Optically active chiral Ag nanowires

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Chiral Ag nanowires (CAGNWs), fabricated inside chiral carbon nanotubes (CCNTs), exhibit strong circular dichroism (CD) signals in the visible and near-IR regions. Enantiopure CCNTs were prepared by carbonization of the self-assembled chiral polypyrrole nanotubes according to our previous report. Ag ions could be easily introduced into the chiral pores of CCNTs due to the capillary phenomenon. After hydrogen reduction, the optically active CAGNWs formed inside the channels of the CCNTs. The helical channels in the CCNTs played a predominant effect on the chiral formation of the CAGNWs. This system provides new insight into the fabrication as well as the study of optical activity (OA) of chiral inorganic nanomaterials. Such novel chiral inorganic material will bring new opportunities in non-linear optics, biosensors and chiral recognition.

INTRODUCTION

Metallic nanomaterials (nanowires and nanoparticles) are widely considered as potential structural and functional building-blocks for materials in catalysis, separation, optics, and nanoelectronics [1–4]. Many properties of these materials are predicted to be dependent on their size, shape, and spatial arrangement [5,6]. Among them, the chirality of metallic nanomaterials receives arising attention because it offers the ability to achieve strong optical activity (OA) over a broad spectral range [7–9]. This is the effect of the difference in speed and absorption of the left- and right-handed circularly polarized light when passing through the chiral materials. Such chiral plasmonic nanostructures provide potential applications in asymmetric catalysts [10,11], optical devices [12] and biological sensors [13–16].

Since Schaaff and Whetten [17] firstly reported the chiral glutathione-protected Au nanoparticles (NPs) exhibiting particular OA in surface plasmon resonance, diverse types of chirality in metal NPs have been found to create plasmonic circular dichroism (CD) [18]. These systems include metal NPs capped with various small chiral molecules, or biological macromolecules such as DNA [19–22], amino acids [23–28], peptides [29–31], and pro-

teins [32,33]. Moreover, MacLachlan's group used chiral nanocrystalline cellulose as hard template to prepare chiral nematic cellulose-silver [34] and -gold [35] NP composites. However, these types of chirality in metal NPs rely on the capped chiral molecules, which are unstable under severe conditions, such as high temperature.

Recently, we have obtained chiral arrangement of Ag NPs and nanowire arrays in chiral mesoporous silica by hard template method [36,37], which resulted in the OA in surface plasmon resonance based on chiral superstructure of assembled NPs. However, the origin of the chiral OA by hard template method is so complicated that more efforts are needed to reveal the mechanism.

Herein, we present the synthesis of chiral Ag nanowires (CAGNWs) which features collective intrinsic property of OA by a simple hard template method. Notably, the Ag nanowires are chiral, which are extremely rare [38–41]. For the preparation of ordered nanoarchitecture, hard template method has many advantages, especially in its stability, predictability, controllability and versatility. The synthesis method involves directly casting of Ag ions in chiral carbon nanotubes (CCNTs), subsequent reduction of the metal precursors into CAGNWs in H_2 . The resulted materials with CAGNWs embedded, which endows them distinct OA, responding to circularly polarized light. To the best of our knowledge, this is the first example of organizing metal into CCNTs with OA, and such method can be extended for preparing other functional metal composites.

As shown in Scheme 1a, the CCNTs were synthesized by the method described in our previous report [42]. Fig. 1a shows the chiral double helix carbon nanotubes. The white colour region in the middle of chiral carbon nanotube stands for helical pores after carbonization in Ar. Then, CCNTs were employed as hard templates to fabricate CAGNWs. Silver ions could be easily introduced into the chiral pores of CCNTs due to the capillary phenomenon. After hydrogen reduction, the CAGNWs were formed inside the channels of the CCNTs by the impregnation of $AgNO_3$ (Scheme 1b). The gray colour region in the middle of chiral

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Scheme 1 Schematic illustration of the synthesis of CAgNWs with OA. (a) CCNTs prepared by carbonization of CPPy synthesized by self-assembling of *N*-stearyl-D-glumatic acid (C_{18} -D-Glu) and pyrrole. (b) CAgNWs prepared from CCNTs.

carbon nanotube in Fig. 1b represents the formation of chiral Ag nanowire. This procedure granted the samples with left- and right-handed helical orientations, which were denoted as L- and R-C-Ag, respectively.

