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Growth of Pd, Pt, Ag and Au nanoparticles on carbon nanotubes

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By thermal decomposition of metal salts, palladium, platinum, silver and gold nanoparticles, with average size of 7 nm, 8 nm, 17 nm and 8 nm, respectively, were grown on carbon nanotubes. TEM observations showed that most of the nanoparticles synthesized stuck on the outer surface of the carbon nanotubes. The size of nanoparticles can be adjusted by changing the metal to carbon ratio. Small nanoparticles are prone to agglomerate under intense bombardment from the electron beam. By comparison, nanoparticles were scarcely found on graphite or active carbon using the same synthesis process. HRTEM and XRD investigations revealed the well-crystallized structure and a lattice contraction of these nanoparticles.

Introduction

Metal nanoparticles have unique properties compared with their counterparts—normal metals. For example, Au is an excellent catalyst for total oxidation of CO only when its size is as low as ~2 nm.[1] Metal nanoparticles also exhibit abnormal non-linear optical limiting behavior.[2] Thus, such particles can be efficiently applied in industrial catalysis, electronic devices, gas sensing and coatings.[3] Normally, metal nanoparticles can be prepared by impregnation, precipitation and so-called atomic layer epitaxy techniques. Ayyappan *et al.* reported that nanoparticles of Ag, Au, Pd and Cu could be obtained by the reduction of the corresponding metal salts by using ethanol as the reducing agent under refluxing conditions.[4] In order to control the formation of the metal colloids and to stabilize them, a protective agent such as poly(vinylpyrrolidone) (PVP) is required. However, particle agglomeration remains a problem as encountered by Paszti *et al.* in the production of Cu and Ag nanoparticles by using the laser ablation method.[5]

The discovery of carbon nanotubes has generated substantial research activities worldwide.[6,7] Different from graphite and diamond, carbon nanotubes are one-dimensional tube-like carbon materials. The carbon layer is rolled up cylindrically with diameters in the nanoscale range. The structure and morphology of this material enable it to act as a specific template in synthesizing nanorods and nanoparticles.[8–10] In most cases, nanorods and nanoparticles are formed inside the tubes.[8,9] In our previous report, Cu nanoparticles and fibers were successfully synthesized by simple solid-state reaction between carbon nanotubes and a Cu salt.[11] In this work, we attempted to extend this method to prepare several commonly used metal nanoparticles. Experimental results demonstrated that Pd, Pt, Ag and Au nanoparticles with size from <5 to tens of nanometers can be synthesized following a similar process. XRD and HRTEM were applied to study the structural properties of these nanoparticles. For clear illustration, Pd samples were studied in more depth for comparative and characteristic studies.

Experimental

The carbon nanotubes were prepared by catalytic disproportionation of CO, which has been shown to be able to produce highly (>95%) purified, size-controllable tubes.[12] The average diameter of carbon nanotubes used in this work is ~20 nm. The Pd, Pt, Ag and Au nanoparticles were prepared by solid-state reaction between carbon nanotubes and the corresponding metal salts. The preparation process includes the following steps: (1) fully dispersing the carbon nanotubes in distilled water or acetone in an ultrasonic bath; (2) adding a soluble metal salt, ~2 mol% relative to carbon, to the suspension and stirring strongly at 373 K until all the solvent had evaporated; (3) decomposing and reducing the above mixture at temperatures from 573 K to 973 K depending on the metal salt used under an H_2 atmosphere for 2 hours then allowing to cool naturally. The metal salts used and the decomposition conditions are described in the caption of the TEM image of each sample. In order to verify the unique function of carbon nanotubes, graphite and active carbon were also mixed with $HPdCl_3$ and subjected to the same preparation procedure as that for the carbon nanotubes described above. We refer to these two samples as the graphite Pd sample and active carbon Pd sample, respectively.

Low and high resolution TEM (HRTEM) observations were conducted on JEM-100CX and Philips CM300 electron microscopes, respectively. Samples were attached to the TEM grid in two ways: either by directly sticking the sample on the TEM grid or by first dispersing the sample in distilled water in an ultrasonic bath then depositing a droplet of the suspension onto the grid and drying. A Philips PW 1710 diffractometer with CuKα irradiation was used in the measurements of X-ray diffraction patterns of the samples.

