agent. Chen and coworkers<sup>8–10</sup> fabricated silver–PPy coaxial nanocables by a redox reaction of silver nitrate and pyrrole with the assistance of poly(vinyl pyrrolidone) (PVP). To the best of our knowledge, there have been no reports on multilayer nanocables of noble metal/conducting polymers. In addition, conducting-polymer hollow nanostructures encapsulating guest species have attracted considerable research attention.<sup>11,12</sup> For example, Chen et al.<sup>12</sup> synthesized PPy hollow nanospheres containing movable Ag cores by a photoreduction process,

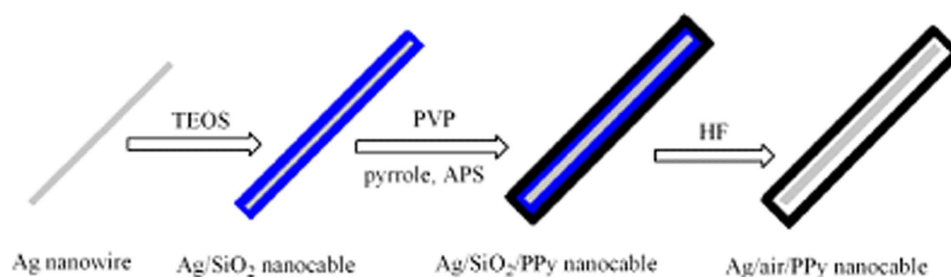
which may find potential application as a new drug-delivery system.

In this article, we report the synthesis of Ag/SiO<sub>2</sub>/PPy nanocables and Ag/air/PPy nanocables (Scheme 1). In this process, monodispersed silver nanowires (Ag NWs) were prepared first. Subsequently, the Ag NWs were coated with SiO<sub>2</sub> via the base-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS). PVP molecules were adsorbed onto the surface of Ag/SiO<sub>2</sub> to provide active sites for the growth of PPy.<sup>13–15</sup> Finally, the midlayer SiO<sub>2</sub> of the product was selectively etched by 10 wt % HF acid, and Ag/air/PPy nanocables were obtained. The doped PPy nanotubules could be covered by Au nanocrystals, and the as-prepared PPy–Ag composites exhibited an excellent surface-enhanced Raman scattering (SERS) ability.<sup>16</sup> In this study, Ag nanostructures were fabricated on Ag/SiO<sub>2</sub>/PPy nanocables by a silver-mirror reaction, and its application in SERS was investigated.

### EXPERIMENTAL

#### Materials

Pyrrole, ammonium persulfate (APS), silver nitrate, glucose, aluminum nitrate, 2-propanol, Rhodamine B (Rh B), and hydrofluoric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). TEOS and PVP (weight-average molecular weight = 550,000) were obtained from Sigma-Aldrich. Pyrrole monomer (Milwaukee, Wisconsin) was distilled under reduced pressure before use, and other reagents were used as received without further treatment.



**Scheme 1.** Scheme of the preparation of the coaxial Ag/SiO<sub>2</sub>/PPy nanocables. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Preparation of the Ag/SiO<sub>2</sub> Nanocables

Ag NWs were synthesized by a polyol process.<sup>17</sup> Ag NWs (0.02 g) were dispersed in a mixed solution including 30 mL of 2-propanol, 4 mL of deionized water, and 0.5 mL of a 30% ammonia solution. Subsequently, 10 mL of TEOS in 2-propanol (0.1M) was dropped under vigorous stirring, and the reaction was allowed to continue for 30 min. The product was separated by three cycles of centrifugation/separation.

### Preparation of the Ag/SiO<sub>2</sub>/PPy Three-Layer Nanocables and Ag/Air/PPy Nanocables

Ag/SiO<sub>2</sub> nanocables (0.01 g) and PVP (0.02 g) were added to 10 mL of deionized water, and the mixed solution was stirred for 24 h to ensure that the surface of the Ag/SiO<sub>2</sub> nanocables was adequately adsorbed by PVP. Excess PVP molecules were removed by centrifugation and washed with deionized water. The previous composite was redispersed in 10 mL of deionized water via ultrasound, and different amounts of pyrrole monomer (5 and 10 μL) were added under stirring. After 2 h, 5 mL of an APS aqueous solution was dropped into the previous solution. The reaction was allowed to proceed for 12 h, and the resulting product was washed by deionized water and dried at 50°C for 24 h *in vacuo*.

