

Palladium Nanoclusters Deposited on Single-Walled Carbon Nanohorns

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This study reports a direct route for deposition of Pd nanoclusters on single-walled carbon nanohorns (SWNHs) in a one step reaction involving chemical reduction of metal ions in the presence of a polymer-stabilizer. The applied strategy provides small Pd nanoclusters with an average diameter of ~ 2.3 nm robustly attached to the nanotubular carbon. The attachment is mediated by the polymer (poly(vinylpyrrolidone), PVP) used to stabilize the nanoclusters.

The extensive research on the synthesis and purification of carbon nanotubes (CNTs) in the past decade has significantly advanced our understanding of the physical and chemical properties of the material and broadened its applications beyond the early predictions. The fabrication of nanoparticles–carbon nanotubes hybrid materials^{1–8} offers a considerable scope for development of novel materials, which can find applications in catalysis, fuel cells, and nanoelectronics. These applications require uniform nanoparticles attached to the nanotube surface. However, deposition of uniform nanosize metal particles on graphitic surface has proved to be a considerable challenge. Due to the weak interactions between the graphene walls of carbon nanotubes and most metals, many techniques for deposition of metal on CNTs have led to the formation of nanowires^{9–11} or coatings.^{3,5} Advances in the chemistry of CNTs have afforded the development of a number of strategies for functionalization of CNTs,^{12,13} which have opened new opportunities for synthesis of hybrid nanostructures. Various chemical routes have been explored for controlled deposition of nanoscale metal clusters on CNTs.^{8,14,15} By tailoring the chemistry of CNTs successful attachment of quantum dots, including Au,¹⁴ TiO₂,¹⁶ CdSe,^{15,16} and CdTe⁸ has been achieved. Although the deposition of metal nanoparticles on CNTs has been demonstrated,^{2,17} agglomeration of the particles remains a major issue.

Here we report a direct route for deposition of Pd nanoclusters on single-walled carbon nanohorns (SWNHs) in a one step

reaction involving chemical reduction of the metal ion in the presence of a stabilizer. The applied strategy provides small Pd nanoclusters with a diameter of ~ 2.3 nm, robustly attached to the nanotubular carbon. The attachment is mediated by a polymer (poly(vinylpyrrolidone), PVP), which is used to stabilize the nanoclusters. The hybrid material is of potential interest in a number of aspects. Nanoscale metal clusters deposited on a high surface area carbon support are of considerable interest to catalysis. PVP-stabilized Pd nanoparticles have been shown to effectively catalyze Suzuki cross-coupling reactions.¹⁸ The synthesis of SWNH–metal assemblies opens new opportunities to study the effect of heteroatoms in carbon nanostructures on their ability to adsorb supercritical gases. Because Pd has been shown to form ohmic contacts with CNTs,¹⁹ Pd–CNT heterostructures are of fundamental and practical interest for the assembly of integrated nanometer-scaled circuits.

SWNHs have nanotubular structure. The nanohorn units consist of graphene cylinders with a typical diameter of 2–3 nm and several tens of nanometers in length, which are capped with horn-shaped tips. They aggregate in spherical assemblies with nanospace between the adjacent nanohorns, which determines their intrinsic porosity. The adsorption of various species such as water,²⁰ methane,²¹ H₂,²² and C₆₀²³ in SWNHs has been reported.

Dahlia-SWNHs were produced by laser ablation of graphite in Ar (101.3 kPa).²⁴ The nanohorns were opened by heating in O₂ at 693 K for 10 min; the sample is denoted as o-SWNHs. The treatment is necessary to open the nanohorns, which increases the surface area of SWNHs.^{23,25} Pd nanoparticles were deposited on o-SWNHs from an aqueous solution of PdCl₂ by in situ reduction of [PdCl₄]^{2–} with ethanol in the presence of PVP as a stabilizing polymer. The size and size distribution of the nanoparticles depend on the concentration of the polymer,

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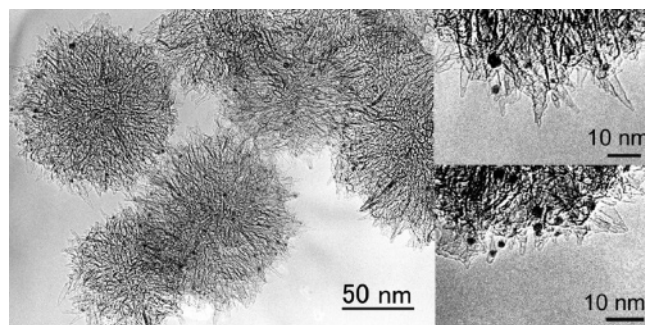


Figure 1. TEM micrographs showing the distribution of Pd nanoclusters in Pd/o-SWNHs.

