

## Original Paper

# A Facile Method to Fabricate Palladium Nanoparticles Arrangement on Single-Walled Carbon Nanotubes

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We report here a facile solution-chemical route to site-selectively deposit and arrange palladium (Pd) nanoparticles on single-walled carbon nanotubes (SWCNTs). Sodium dodecyl sulfate (SDS) previously formed supramolecular self-assembly on the walls of SWCNTs, which may act as adsorption sites of Pd (II) ions on SWCNTs. The Pd nanoparticles reduced by photo-reduction process and formed one-dimensionally ordered arrangement on the surface of SWCNTs with a variety of helices and tilted angles. The distance of periodic Pd nanoparticles arrangement was 5 nm. The structure (distance, helix and tilted angle) of the ordered arrangements were determined by the supramolecular self-assembly of SDS wrapped on SWCNTs. Increasing the concentration of Pd (II) ions, it was succeeded in high-density deposition of Pd nanoparticles on SDS-functionalized SWCNTs.

**Key Words:** *Single-Walled Carbon Nanotubes, Palladium Nanoparticles, SDS, Supramolecular self-assembly, Arrangement*

## 1. Introduction

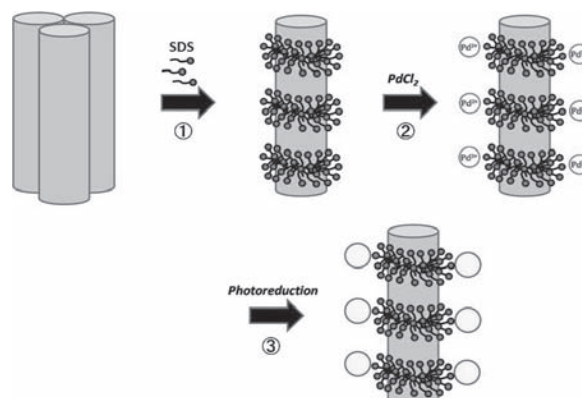
Carbon nanotubes (CNTs) have been one of the most extensively studied nanostructured materials since it was discovered in 1991 because of their great potential applications in many fields[1-4]. Surface functionalization of CNTs currently attracts significant research interest because CNTs are regarded as ideal templates for the decoration of functional nanoparticles[5]. Such decoration of CNTs can change the surface physical, chemical and electronic properties. It provides a simple route easy achieved to synthesis of various heterogeneous nanostructures for the applications of high-performance catalyst, fuel cells and (bio)chemical sensors. In this research filed, it is still a great challenge to design and control ordered heterogeneous nanostructures on the surface of CNTs. Many research groups have focused on the ordered self-assembly behavior of polymers and/or other organic macromolecules on the surface of CNTs[6-15]. For example, Li's group reported the formation of alternating periodic patterns of copolymers on the surface of CNTs[12-14]. Based on this approach, they succeeded in immobilization gold nanoparticles on the block copolymer/CNT hybrid to construct designed heterogeneous nanostructures on one-dimensional CNTs[15].

On the other hand, we consider surfactant-functionalized CNTs are also a charming approach to synthesize the ordered heterogeneous nanostructures. Surfactants have been widely studied because of the advantages on dispersing CNTs in water and changing the surface physical properties of CNTs[16,17]. SDS is one of the most typical surfactant to this subject[18,19]. In this case, the alkyl group of SDS is adsorbed on the CNTs by the hydrophobic interaction, and the hydrophilic part is oriented toward to aqueous phase. Because CNTs are rolled-up grapheme sheets, the SDS forms a similar supramolecular self-assembly with half-cylinder structure on the surface of CNTs[20]. Therefore, such supramolecular nanostructure of SDS-functionalized CNTs are regarded as an ideal template to construct designed heterogeneous nanostructures on CNTs. Recently, we have reported the site-selective deposition and arrangement of Pd nanoparticles on SWCNTs by utilizing the supramolecular self-assembly of SDS acted as a soft template[21]. Using this simple solution chemical approach, we have succeeded in formation of high ordered CNT-Pd heterogeneous nanostructures. Since Pd is a high-performance