Ag/air/PPy nanocables were obtained by the immersion of the Ag/SiO<sub>2</sub>/PPy three-layer nanocables into a 10% HF aqueous solution for 24 h. Then, the product was centrifuged and washed with deionized water. Finally, the sample was dried at 50°C for 24 h *in vacuo*.

### Fabrication of a Flowerlike Ag Nanostructure on the Ag/SiO<sub>2</sub>/PPy Multilayer Nanocables

Ag/SiO<sub>2</sub>/PPy multilayer nanocables (0.01 g) were dispersed in 5 mL of an aluminum nitrate aqueous solution (1M) for 24 h. Subsequently, 1 mL of an Ag(NH<sub>3</sub>)<sub>2</sub>OH–glucose solution was added, and the silver-mirror reaction was carried out for 30 min at room temperature according to previous reports.<sup>18,19</sup> The as-prepared Ag/SiO<sub>2</sub>/PPy–silver composites were immersed in an Rh B aqueous solution with different concentrations for 1 h. Then, the substrates were dried with an N<sub>2</sub> flow for SERS measurement.

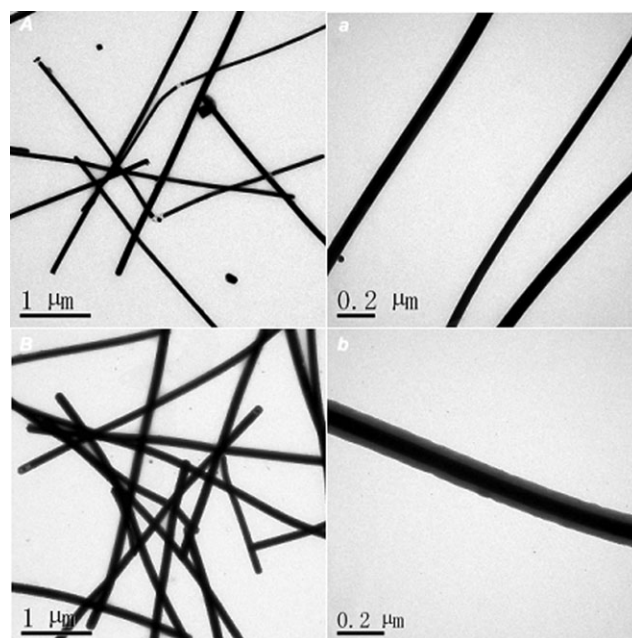
### Instrumentation

Transmission electron microscopy (TEM; H-7650) Hitachi (Tokyo, Japan) and scanning electron microscopy (SEM; SU-70) Hitachi (Tokyo, Japan) were used to observe the morphologies of the nanocomposites. The products were characterized by Raman spectroscopy (HR800) (HORIBA Jobin Yvon (Paris, France), X-ray photoelectron spectroscopy (XPS; Axis Ultradld)

