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Arrangement of Pd nanoparticles on SDS-functionalized single-walled carbon nanotubes[†]

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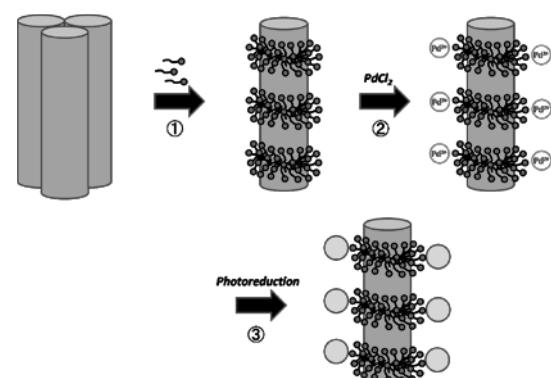
1. Introduction

Carbon nanotubes (CNTs) have many unique physical, electrical, mechanical and chemical properties and represent one of the most extensively studied nanostructured materials because of their potential applications in many fields. Surface functionalization and hybridization of CNTs currently attracts significant research interest because CNTs are ideal templates for the decoration of functional nanoparticles. Among these research branches, one of the most attractive topics is to construct designed and controllable heterogeneous nanostructures on one-dimensional CNTs with sub ten nanometers diameter. Polymers and many organic molecules seem to be candidates for this objective because they are reported to form ordered self-assembly nanostructures on CNTs, which provide suitable combination sites to arrange metal nanoparticles or quantum dots on CNTs by the specific bonding interactions between the nanoparticles and the terminal groups of organic molecules.[1] Surfactant-functionalized CNTs are now also considered as another approach to control the designed heterogeneous nanostructures on one-dimensional CNTs. Surfactants have been widely studied because of the advantages of dispersing CNTs in water and changing the surface physical properties of CNTs. SDS is one of the well known surfactants to disperse and functionalize CNTs in water. It is also reported that SDS forms a supramolecular self-assembly with half-cylinder structure on the surface of CNTs.[2] The nanostructural pattern of SDS-functionalized CNTs represents an ideal template to construct designed one-dimensional heterogeneous nanostructures on the surface of CNTs. In this study, we report site-selective deposition and patterning of Pd nanoparticles on SWCNTs by utilizing the supramolecular self-assembly of SDS acting as a soft template. Since Pd nanoparticles have great applications in fuel cell, high-performance catalyst and hydrogen storage, it is of many scientific interests to construct ordered one-dimensional Pd nanostructures on SWCNTs.

2. Experiment

The experimental approach for the site-selective synthesis of Pd nanoparticles templated by supramolecular self-assembly of SDS-functionalized SWCNTs is described

in **Scheme 1**. SWCNTs (5mg, 0.05 wt %) in aqueous solution (10 ml, containing 0.5 wt % SDS) were mixed for 8 hours assisted by ball-milling as previously described [3, 4]. The SWCNTs were essentially bundles with an average diameter 50 nm. The bundles of SWCNTs were separated into individual nanotubes and/or small bundles, and dispersed in an SDS aqueous solution by ultrasonic treatment. SDS molecules were adsorbed onto the surfaces of SWCNTs to form half-cylindrical supramolecular self-assembly oriented perpendicular to the CNT axis. A 2 ml aqueous solution of palladium chloride (20 mM) was added to the SDS-functionalized SWCNTs solution. Since SDS is an anionic surfactant, Pd (II) cations were selectively absorbed onto the walls of SWCNTs along the helix of the half-cylinders of SDS due to the electrostatic interaction between Pd (II) cation and the anionic groups of sulfate in SDS molecules. The mixed solution was then irradiated for 60 min by a UV lamp ($\lambda = 254$ nm). Consequently, Pd nanoparticles were site-selectively reduced by a photoreduction reaction and formed ordered nanostructures on the surface of SWCNTs which used the supramolecular self-assembly of SDS as a soft patterning template. The resulting nanostructures were characterized by scanning electron microscopy (SEM, SU-70, Hitachi, Japan) and transmission electron microscopy (TEM, JEM-2100F, JEOL).



Scheme 1. A schematic approach for the arrangement of Pd nanoparticles on the SDS-functionalized SWCNTs.

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3. Results and Discussions

Figure 1 shows the SEM image of pristine SWCNTs (A) and TEM images of SDS-functionalized SWCNTs (B, C). The pristine SWCNTs are almost ca. 50 nm bundles and twisted together due to the van der Waals interaction (Fig. 1A). After dispersing in SDS aqueous solution, the large bundles of pristine SWCNTs were effectively separated into small bundle and/or individual SWCNTs (Fig. 1B). Figure 1C shows a high-resolution TEM photograph of SDS-functionalized SWCNTs. We can clearly observe the ordered supramolecular self-assembly of SDS half-cylinders wrapped on the surface of SWCNTs. The ordered nanostructures of SDS with varying tilt angles can be clearly observed in this photograph. The tilt angles of helices depend on the diameter of the CNTs.[2] The lateral striations of SDS supramolecular self-assembly were 4.5 ± 0.5 nm. This value is agrees well with the previous research.[2] The supramolecular self-assembly of SDS half-cylinders provide a soft template to deposit and arrange metal nanoparticles on the surface of SWCNTs to construct ordered heterogeneous nanostructures.