EXPERIMENTAL DETAILS

Preparation of chiral hard templates of CCNTs

Firstly, the CCNTs derived from chiral polypyrrole (CPPy) nanotubes by carbonization in an inert gas were synthesized by a modified method according to our previous report [42]. Typically, the molar composition of lipid amphiphilic molecule:ammonium persulfate (APS):pyrrole: methanol:water was 1:40:40:5351:57081. In a typical synthesis, 0.06 mmol of C_{18} -D-Glu was dissolved in 10.2 g methanol at room temperature, and then 2.4 mmol pyrrole and 60 mL deionized water were added. The solution was stirred for 10 min, and then a precooled aqueous solution of APS (2.4 mmol in 1.2 mL deionized water) were added to the mixture and stirred for a further 30 min. A brown solid was obtained after filtrating and thrice-washing with water and ethanol, followed by drying for 12 h at 40°C in vacuum. For the carbonization of the CPPy nanotubes, the synthesized products were heated at a rate of 1.5°C min⁻¹ to 550°C under Ar flow, for 6 h. After slowly cooling the sample to room temperature, CCNTs were obtained.

Synthesis of CAgNWs@CCNTs

In a typical synthesis, CCNTs powder (20 mg) was dispersed in an aqueous solution of $AgNO_3$ (2 mL, 10 mg mL⁻¹), and then stirred for 30 min at room temperature. The mixture was reacted statically for 3 h. The water was evaporated

slowly in a rotary evaporator and then washed with acetone to remove the Ag ions bounded to the outer surface of the CCNTs. Subsequently, the obtained solids were dried in a vacuum oven at room temperature. The collected samples were placed in a tube furnace, and the metal precursors were reduced under a constant H_2 flow at 120°C for 6 h. The temperature was increased from room temperature to the desired temperature at a rate of 1.0°C min⁻¹. A dark yellow powder was collected after the tube furnace was cooled to room temperature.

Characterization

The microscopic characteristics of the samples were observed with JEOL JSM-7401F scanning electron microscope (SEM). Transmission electron microscopy (TEM) observation was performed with a JEOL JEM-2100 microscope operating at 200 kV. The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2000 powder diffractometer equipped with Cu K α radiation. The solid-state diffuse-reflectance circular dichroism (DRCD) and diffuse reflectance UV/vis (DRUV/vis) spectra of the powder samples were obtained on a JASCO J-815 spectropolarimeter fitted with a DRCD apparatus.

RESULTS AND DISCUSSION

Figs 1a₁ and b₁ show the SEM images of the CCNTs. These samples are composed of exclusively left- or right-handed double helical fibers with uniform morphology. The outer

Figure 1 SEM images of the antipodal CCNTs (a₁ and b₁) and the CAgNWs obtained by reduction in H_2 (a₂–a₃ and b₂–b₃). (a, left-hand; b, right-hand).

diameters of the CCNTs are ~ 100 nm and the pitch length is estimated to be ~ 200 nm (the length between the arrows indicated in Figs 1a₃ and b₃ is the pitch length). After the uniform filling of Ag NWs into the CCNTs by hydrogen reduction, the outer diameters slightly decrease due to the shrinkage by hydrogen reduction at high temperature for a long time. However, the double helical morphology is well-maintained even after long-time reduction in H₂, which shows the high memory capability of morphology (Figs 1a₂ and b₂). Figs 1a₃ and b₃ are high resolution SEM images of L-C-Ag and R-C-Ag, respectively. Obviously, there is no Ag NPs on the surface of the CCNTs.

Figs 2a and b are the TEM images of the Ag NWs within the L-C. Dark, wirelike objects with a uniform diameter of about 10 nm are observed within the CCNTs, which is smaller than the diameter of the channel (~ 20 nm) [42]. When the helical radius is larger than the diameter of single chiral fibers which form double helix, the helical pores will form in the middle of the double helical carbon nanotubes. Along with the shrinkage of the outer diameter, the channels also shrink by hydrogen reduction at high temperature for a long time. Although the single stranded helical morphology of Ag NW inside the CCNT can be clearly observed from the TEM images (Fig. 2b), it is hard to clearly see the pitch length of single stranded helical Ag NW due to the high pitch length/diameter ratio. It can be observed that the Ag NWs are not continuous in some areas because the CCNTs are so long that the Ag ions are unable to fill all

Figure 2 TEM images (a and b) of the L-C-Ag. The L-C-Ag (c) and its corresponding EDX result (d).

of the pores. Fig. 2c shows the single L-C-Ag. As shown in Fig. 2d, the energy dispersive X-ray detector (EDX) analysis of the L-C-Ag indicates that Ag element is in each carbon nanotube. The results suggest that these Ag NWs are oriented in the helical pores.