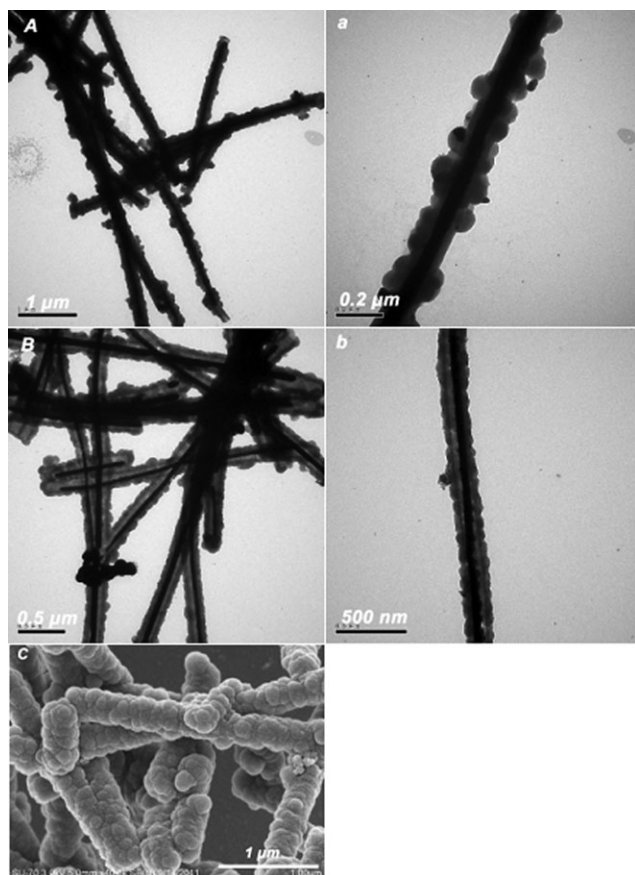
(SHIMADZU) (Tokyo, Japan), and X-ray diffraction (XRD; Rigaku D/max-1200) (Tokyo, Japan). Thermogravimetric analysis was conducted with a PerkinElmer thermogravimetric analyzer (TG–DTA SSC-5200) PerkinElmer (Waltham, Massachusetts, USA) from 20 to 900°C in O<sub>2</sub> (10°C/min). SERS spectroscopy was carried out on an RM2000 microscopic confocal Raman spectrometer (Renishaw PLC) (Gloucestershire, England) with an air-cooled He–Ne laser operating at 514 nm and focused on a spot of approximately 1 μm with a 20× long working distance objective. The spectra were accumulated three times for 10 s each.

## RESULTS AND DISCUSSION

Figure 1(A) shows the TEM image of the Ag NWs, which indicates the relative uniformity in diameter. Figure 1(a) shows a higher resolution TEM image of the single Ag NWs about 60 nm in diameter. Figure 1(B) shows a typical TEM image of some Ag/SiO<sub>2</sub> coaxial nanocables that were synthesized with the sol–gel approach. The clear dark–light contrast indicated a



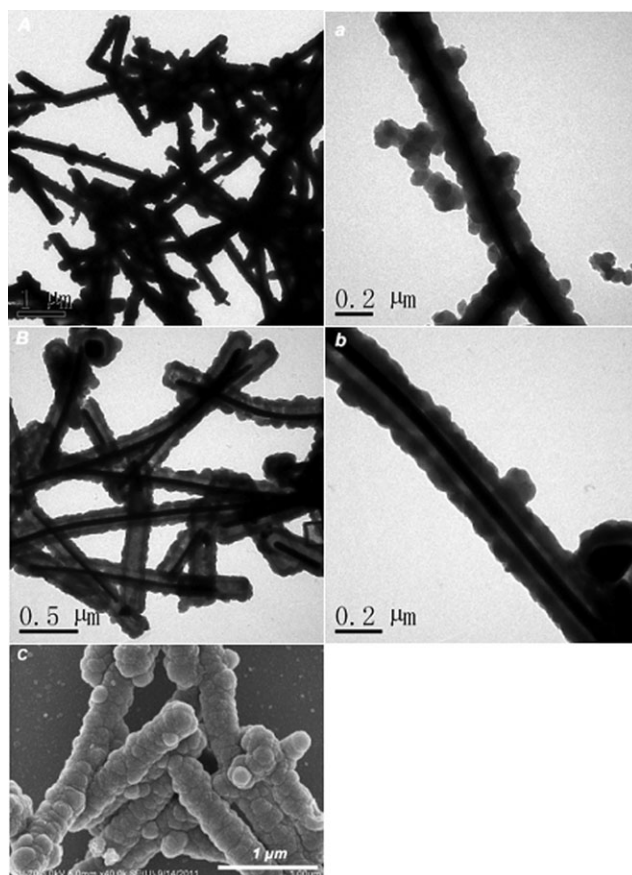
**Figure 1.** TEM images of the (A) Ag NWs and (B) Ag/SiO<sub>2</sub> nanocables and higher magnification TEM images of the (a) Ag NWs and (b) Ag/SiO<sub>2</sub> nanocables.