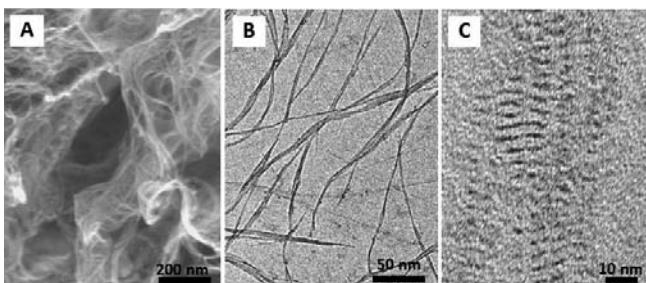


Fig. 1. TEM images of (A) pristine SWCNTs and (B,C) fine dispersed SDS-functionalized SWCNTs.

The photo-reduction reaction of palladium chloride in the suspension of SDS-functionalized SWCNTs was characterized by the UV-Vis absorption spectroscopy. The palladium chloride aqueous solution shows a clear absorption at 420 nm, which originates from the $d-d$ electron transition of Pd (II) ions. After irradiation by UV light, The absorption band of Pd (II) ions at 420 nm disappeared completely when Pd nanoparticles were reduced and deposited on SWCNTs. This suggests the complete reduction of Pd (II) ions and deposition of Pd nanoparticles onto the surface of SWCNTs.

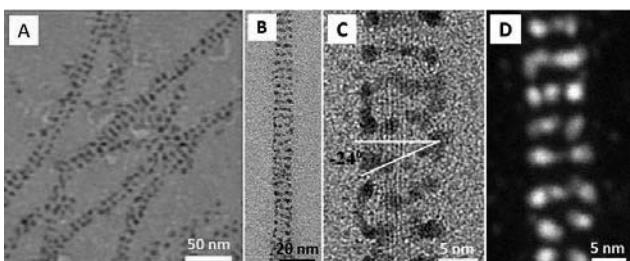


Fig. 2. TEM images of Pd nanoparticles selectively deposited on the SDS-functionalized SWCNTs.

Figure 2 shows the high-resolution TEM images of resulting nanostructures of Pd nanoparticles on the surface

of SDS-functionalized SWCNTs. It is clearly observed that Pd nanoparticles formed ordered nanostructures that Pd nanoparticles arranged on the surface of SWCNTs (Fig. 2A). These nanostructures are very similar to those using copolymers as a soft template.[1] Since SDS, the soft template, formed a periodic supramolecular self-assembly on SWCNTs, the deposited Pd nanoparticles also formed ordered periodic nanostructures on the surface of SWCNTs. Such periodic nanostructures were clearly observed by high-resolution TEM (Fig. 2B). The Pd nanoparticles have a size of 2.5 ± 0.5 nm. The inter-nanoparticle distance was 4.5 ± 0.5 nm along the orientation parallel to the tube axis. This value is the same to the lateral striations of SDS half-cylinders that were shown in Fig. 1C. This observation indicates that the Pd nanoparticles were selectively deposited onto the SDS-functionalized SWCNTs along the half-cylinders of SDS supramolecular self-assemblies wrapped around the SWCNTs. Figure 2C shows a high resolution image of Pd nanoparticles forming ordered nanostructures wrapped around the SWCNTs. The nanostructures have a right helix twist with a tilt angle of -24° relative to the tube axis. In our experiment, we observed that the ordered nanostructures of Pd nanoparticles have various helices and tilt angles wrapped around SWCNTs. It indicates that the tilt angle of Pd nanostructures depends on the various helices of SDS supramolecular self-assembly on the surface of SWCNTs. Figure 2D shows a dark field STEM image of Pd nanoparticles wrapped around SWCNTs. The ordered nanostructures of Pd nanoparticles arranged on SWCNTs were also clearly confirmed by the STEM observation.

The crystalline structures of Pd nanoparticles were also confirmed by powder X-ray diffraction (XRD) measurement. There sharp diffraction peaks were clearly observed in the XRD profile, which were assigned to (111), (200) and (220) planes of Pd nanoparticles.

In this study, we found that increasing the concentration of the palladium chloride aqueous solution resulted in a significantly higher density of site-selectively deposited Pd nanoparticles. The average size of Pd nanoparticles slightly increased to 3.2 ± 0.5 nm. In the case of high coverage, it is found that the disordered Pd nanoparticles increased when larger numbers of Pd nanoparticles deposit onto the SDS functionalized SWCNTs. This may due to the deposition rate of Pd nanoparticles being higher than the equilibrium rate of Pd absorbed to SDS molecules on the surface of SWCNTs.

4. Conclusions

In summary, we report a route to site-selectively deposit and arrange Pd nanoparticles on the surface of SDS-functionalized SWCNTs. SDS formed supramolecular self-assembly wrapped around SWCNTs. The terminal functional group of SDS provided the combination site to immobilize Pd nanoparticles. Pd nanoparticles are arranged on the surface of SWCNTs and form ordered periodic nanostructures. By control of the concentration of Pd (II) ions, it also allows high density deposition of Pd nanoparticles on SWCNTs. This is very important for the potential applications of these kinds of heterogeneous

nanostructures. This approach is easily applied to a variety of metal nanoparticles and/or quantum dots. It represents a potential and simple chemical route to arrange nanoparticles and/or quantum dots to form ordered heterogeneous nanostructures on CNTs by utilizing organic molecules as soft templates.

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