Results and discussion

Pd, Pt, Ag and Au nanoparticles with size distribution from <5 nanometers up to tens of nanometers were synthesized by the above-mentioned process. TEM images of the Pd, Pt, Ag and Au nanoparticles together with their histograms are shown in Figs. 1–4, respectively. The histograms were constructed by counting hundreds of nanoparticles spread on different regions of the TEM grid. The average sizes of the Pd, Pt, Au and Ag nanoparticles are 7 nm, 8 nm, 8 nm and 17 nm, respectively. Pd and Pt samples not subjected to ultrasonic pretreatment are shown in Fig. 1(a) and 2(a). It can be seen that most of the nanoparticles are attached on the outer surface of the carbon nanotubes. The size of nanoparticles is comparable to the diameter of carbon nanotubes. By comparison, larger particles rather than nanoparticles were observed by TEM for graphite and active carbon Pd samples, which revealed the unique

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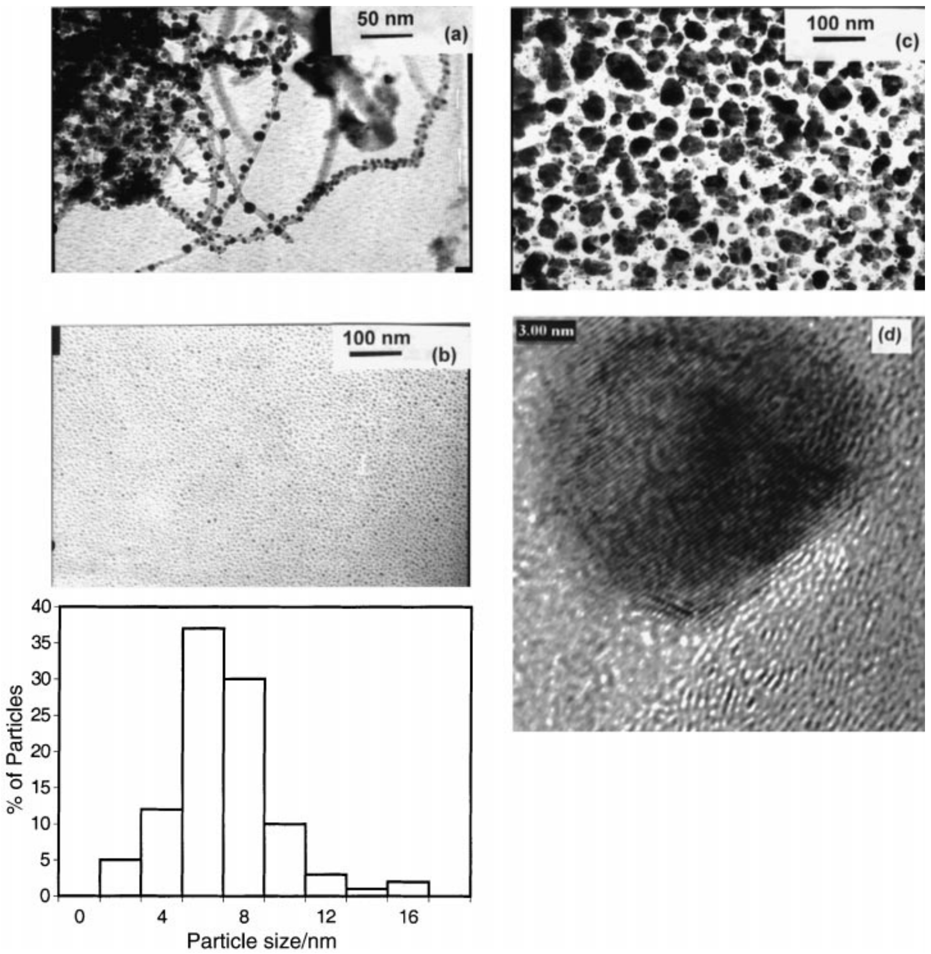

Fig. 1 TEM images of Pd samples prepared by solid-state reaction between $HPdCl_3$ and carbon nanotubes at 873 K under a flow of H_2: Pd/C is about 1/50. (a) Samples directly attached to the grid; (b) samples after ultrasonic treatment (with associated histogram); (c) sample under intense bombardment of the electron beam; (d) high resolution image of an individual Pd particle.

template function of carbon nanotubes in tailoring the size of metal particles. Fig. 1(b), 3 and 4 show the TEM images of samples after ultrasonic treatment. Most of the nanoparticles were detached from the carbon nanotubes and were spread on the grid. Detached nanoparticles were also observed if samples were simply immersed in distilled water and a droplet placed on to the TEM grid. It seems that the adhesion of the nanoparticles to carbon nanotubes is not strong and probably due to van der Waals forces.

The average size of metal nanoparticles depends on the carbon/metal ratio. The experimental results demonstrated that, in the case of the Pd sample, if Pd/C was increased to 1/10, the average size of the Pd particles was above 15 nm. If, however, the Pd content was decreased (Pd/C = 1/100), most of the nanoparticles were below 5 nm.

