Heteropoly Acid-Assisted Fabrication of Carbon Nanostructures under Ambient Condition
(Supporting information)

1. Experimental details.

All the reagents were purchased from Beijing Chemical Reagent (Beijing, China). AgNO₃, H₃PW₁₂O₄₀•nH₂O, C₂Cl₄, CCl₄, ethanol, and nitric acid were commercially available reagent grade without further purification. All solid samples were dried under vacuum at 60°C for 8-10 h before measurement.

The XRD patterns were obtained on a Rigaku D/max 2500V PC diffractometer using CuKα radiation. JEM-2010 and JEM-2010F transmission electron microscopes were used to examine the morphology of nanostructured carbons. SEM images were obtained with a JEOL JSM-840 operating at 20 kV and a FEG-XL30, FEI Company. Raman spectrum was recorded at room temperature on a Spex 1403 Raman spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm.

Synthesis of SWNT, CNS and other nanostructured carbons via H₃PW₁₂O₄₀-assisted electrochemical reduction of CCl₄/C₂Cl₄ is described briefly as follows. 0.1g H₃PW₁₂O₄₀, 10 ml ethanol, and 10 ml C₂Cl₄/CCl₄ (1:1 in molar ratio) were mixed and stirred into a clear homogeneous phase. Electrolysis was carried out under 100-200 volt (DC) and 10-100 mA. With the anode and cathode separated 1-2 cm, the nanostructured carbon was obtained on the cathode after several hours. One to two drops of the mixture from the electrolytic cell after electrolysis were added to a large amount of deionized water. White AgCl precipitate was formed upon addition of AgNO₃ aqueous solution to the above solution. The C₂Cl₄ and CCl₄ reacted to form carbon and chlorine via this electrolytic process. The electrochemical process can be described as follows.

Anode:  4Cl⁻ - 4e → 2Cl₂                   (1)
Cathode:  C₂Cl₄ + 4e → 2C + 4 Cl⁻
and  CCl₄ + 4e → 2C + 4 Cl⁻                 (2)

For fabrication of COS at room temperature, the method employed is as follows. Graphite rods, which were purchased from China National Medicines Shenyang Co. Ltd, were used as electrode for the electrolysis (300 mA) of H₃PMo₁₂O₄₀ solution (20 mM). The graphite powder in the solution formed from erosion of graphite was collected, and cleaned via 3 cycles of centrifugation/wash/re-dispersion in water and alcohol, respectively. After
oven-dried at 90 ºC for 5 hours, the samples were ball milled (400 r/min) for 24 h, and the products containing COS were finally collected. Counting COS on randomly selected grids in TEM, the yield was estimated to be about 30 %.

2. Characterization

Before XRD measurement, Ni particles in the products were removed by sonicating in 37 wt% hydrochloric acid for 2 h. The XRD pattern of the as-obtained product on cathode is shown in Figure S1, which demonstrates that the product on the cathode is made of carbon. The three XRD peaks can be assigned to (002), (100), and (101) of carbon.

![Figure S1 XRD pattern of the as-obtained carbon on the cathode](image1)

Figure S1 XRD pattern of the as-obtained carbon on the cathode

![Figure S2 TEM image of the as-obtained products on the cathode](image2)

Figure S2 TEM image of the as-obtained products on the cathode
Figure S3 SEM image of the as-obtained products on the Ni cathode

Figure S4 SEM images of (a) SWNT and (b) CNS grown on the Ni micro-particle

Figure S5 TEM images of as-obtained SWNT

Figure S6 Raman spectrum of the as-obtained SWNT
Figure S7 TEM and HRTEM images of as-synthesized CNS

Figure S8 HRTEM images of (a) onion-like closed-carbon nanostructures and (b) disorder graphite sheets

Figure S9 SEM images of different morphological nanostructured carbons