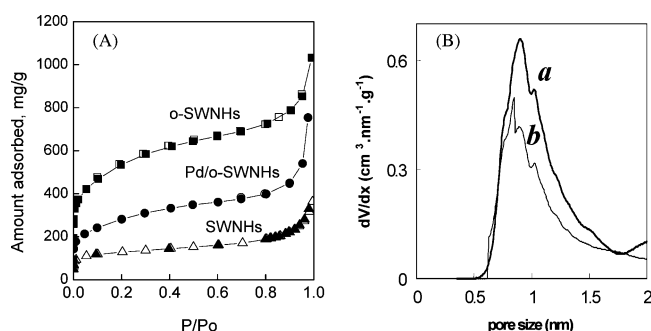


Figure 2. (A) Nitrogen adsorption isotherms at 77 K of (Δ) as-prepared SWNHs, (\square) o-SWNHs, and (\circ) Pd-loaded o-SWNHs (Pd/o-SWNHs). Closed and open symbols denote adsorption and desorption, respectively. The adsorption isotherms of N_2 were measured volumetrically at 77 K on an Autosorb-1, Quantachrom. The samples were treated at 423 K and 10^{-4} Pa for 2 h prior to the adsorption measurements. (B) Micropore size distribution curves of (a) o-SWNHs refluxed in a solution of water and methanol without Pd and (b) Pd/o-SWNHs. The distributions are calculated using the Saito–Foley method.

solvent and reducing agent.²⁶ In a typical experiment an aqueous solution of 2 mM H_2PdCl_4 (15 mL) and PVP (K30, average molecular weight 40 000) was mixed with 21 mL of water and 14 mL of EtOH. The synthesis was conducted at a molar ratio of PVP:Pd = 10:1, calculated for monomer units of PVP. The mixture was refluxed for 1 h at 343 K under air and after cooling to room temperature, 40 mg of single-walled carbon nanohorns (o-SWNH) were added. The mixture was refluxed for additional 1 h, the black residue was filtrated and dried in a vacuum. The amount of deposited palladium on SWNHs is 2.6% as estimated by TGA.

The TEM observations revealed that the Pd particles are relatively homogeneous in size with an average diameter of ~ 2.3 nm (Figure 1, see also Supporting Information). Although it is difficult to discern the precise location of the nanoclusters, they appear to be predominantly deposited on the external carbon nanohorn walls. A recent TEM study has shown that heat treatment in oxygen opens two types of paths to the inner space of SWNHs: paths at the tip with a narrow size distribution of 0.5 to 1.0 nm, and paths on the side-walls of SWNHs, which are much wider and can reach several nanometers.²³ Therefore, we assume that migration of Pd particles into the open nanohorns is not excluded considering the small size of the nanoparticles.

Pore structure analysis based on N_2 adsorption at 77 K (Figure 2A) revealed that the surface area and pore volume were reduced after the deposition of Pd on o-SWNHs. The subtracting pore effect method for a standard α_s -plot²⁷ was used to estimate the surface area (a_t) and total pore volume (V_t): for o-SWNHs a_t = 1006 m²/g and V_t = 1.10 cm³/g, and for Pd/o-SWNHs a_t = 675 m²/g and V_t = 0.78 cm³/g. There is a decrease of the