**Figure 2.** TEM images of the (A) Ag/SiO<sub>2</sub>/PPy nanocables and (B) Ag/air/PPy nanocables and higher magnification TEM images of the (a) Ag/SiO<sub>2</sub>/PPy nanocables and (b) Ag/air/PPy nanocables. Reaction conditions: 5  $\mu$ L of pyrrole monomer.

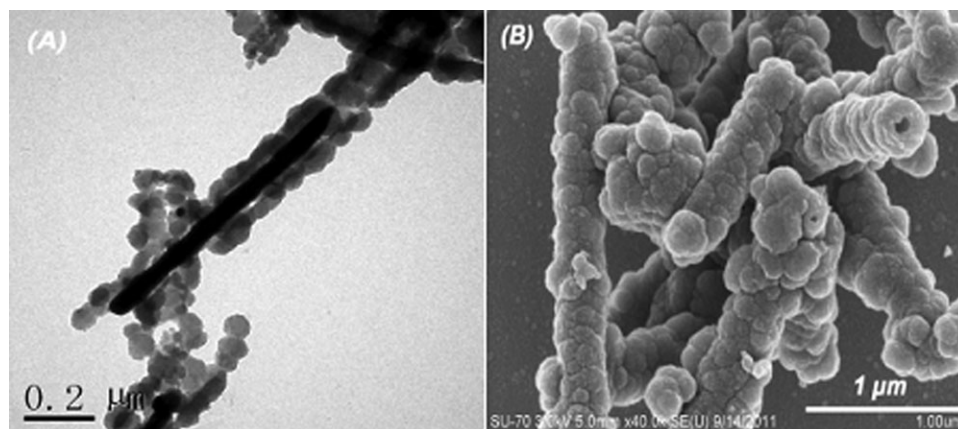
core–sheath nanostructure in the coaxial nanocables. As shown in Figure 1(b), the thickness of the SiO<sub>2</sub> shell was found to be about 30 nm.

Figure 2(A) shows a typical TEM image of the Ag/SiO<sub>2</sub>/PPy nanocables (5  $\mu$ L of pyrrole monomer) and indicates that a large quantity of nanocables with good uniformity were

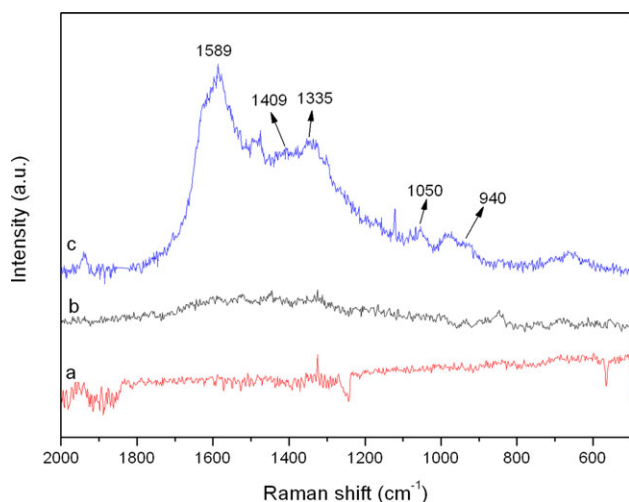


**Figure 3.** TEM images of the (A) Ag/SiO<sub>2</sub>/PPy nanocables and (B) Ag/air/PPy nanocables and higher magnification TEM images of the (a) Ag/SiO<sub>2</sub>/PPy nanocables and (b) Ag/air/PPy nanocables. Reaction conditions: 10  $\mu$ L of pyrrole monomer.