The XRD pattern (Fig. 3) of the L-C shows a broad diffraction peak at $2\theta \approx 25^\circ$ because the CCNTs are amorphous. The wide-angle XRD patterns of the L-C-Ag reveals four diffraction peaks at $2\theta = 38.1^\circ$, 44.3° , 64.5° , and 77.58° (Fig. 3), which are assigned to the (111), (200), (220), and (311) reflections of a face-centered cubic silver lattice, respectively.

The CD can be used to measure the differential absorption of left- and right-handed circularly polarized light, and the CD activity indicates a chiral structure, which can be detected by DRCD. Fig. 4 shows the DRCD spectra of two pairs of the antipodal L/R-C and L/R-C-Ag samples. The

Figure 3 XRD patterns of L-C and L-C-Ag.

Figure 4 DRUV-vis and DRCD spectra of antipodal CCNTs and CAgNWs.

antipodal CCNTs show obvious mirror-image CD signals with a peak at ~ 460 nm, which indicates that the optically active CCNTs can selectively reflect left- or right-handed circularly polarised light in the UV absorption region through a vicinal effect of the helical stacking of carbon nanostructure. A broad absorption band in the range of 350–800 nm is attributed to the CCNTs, resulting from the combination of nano effect, polarization, and π -conjugated structure.

For the L/R-C-Ag materials, the DRCD spectra show the overlapped signals attributed to the CAgNWs and CCNTs. L/R-C-Ags show symmetric sharp peaks at the wavelength of ~ 320 nm and broad peaks in the range of 350–800 nm. The characteristic band at 320 nm of L-C-Ag is a result of the absorption of inhomogeneous Ag NWs near the region of the inter-band transitions due to surface plasmon resonance optical signatures of silver nanowires [43–45]. The decreased intensity of broad peak in range of 350–800 nm also may be due to negative cotton effect on CD signals of L-C-Ag at 350–800 nm based on the coupled dipole and exciton coupling theory. Moreover, the CD intensity of L-C after reduction in H_2 decreases due to partial deformation at high temperature for a long time (as shown in Fig. 5), which leads to the decreased CD intensity in the range of 350–800 nm for L-C-Ag (as shown in Fig. 4).

CONCLUSIONS

In conclusion, we have successfully prepared chiral Ag NWs with a distinct helix by using CCNTs as hard templates. These novel chiral Ag NWs supported by CCNTs exhibit distinctive plasmon CD signals, which originates from the collective plasmon coupling of the CAgNWs. It is possible to produce other metallic chiral NWs by using

metals such as Pt and Au with a similar synthetic procedure. This approach provides the possibility of exploiting the optical and electronic properties of intrinsically chiral metallic compounds for electronics, sensing, and electrochemical applications.

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Figure 5 DRUV-vis and DRCD spectra of CCNTs and CCNTs after reduction in H_2 .

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Author Contributions Che S designed the experiment and led the project. Ma L synthesised the chiral Ag nanowires and performed the SEM, XRD and CD measurements and Huang Z obtained the TEM images. Duan Y, Huang Z and Shen X provided comments and feedback on the manuscript. All authors contributed to the general discussions.

Conflict of interest The authors declare that they have no conflict of interest.

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中文摘要 本文以手性碳纳米管为模板,成功地在其内部形成了手性银纳米线.由于手性排列的银纳米线之间的集合耦合效应,在可见光区和近红外区产生了较强的手性圆二色信号.根据我们先前报道的方法,通过碳化处理自组装合成的手性吡咯碳纳米管得到了单一手性的碳纳米管.由于毛细管效应,银离子能够很容易地进入手性碳纳米管的手性孔道中,然后再通过氢气高温还原,在其管内得到了具有光学活性的手性银纳米线.手性碳纳米管内的螺旋孔道对手性银纳米线的形成起模板作用.该合成体系将有助于理解具有手性光学活性的无机材料的形成及其机理.这种新颖的手性无机材料也将有机会应用到非线性光学器件、生物传感和手性识别等领域.