It was found that under TEM observations the size and the shape of small nanoparticles changed with the intensity of the electron beam. In the case of the Pd sample, as the electron beam intensity was gradually increased, smaller particles moved along the tubes or the grid and merged with each other leading to larger particles (compare Fig. 1(b) with 1(c)). Compared with Pd and Pt samples, Ag and Au nanoparticles agglomerated more readily under the same intensity of the electron beam. It was found that during the agglomeration, small nanoparticles first became round-shaped then moved quickly until merging with other particles. This suggests that these small nanoparticles may melt under the intense bombardment of the electron beam. The heat for the melting may arise from the energy released when the electron beam passes through the nanoparticles. If the heat conduction capability between the nanoparticles and the TEM grid is not

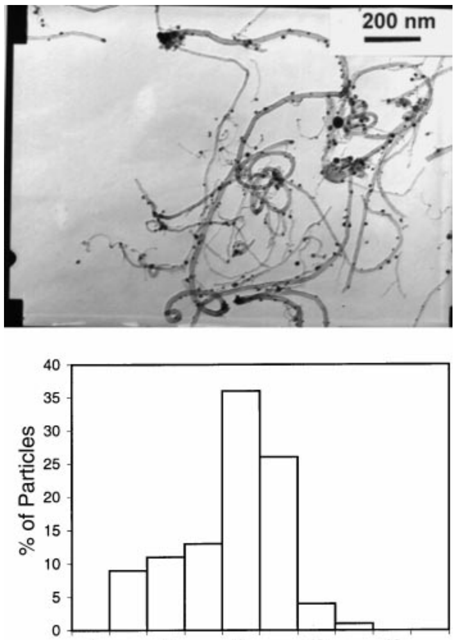

Fig. 2 TEM image and histogram of a Pt sample prepared from H_2PtCl_6 and carbon nanotubes at 873 K. The sample was directly attached to the grid.

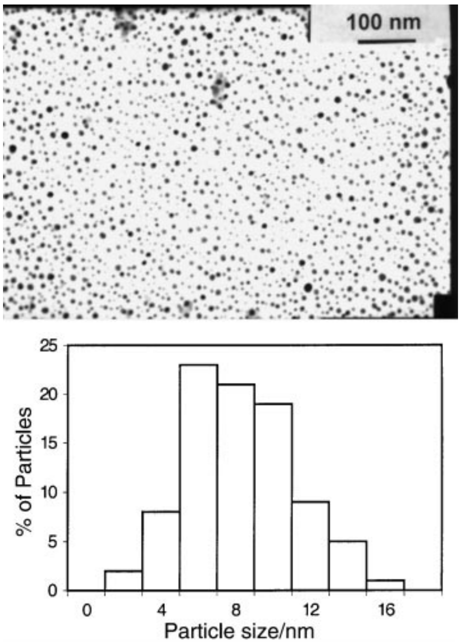

Fig. 3 TEM image and histogram of an Au sample prepared from $HAuCl_4$ and carbon nanotubes at 673 K; the sample was subjected to ultrasonic treatment.

high enough, the temperature of the particles will rise and thus cause melting and agglomeration of small particles.

The prepared nanoparticles are well crystallized. The Pd sample, for example, was characterized by HRTEM and XRD. Fig. 1(d) shows the HR-TEM image of an individual Pd particle with its carbon nanotube template lying on the left. Fringes corresponding to Pd(111) lattice structure were clearly seen. The lattice constant of Pd is around 0.39 nm, which was calculated by using the interlayer distance of the carbon nanotubes ($\sim$0.35 nm) as reference. XRD measurements also demonstrated the well-crystallized structure of these nanoparticles. Fig. 5 shows the XRD pattern of the Pd sample. It was found that strong diffraction peaks assigned to polycrystalline Pd[13,14] were developed. Diffraction peaks of carbon nanotubes (2θ around 26°) were weak and broad. Although Pd only comprises a small portion ($\sim$2 mol%) of the sample, its peaks are much stronger and sharper than those of carbon nanotubes, revealing the high crystallinity of these nanoparticles. The average size of the nanoparticles can be calculated using the Sherrer equation from XRD spectra (eqn. (1)):[15]

$$D_x = K\lambda/\beta_{1/2}\cos\theta \quad (1)$$

where D_x is the average diameter, $\beta_{1/2}$ is the full width at half maximum (FWHM) of the diffraction peak, and K is a constant. In the case of Pd samples, for calculations we used the FWHM of the narrow Debye–Sherrer line at $2\theta = 40.415°$, which corresponds to the Bragg diffraction from the Pd(111) planes. The result of 7 nm matches well with the average size observed from TEM.