metal material that has been extensively studied for possible applications in fuel cell, high-performance catalyst and hydrogen storage[22,23], high-density deposition of Pd nanoparticles on SWCNTs is also very important for their many potential applications. In this article, we report the control of the ordered Pd nanostructures on SDS-functionalized 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 (5 mg, 0.05 wt%) in aqueous solution (10 ml, containing 0.5 wt% SDS) were sonicated for 8 hours assisted by ball-milling as previously described[24,25]. 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-assemblies oriented perpendicular to the CNT axis[20]. A 2 ml aqueous solution of palladium chloride was added to the SDS-functionalized SWCNTs solution. Two samples solutions were prepared in this study. Sample A used 20 mM



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

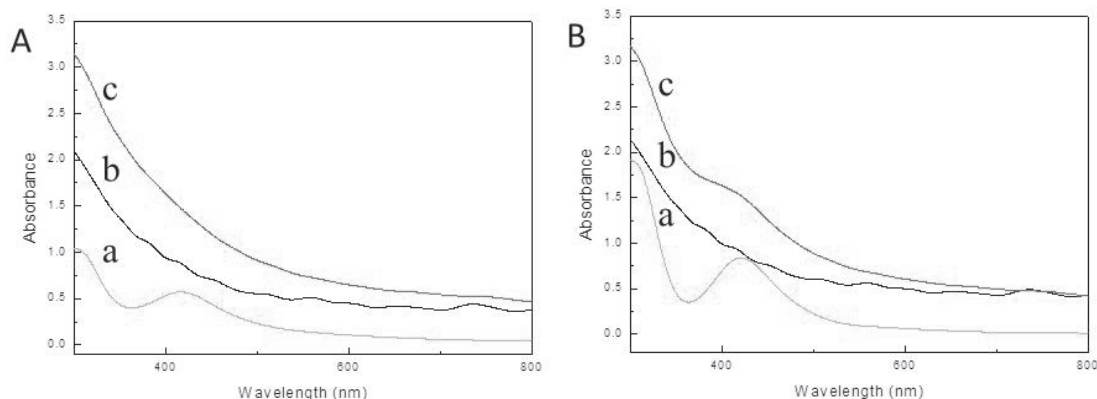


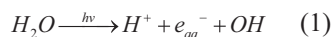
Fig.1 UV-Vis absorption spectrum of sample A (A) and sample B (B). In sample A, the concentration of PdCl<sub>2</sub> was 20 mM while in sample B it was 50 mM. (a) Palladium chloride aqueous solution, (b) SDS-functionalized SWCNTs aqueous dispersion and (c) Pd nanoparticles decorated SWCNTs aqueous dispersion.

palladium chloride, and sample B used 50 mM palladium chloride. 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 ordered heterogeneous nanostructures have been characterized by transmission electron microscopy (TEM, H800, Hitachi, Japan) on carbon-coating Cu grid operated at 200 kV.

### 3. Results and Discussions

UV-Vis absorption spectroscopy was used to characterize the photo-reduction reaction of Pd (II) ions in the dispersion of SDS-functionalized SWCNTs. Figure 1 shows UV-Vis absorption spectra of the samples A and sample B. The palladium chloride aqueous solution shows a clear absorption peak at 420 nm, which originates from the *d-d* electron transition of Pd (II) ions[26]. The SDS-functionalized SWCNTs aqueous solution shows numerous absorption peaks in the wavelength region of 400-800 nm which originate from the van Hove maxima electronic density of the quasi one-dimensionality of the SWCNTs[27]. SDS has no absorption peak between this region. In sample A, the absorption band of Pd (II) ions at 420 nm disappeared completely when Pd nanoparticles were reduced and deposited on SWCNTs. It indicates that all of Pd (II) ions were completely reduced by photo-reduction within 1 hour under the irradiation of 254 nm UV light. But in sample B, after 1 hour irradiation by 254 nm UV light, a weak absorption peak can be observed at 420 nm. It indicates that a part of Pd (II) ions was still remained in the solution. Interestingly, the absorption peaks of SWCNTs disappeared in both of the sample A and sample B. This observation is possibly due to the absorption area of the bare surface of the SWCNTs being dramatically reduced. It suggests the deposition of Pd nanoparticles onto the surface of SWCNTs.