achieved by this approach. Figure 2(a) shows a single Ag/SiO<sub>2</sub>/PPy nanocable about 200 nm in diameter. The PPy shell composed of granular structures was evident because the pyrrole monomers were adsorbed on the surface of the SiO<sub>2</sub> spheres and *in situ* polymerized to form granular PPy shell structures. The morphologies of the PPy layer were further confirmed by



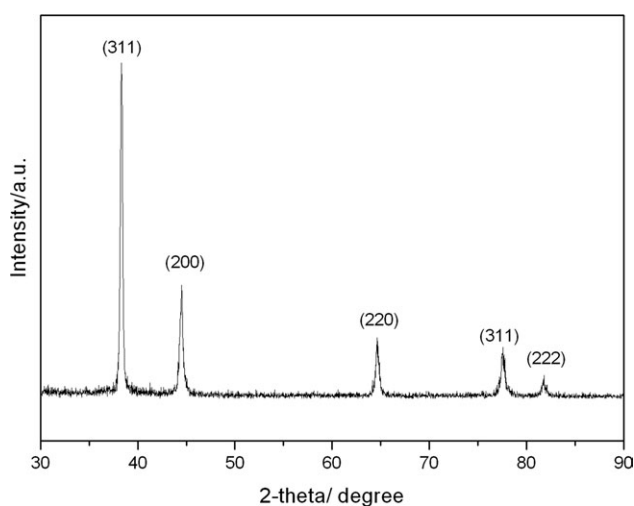
**Figure 4.** TEM and SEM images of the broken Ag/air/PPy nanocables.



**Figure 5.** Raman spectra of the (a) Ag NWs, (b) Ag/SiO<sub>2</sub> nanocables, and (c) Ag/SiO<sub>2</sub>/PPy coaxial nanocables. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

SEM imaging [Figure 2(C)]. Ag/air/PPy nanocables were obtained by the removal of the middle SiO<sub>2</sub> layer with an HF aqueous solution [as shown in Figure 2(B)]. The TEM image of a single Ag/air/PPy nanocable is shown in Figure 2(b). Ag NWs surrounded by a PPy shell were clearly observed, and the thickness of the PPy layer was about 60 nm.

The influence of the amount of pyrrole monomer on the morphologies of the products was investigated. The TEM images of the relevant Ag/SiO<sub>2</sub>/PPy nanocables with an amount of pyrrole monomer of 10  $\mu$ L are shown in Figure 3(A). Figure 3(a) shows a single Ag/SiO<sub>2</sub>/PPy nanocable 250 nm in diameter. The TEM image of the Ag/air/PPy after the removal of the SiO<sub>2</sub> layer is shown in Figure 3(B). The thickness of the PPy layer was about 70 nm [Figure 3(b)]. When we compared Figures 2(b) and 3(b), we found that the thickness of PPy increased with increasing pyrrole monomer. The morphologies of the granular PPy layer structure on the Ag/SiO<sub>2</sub> nanocables