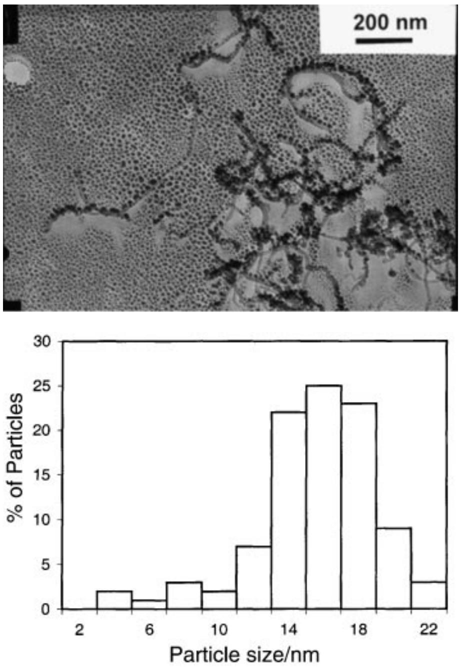

Fig. 4 TEM image and histogram of an Ag sample prepared from $AgNO_3$ and carbon nanotubes at 573 K; the sample was subjected to ultrasonic treatment.

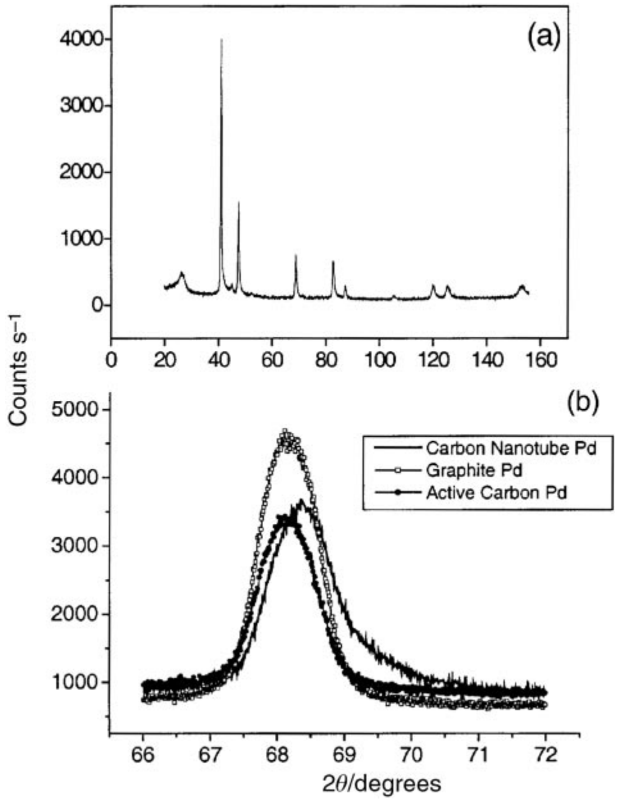

Fig. 5 XRD patterns of Pd samples. (a) Wide scan of the carbon nanotube Pd sample; (b) narrow scan of the Pd(220) diffraction of carbon nanotube, graphite and active carbon Pd samples, respectively.

Wasserman and Vermaak's work has shown that the (220) reflection of Pd can be used to measure the lattice contraction.[16,17] Narrow scans of Pd(220) reflections of carbon nanotube, graphite and active carbon Pd samples under same conditions are shown in Fig. 5(b). Peak positions and FWHMs are listed in Table 1. The peak positions and FWHM of graphite and active carbon Pd samples are almost the same, while an increase in peak position value and broadening in peak width were observed for the carbon nanotube Pd sample. The lattice constant of Pd in graphite and active carbon samples is 0.38910 nm, very close to that of bulk Pd (0.38893 nm) while for the carbon nanotube Pd sample, it is

Table 1 Peak positions and FWHM of Pd(220) in Pd samples prepared by difference carbon template

Template	Peak position (2θ)/°	FWHM/2θ
Carbon nanotube	68.360	1.142
Graphite	68.100	1.013
Active carbon	68.108	1.009

0.38780 nm. This result coincides with the Pd lattice contraction trend reported by Lamber *et al.* who found a decrease in the Pd lattice parameter with decrease in the size of palladium clusters.[18] These XRD discrepancies between graphite, active carbon and carbon nanotube Pd samples agree well with what has been observed in TEM and further demonstrate the template behavior of carbon nanotubes in tailoring the size of metal particles.

Summary

Carbon nanotubes have been demonstrated as efficient templates in the synthesis of nanoscale metal particles. TEM observations showed that Pt, Pd, Au and Ag nanoparticles developed on the outer surfaces of carbon nanotubes. Metal nanoparticles supported on carbon nanotubes could be used as efficient catalysts for some environmentally beneficial reactions. Furthermore, carbon nanotubes attached to metal nanoparticles may have certain applications in electronic devices.

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