Photo-reduction reaction has widely used to fabricate metal nanoparticles and nanostructures[28-31]. In our case, SDS acts as a template that absorb Pd (II) ion on the surface of SWCNT by its negative functional group. Pd is reduced by a photo-reduction reaction: The hydrated electrons formed in the radiolysis of the aqueous solvent water molecules were [32].



And that Pd<sup>2+</sup> ion was reduced by the hydrated electron[33,34].

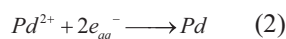


Figure 2(A) is a typical TEM photograph of dispersed SWCNTs. It is well known that the pristine SWCNTs are large bundles having an average diameter 50 nm due to the strong van der Waals interaction. When dispersing in SDS aqueous solution, the large bundles of pristine SWCNTs were effectively separated into small bundle and/or individual SWCNTs, as shown in Fig.2(A). We have observed that SDS molecules were formed ordered supramolecular self-assembly on the surface of SWCNTs[21]. Figure 2(B) shows a high magnification TEM photograph of dispersed SWCNTs. It can be observed the periodic ordered nanostructures formed on SWCNTs, which are the supramolecular self-assembly of SDS.

The morphology and structure of the resulting ordered SWCNT-Pd nanostructures were also characterized by TEM observation. Figure 3(A) shows a typical TEM photograph of sample A. It is clearly observed that Pd nanoparticles formed ordered structures that Pd nanoparticles arranged on the surface of SWCNTs. Since SDS, the soft template, formed periodic supramolecular self-assembly on SWCNTs, the deposited Pd nanoparticles also formed ordered periodic nanostructures on the surface of SWCNTs. Such ordered nanostructures were clearly observed from high-resolution TEM photograph as shown in Fig.3(B).

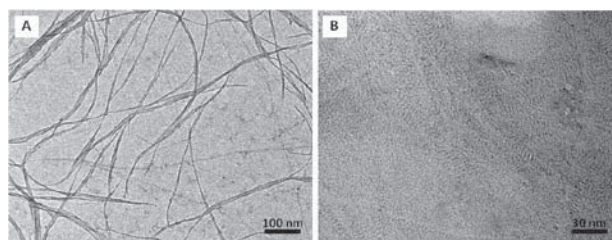


Fig.2 TEM images of fine dispersed SDS-functionalized SWCNTs. (A) Low magnification and (B) high magnification.

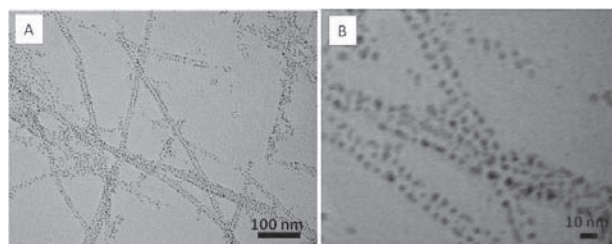


Fig.3 TEM images of Pd nanoparticles selectively deposited on the SDS-functionalized SWCNTs in sample A. (A) Low magnification and (B) high magnification.