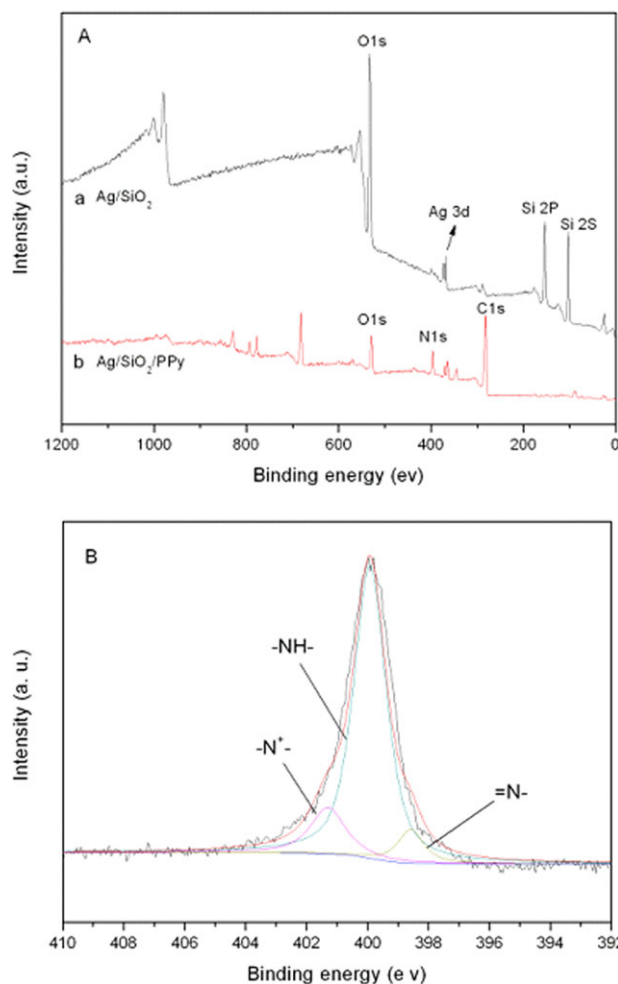


**Figure 6.** XRD scattering pattern of Ag/SiO<sub>2</sub>/PPy.

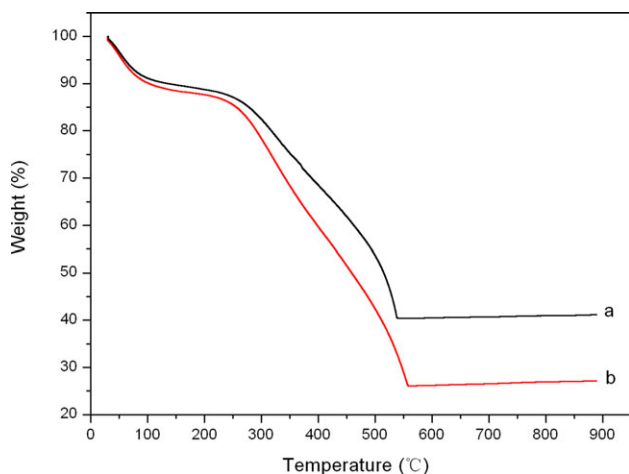
are shown in Figure 3(C) and were similar to those shown in Figure 2(C).

In this study, 10 wt % HF acid was selected to etch the SiO<sub>2</sub> midlayer of the Ag/SiO<sub>2</sub>/PPy nanocables according to the work of Yao et al.<sup>20</sup> In their study, Ag/PPy on SiO<sub>2</sub> spheres were treated with 10 wt % HF acid to remove SiO<sub>2</sub>; however, they did not investigate whether HF acid could etch the Ag core. It could be assumed that the dilute HF acid (10 wt %) and short etching time (24 h) might have had less influence on the Ag core. In our study, we did find that a few of Ag NWs in the Ag/air/PPy nanocables were also etched with HF acid to etch the SiO<sub>2</sub> midlayer [shown in Figure 4(A)]. In addition, the broken ends of a few of the Ag/air/PPy nanocables were also found [shown by arrows in Figure 4(A,B)].

The Ag NWs, Ag/SiO<sub>2</sub> nanocables, and Ag/SiO<sub>2</sub>/PPy nanocables were investigated by Raman spectrum analysis. The Raman spectra of the Ag NWs and Ag/SiO<sub>2</sub> nanocables are shown in Figure 5(a,b), respectively. Compared with Figure 5(b),



**Figure 7.** (A) XPS survey spectra of the Ag/SiO<sub>2</sub> nanocables and Ag/SiO<sub>2</sub>/PPy nanocables and (B) N 1s spectrum of the Ag/SiO<sub>2</sub>/PPy nanocables. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** Thermogravimetry curves of the Ag/SiO<sub>2</sub>/PPy nanocables with (a) 5 and (b) 10  $\mu\text{L}$  of pyrrole. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