parameters by about 30% after deposition of palladium. The decrease in the parameters is not due to the preparation conditions (reflux at 343 K) because almost identical nitrogen isotherms were obtained for nontreated o-SWNHs and nanohorns refluxed in a solution of water and ethanol (see the experimental details above) in absence of Pd salt. Also, it should be noted that because the amount of Pd is very small (2.6 wt %) the surface of the palladium clusters is negligible compared to that of SWNHs and the adsorption takes place mainly on the carbon nanohorn surface. Therefore, we assign the decrease in the surface area and pore volume to the deposition of palladium nanoclusters. This is supported by the analysis of the pore size distribution curves (Figure 2B). The pore size distribution of Pd/o-SWNHs shows a decrease of the fraction of pores with a size < 2 nm as compared to o-SWNHs. Based on the adsorption analysis, it is reasonable to assume that some Pd nanoparticles and PVP are placed inside the nanopores of o-SWNHs and/or the nanopore entrances, which restricts the access of the adsorbate molecules to part of the pores. o-SWNHs have a heterogeneous pore structure, which consists of interstitial pores, formed between the individual nanohorns, and internal pores, which comprise the internal cylindrical space of the nanohorns. To further understand the spatial positioning of the Pd nanoclusters in the pore structure of SWNHs, we deposited Pd on as-prepared SWNHs, which has closed nanohorns and thus interstitial pores only. The deposition of Pd reduced the pore structure parameters by $\sim 15\%$. The comparison with the 30% decrease of the parameters for o-SWNHs, clearly indicates that the deposited Pd clusters block partially both interstitial and internal pores. Locking the palladium nanoparticles in the pores of SWNHs should restrict their migration and aggregation, a drawback often observed in supported metal nanoparticles. Indeed, we found that heat treatment of Pd/o-SWNHs at 423 K in a vacuum (10^{-4} Pa) for 2 h (the same conditions were used for pretreatment of the samples prior the adsorption measurements) did not change the size and distribution of the Pd clusters (see Supporting Information).

To evaluate the role of PVP in blocking the porosity of SWNHs, we treated Pd/o-SWNHs at 673 K for 2 h. The treatment should decompose the PVP (see TGA data in Supporting Information), and the fact that the nitrogen adsorption isotherms of the sample before and after treatment were almost identical indicates that the Pd nanoparticles are responsible for the reduced pore volume and surface area.

One question that arises is what is the mechanism of attachment of Pd clusters to the SWNHs. In the applied procedure, the nanohorns are added to the solution after the formation of Pd clusters is almost completed; note that within 30 min a significant part of $[PdCl_4]^{2-}$ is reduced to Pd^0 .²⁶ Therefore the formation of Pd nanoclusters does not occur on the outer or internal surface of the nanohorns. Because the synthetic procedure provides Pd nanoclusters coated with PVP,^{26,28} the polymer molecules should mediate the interaction between the nanohorn surface and Pd clusters. PVP has been shown to associate robustly with CNTs.²⁹ We assume that PVP adsorbs on SWNHs by hydrophobic interactions between the alkyl chains of PVP and the nanohorn walls, whereas the carbonyl groups from the pyrrolidone ring of the PVP coordinate to the surface Pd atoms.²⁸

The oxidation state of the deposited Pd was studied by XPS. The measurements were carried out using PHI Quantum-2000 spectrometer with Al K α X-ray (1486.6 eV). The pressure in the analysis chamber was below 1.2×10^{-8} Pa. The samples were mounted on an In sheet. Figure 3 shows the Pd3d spectrum,

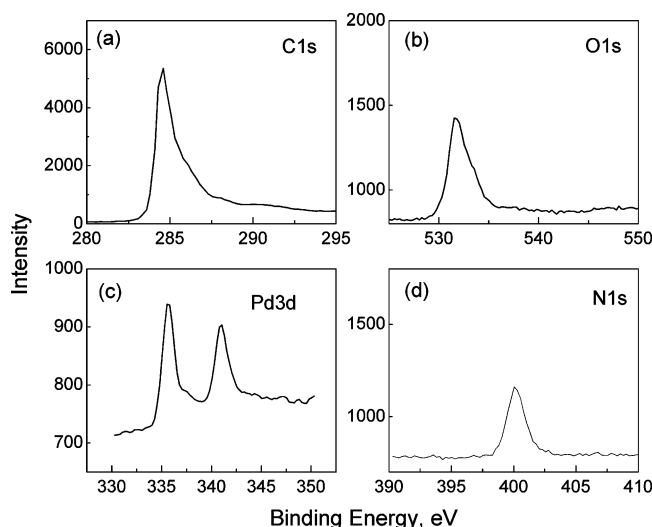


Figure 3. XPS spectra of Pd/o-SWNHs: (a) C1s, (b) O1s, (c) Pd3d, and (d) N1s.