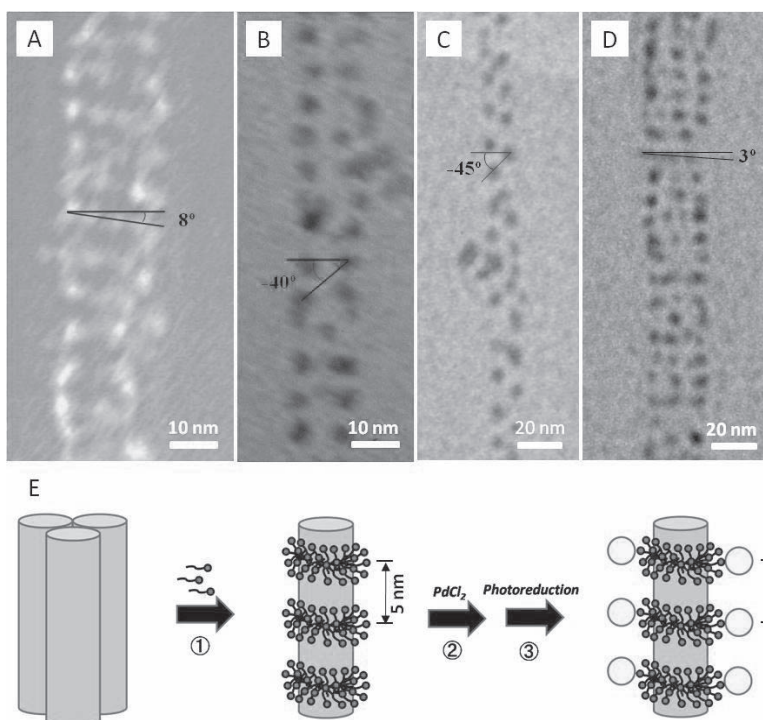


Fig.4 TEM photographs of Pd nanoparticles arrangements with a unique helical nanostructure on individual SWCNT in sample A. (A) Pd nanoparticles wrapped in a left helix with a tilt angle of  $8^\circ$  relative to the nanotube axis. (B) Pd nanoparticles wrapped in a right helix around a SWCNT with a tilt angle of  $-40^\circ$ . (C) Pd nanoparticles wrapped in a right helix around a SWCNT with a tilt angle of  $-45^\circ$ . (D) Pd nanoparticles organized as a helix wrapped around the tube with a tilt angle of  $3^\circ$ . (E) A schematic presentation to the formation of helical structure of Pd nanoparticles arrangement.

It is reported that the supramolecular self-assembly of SDS form a variety of helix on CNTs due to the diameter of CNTs[20]. We observed the helix and tilted angle of Pd nanoparticle arrangement on the SDS-functionalized SWCNTs. Figure 4(A)-(D) exhibit four individual SWCNTs that arranged by Pd nanoparticles with different helices and tilted angles. The Pd nanoparticles have an average size of 3 nm. The inter-nanoparticle distance was 5 nm along the orientation parallel to the tube axis. This value is the same to the lateral striations of SDS half-cylinders that reported elsewhere[20]. 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 [Fig.4(E)].

Increasing the concentration of the palladium chloride aqueous solution resulted in a significantly higher density of site-selectively deposited Pd nanoparticles [Fig.5(A)]. The average size of Pd nanoparticles slightly increased to 4 nm. We have also observed the helical structures on this sample. Figure 5(B) shows Pd nanoparticles that had left helices which were tilted by  $18^\circ$  relative to the tube axis and formed clear lines by linked with the neighboring Pd nanoparticles. Figure 5(C) exhibits a right helix of Pd nanoparticles wrapped on the surface of SWCNT with a tilt angle of  $-24^\circ$  relative to the tube axis. It is found that the disordered Pd nanoparticles increased when larger numbers of Pd nanoparticles deposit onto the SDS functionalized SWCNTs. This made it difficult to distinguish the ordered nanostructures of Pd nanoparticles wrapped around the SWCNTs. But anyway, since Pd is a high-performance metal material that has been widely studied for possible applications in many fields[22,23], it is no doubt that to increase the coverage of Pd nanoparticles on SWCNTs may enhance high performance for this SWCNT-Pd heterogeneous nanostructures. On the other hand, if we can find a suitable condition to control the experiment, it is possible to synthesize novel Pd nanorings wrapped around SWCNTs.

In this experiment, we also observed some interesting ring-structure of SWCNTs. Figure 6(A) is a SWCNTs ring that decorated by Pd nanoparticles observed in sample A. Figure 6(B) is a very similar nanoring observed in sample B. In both of them, Pd nanoparticles form ordered arrangements wrapped around SWCNTs, just the same to those in linear SWCNTs. It suggests that this facile solution chemical route is suitable for many other kinds of CNTs.