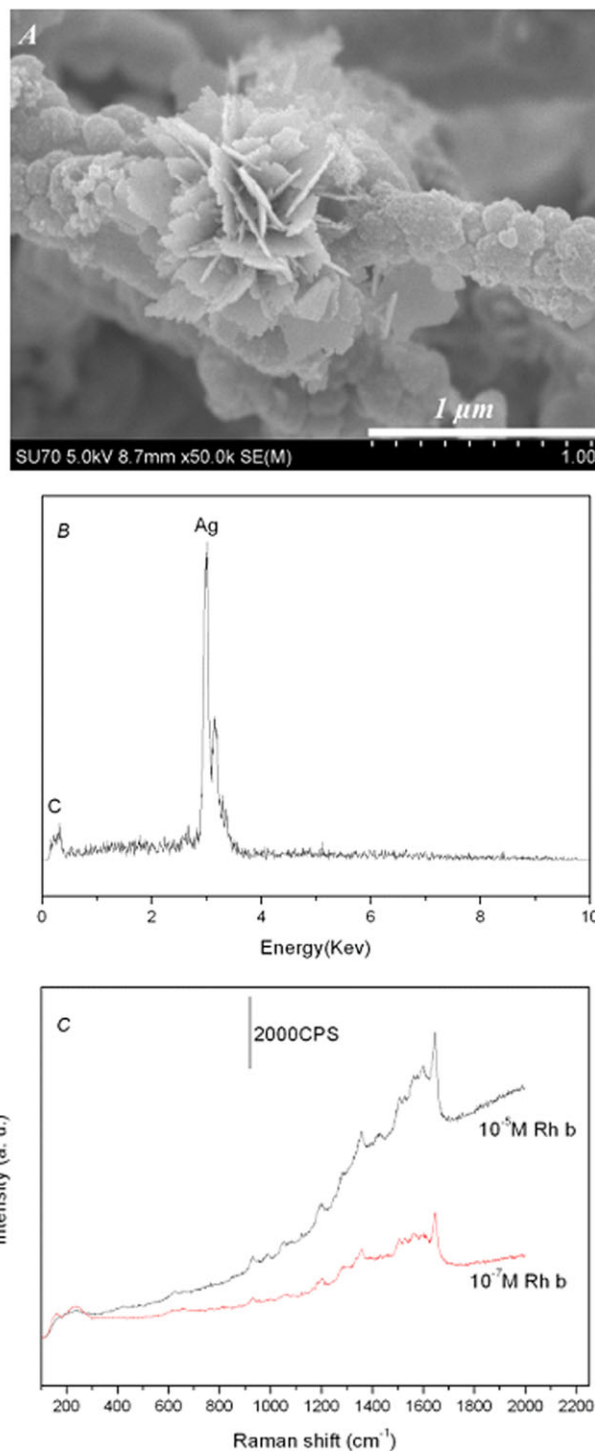
Figure 5(c) shows that the peaks at 1589 and 1409  $\text{cm}^{-1}$  were due to the C=C stretching of the PPy backbone and an anti-symmetric C—N stretching band, respectively. The band at 1335  $\text{cm}^{-1}$  was associated with the ring stretching of PPy. The band at 1050  $\text{cm}^{-1}$  was assigned to the C—H in-plane deformation of PPy, and that at 940  $\text{cm}^{-1}$  was assigned to ring deformation. The results were in good agreement with the reported data,<sup>21,22</sup> this implied that the PPy layer was coated successfully on the surface of the Ag/SiO<sub>2</sub> nanocables.

The XRD pattern of Ag/SiO<sub>2</sub>/PPy is given in Figure 6. The four main diffraction peaks at  $2\theta = 38.2, 44.4, 64.5,$  and  $77.5^\circ$  corresponded to Bragg's reflections from the (111), (200), (220), and (311) planes, respectively, of the Ag. These results were in accordance with reported data,<sup>23</sup> which confirmed the presence of Ag.