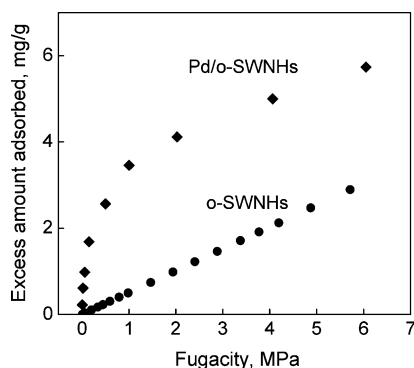


Figure 4. Hydrogen adsorption at 303 K on (●) o-SWNHs and (◆) Pd/o-SWNHs. The excess adsorbed amount is reported per mass of sample.

which has two photoemission peaks at binding energies (BE) of 335.6 eV (Pd3d_{5/2}) and 340.85 eV (Pd3d_{3/2}).

The observed BEs are slightly higher than the values for bulk Pd due to a size dependent effect of the core level. It is known that a decrease of the cluster size shifts the core level peaks to higher BE.³⁰

The binding energy of Pd3d_{5/2} is indicative of nanometric palladium in metallic state (Pd⁰) and cannot be associated with PdO (BE = 336.5 eV). The XPS measurements also show presence of O and N (Figure 3). O-atoms are associated with oxygen groups in the nanohorns and PVP, and the N-atoms are due to presence of PVP on the surface. Overlapping of the O1s and Pd3p_{3/2} spectra does not allow a precise quantitative estimation of the surface composition. To a good approximation, the amounts of Pd, O, and N calculated from the area of the corresponding peaks are 0.3, 5.8, and 3.0 at. %, respectively. The amount of Pd, calculated from XPS, is consistent with the values obtained by elemental analysis and TGA.

The pore structure parameters of Pd/o-SWNHs (surface area of 675 m²/g, micropore volume of 0.35 cm³/g and pores size <2 nm) are ideally suited for adsorption of supercritical gas. To demonstrate the effect of the Pd clusters on the adsorption behavior of the hybrid material, we utilized H₂ as a model supercritical gas. Pd/o-SWNHs show a significantly enhanced hydrogen capacity (Figure 4). More importantly, the H₂ isotherm of Pd/o-SWNHs exhibits different behavior as compared to o-SWNHs; the isotherm of o-SWNHs shows a linear increase with the pressure, indicating weak interactions between the

hydrogen molecules and SWNHs, whereas the isotherm of Pd/o-SWNHs exhibits a steep uptake at low H₂ pressure and a linear increase with the pressure above 1 MPa. The hydrogen uptake on Pd/o-SWNHs is slow, reaching equilibria after about 3 h. The trend of the isotherm and the long equilibration time is indicative of chemisorption and it suggests that the dispersed Pd-clusters have a significant contribution to the hydrogen uptake. Bulk Pd and Pd nanoclusters are known to store reversibly large amounts of hydrogen. The maximum H/Pd ratio for bulk Pd is about 0.7 and it decreases with decreasing the cluster size. The calculated H/Pd ratio for the Pd/o-SWNHs is $\gg 1$, suggesting that part of the hydrogen is stored within the nanohorns. The high hydrogen capacity of Pd/o-SWNHs has implications for catalytic activity of this material in hydrogenation reactions.

In summary, this study reports a general strategy for deposition of small metal nanoparticles on nanostructured carbon. The technique is general and can be applied to a variety of other metals such as Au and Pt. The synthesis of metal nanoparticles involves polymer, which acts as a protecting agent for the metal clusters and an intermediate for their attachment to the graphitic surface. Using PVP as an intermediate has an advantage over other protecting agents as it associates strongly with carbon nanotubular structures, providing a robust attachment of the metal nanoparticles. The catalytic properties of the Pd/o-SWNH hybrid material are currently under study.

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Supporting Information Available: TEM micrographs and thermogravimetric analysis of Pd/o-SWNHs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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