The crystalline structure of Pd nanoparticles was characterized by a powder X-ray diffractometer (XRD) system (JDX-3530M, JEOL). Figure 7 shows a XRD pattern of Pd nanoparticles that were deposited and arranged on SDS-functionalized SWCNTs. The SWCNTs supported Pd nanoparticles revealed three diffraction peaks at  $2\theta = 40.3, 46.7$  and  $68.4^\circ$ , which are assigned to the (111),

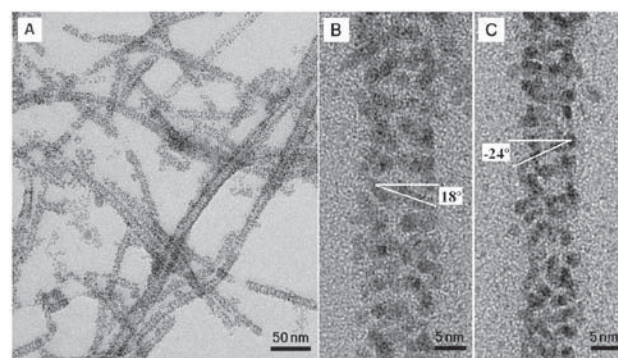


Fig.5 TEM photographs of the high-density deposition of Pd nanoparticles on SDS-functionalized SWCNTs in sample B. (A) A low magnification photograph. (B) Left helix of the Pd nanoparticles wrapped around a SWCNT with a tilt angle of  $18^\circ$  relative to the tube axis. (C) Right helix of Pd nanoparticle decorated SWCNT with a tilt angle of  $-24^\circ$ .

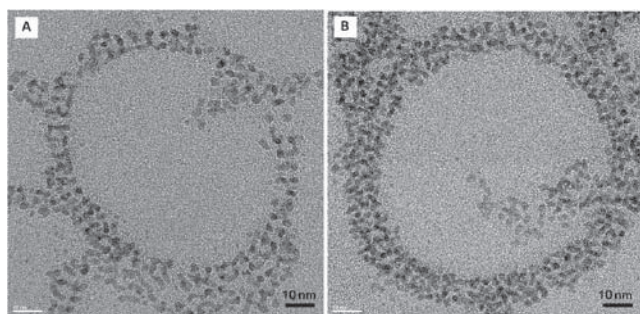


Fig.6 High resolution TEM images of individual SWCNTs nanoring decorated by Pd nanoparticles. (A) Sample A and (B) sample B.

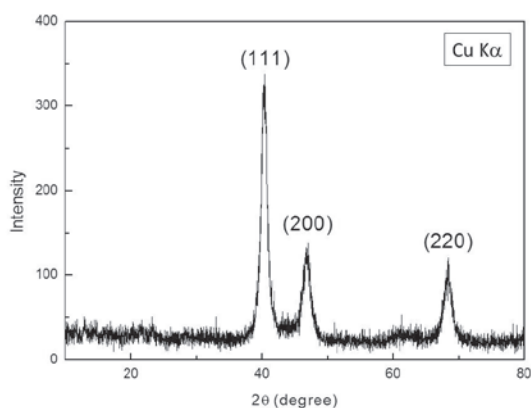


Fig.7 XRD pattern of Pd nanoparticles that deposited and arranged on SWCNTs.

(200) and (220) planes, respectively. The lattice parameters of the Pd nanoparticles evaluated by the XRD measurement were determined to be 0.388 nm, which is in agreement with the standard value (0.389 nm).

#### 4. Conclusion

In summary, we report a facile route to site-selectively deposit and arrange Pd nanoparticles on the surface of SDS-functionalized SWCNTs having sub 10 nm diameter. SDS formed supramolecular self-assembly wrapped around SWCNTs, and acted as a soft template to immobilize Pd nanoparticles. Pd nanoparticles thus are arranged on the surface of SWCNTs and formed ordered periodic nanostructures. By control the concentration of Pd (II) ions, it is also succeeded in the high density deposition of Pd nanoparticles on SWCNTs. This is very important for the potential applications of these heterogeneous nanostructures. Actually, this facile approach is easily applied to arrange a variety of metal nanoparticles and/or quantum dots on SWCNTs. 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 molecule as a soft template.

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