The products were characterized further by XPS. The survey spectra of the Ag/SiO<sub>2</sub> and Ag/SiO<sub>2</sub>/PPy nanocables are depicted in Figure 7(A). In Figure 7(A), curve a shows the Si 2p, Si 2s, and O 1s peaks at 103, 152, and 532 eV, respectively; these were attributed to the SiO<sub>2</sub> layer on the Ag NWs. Two peaks at 368 and 374 eV, corresponding to binding energies of Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub>,<sup>24</sup> respectively, are also shown in curve a. In comparison with curve a, the C 1s and N 1s peaks at 285 and 400 eV, respectively, are shown in curve b and were due to the PPy layer. The peak-fitted N 1s core-line spectrum of the Ag/SiO<sub>2</sub>/PPy nanocables [Figure 7(B)] showed that three nitrogen environments were present. The peaks at 398.6 and 399.8 eV were attributed to the uncharged deprotonated imine (=N<sup>-</sup>) nitrogen species and neutral nitrogen atoms (—NH—) in PPy. The peak at 401.2 eV was assigned to positively charged nitrogen (—N<sup>+</sup>—) species in PPy.<sup>25</sup>

The thermal decomposition curves of Ag/SiO<sub>2</sub>/PPy nanocables with different PPy content are shown in Figure 8. For curve a, the initial weight loss below 100°C is attributed to the evaporation of moisture. Subsequently, successive degradation from about 230 to 550°C corresponds to PPy degradation.<sup>26</sup> Compar-

ing curve a with curve b, it is found that the process and tendency of degradation are almost similar except the final residual weight. The result is attributed to the different thickness of PPy layer in the Ag/SiO<sub>2</sub>/PPy nanocables as shown in Figure 2(b) and Figure 3(b).



**Figure 9.** (A) SEM image of the Ag/SiO<sub>2</sub>/PPy–Ag composites, (B) EDX spectrum of the Ag/SiO<sub>2</sub>/PPy–Ag composites, and (C) SERS spectra of Rh B ( $10^{-5}$  and  $10^{-7}$  M) on the Ag/SiO<sub>2</sub>/PPy–Ag composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

On the basis of previous reports,<sup>23</sup> the  $\text{Al}(\text{OH})_4^-$  species could be formed by the addition of aluminum nitrate to the solution of  $\text{Ag}(\text{NH}_3)_2\text{OH}$ . The cations along the PPy chains (PPy in the oxidized state) could absorb the  $\text{Al}(\text{OH})_4^-$  anions; this favored the growth of flowerlike silver crystals. Silver nanostructures were deposited on the surface of the  $\text{Ag}/\text{SiO}_2/\text{PPy}$  nanocables by the silver-mirror reaction. An SEM image of the flowerlike Ag nanostructures on the  $\text{Ag}/\text{SiO}_2/\text{PPy}$  nanocables is shown in Figure 9(A). The energy dispersive X-ray (EDX) spectrum of the  $\text{Ag}/\text{SiO}_2/\text{PPy}-\text{Ag}$  composites is shown in Figure 9(B). The  $\text{Ag}/\text{SiO}_2/\text{PPy}-\text{Ag}$  composites were used as SERS substrates, and the spectra of the Rh B solution ( $10^{-5}$  and  $10^{-7}$  M) on these substrates are shown in Figure 9(C). We found that the SERS intensity of the peak at  $1645\text{ cm}^{-1}$  was very strong when the concentration of Rh B was  $10^{-5}$  M. When the concentration of Rh B was as low as  $10^{-7}$  M, the peak at  $1645\text{ cm}^{-1}$  was still observed. This indicated that the  $\text{Ag}/\text{SiO}_2/\text{PPy}-\text{Ag}$  composites could be SERS active substrates for the analysis of trace molecules.

## CONCLUSIONS

In summary,  $\text{Ag}/\text{SiO}_2/\text{PPy}$  nanocables were prepared successfully through a simple process, and the thickness of the PPy layer could be controlled by the amount of pyrrole monomer. The  $\text{Ag}/\text{air}/\text{PPy}$  nanocables were obtained by the removal of the midlayer  $\text{SiO}_2$  by HF. By a silver-mirror reaction, a flowerlike Ag nanostructure was formed on the  $\text{Ag}/\text{SiO}_2/\text{PPy}$  nanocables, which could be used as SERS active substrates for trace detection.

## ACKNOWLEDGMENTS

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