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Laser-induced decoration of carbon nanotubes with metal nanoparticles

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Abstract Hybrid nanomaterials consisting of multiwall carbon nanotubes (MWCNT) decorated with noble metal nanoparticles were produced by irradiating aqueous mixed solutions of the separate components with nanosecond lasers pulses at 248 nm. Specifically, the decoration with Au and Pd nanoparticles is discussed. No decoration of the MWCNT was observed by simple mixing with nanoparticle solutions. Hence, a photo-thermal mechanism is suggested, whereby the laser-heating of the nanoparticles induces melting, boiling and subdivision into smaller clusters and atoms, which then attach to the MWCNT.

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1 Introduction

Hybrid nanomaterials, such as carbon nanotube-metal nanoparticle composites, will be important building blocks in a variety of future nanotechnological systems. Such 1D:0D composites can fuse the unique optical, chemical and electrical properties of the individual components, enabling applications in heterogeneous catalysis, molecular sensing [1] and the combination of plasmonics, [2] non-linear optical properties [3] and electronics on the nano-scale.

Various strategies have been adopted to attach metal nanoparticles onto the surface of carbon nanotubes. These include electrodeposition, [4] electrostatic force directed assembly, [5] a variety of chemical functionalisation routes and direct evaporation coating. Covalent surface functionalization with carboxylic acid groups or by coating with a chemical interlinker such as 1-Pyrenemethylamine or pyrene has been used to decorate carbon nanotubes with metal nanoparticles. [6–8] However, the chemical functionalization process is often tedious, with specific functionality often required for each metal and the electronic properties of the carbon nanotubes may be detrimentally modified. [9] Wrapping of nonfunctionalized carbon nanotubes with polymers has also been used to attach gold nanoparticles, [10] but coating with a polymer layer may block electron transport pathways in the nanotube, reducing the conductivity of the composites. Direct thermal or electron beam evaporation of metals onto carbon nanotubes has also been

performed, [11] but this technique would be difficult to scale to treat large volumes of carbon nanotubes.

In this paper, a method for decorating multiwall carbon nanotubes (MWCNT) with gold and palladium nanoparticles is introduced. This method involves the irradiation of mixtures of the individual components, in solution, with short duration laser pulses.

2 Experimental Details

The initial metal nanoparticle solutions were synthesised by two laser-based techniques using the pulses from a Lambda-Physik LPX 210i excimer laser operating at 248 nm, with a pulse duration of 25 ns. In the first technique, 100 mJ laser pulses were brought to a line focus, 7 mm long by 0.5 mm wide, using a cylindrical lens array. This fluence, of nearly 3 J/cm^2, was delivered onto a gold or palladium foil (purity 99.99%) submerged to a depth of 4 mm by de-ionised water. The vessel containing the foil and the liquid were mounted on a computer-controlled motorised X-Y translation stage, so that the whole surface of the metal foil could be utilised. Here, 9000 laser shots were used to produce 8 cm^3 of a metal nanoparticle solution, which remained in solution without the need for any surfactant. The second technique, used only to produce Au nanoparticles involed the UV photo-reduction of an aqueous $AuCl_4^-$ solution. This method was discussed in detail by Inasawa. [12]. A 4 mm depth of a 0.12 mM $AuCl_4^-$ solution was placed in a vessel mounted on the X-Y translation stage. The 15 mJ laser pulses were

defocused to produce a rectangular spot of area 0.4 cm^2. The laser spot was raster scanned over the whole area of the vessel, during the 9000 laser shot irradiation, scanning across the whole area 40 times. This method produced Au nanoparticle solutions with red colorations. However, unlike the synthesis by pulsed laser ablation (PLA), nanoparticle coalescence occurred rapidly, giving the solution a blue-purple color. The MWCNT used in the experiments were grown by chemical vapour deposition (Tsinghua-Nafine Nano-Powder, Commercialization Engineering Centre, China) To produce the MWCNT solution, raw tubes were acid treated using a H_2SO_4/HNO_3 mixture (3:1, 50 ml) and refluxing at 90 °C for 6 h, after which time the acid mixture was decanted. The residue was subsequently re-suspended in deionised water and centrifuged. This process was repeated several times until the pH of the solution reached neutral and was then ultra-sonicated to afford a stable suspension of MWCNT-COOH in aqueous media. This was filtered and the wet material immediatedly mixed with NaOH (aq) (50 ml, 5 M) and sonicated for 10 mins. The solution was filtered, washed with deionised water then re-disolved in water. This process was repeated until CNTs formed a stable aqueous suspension with a neutral pH. After synthesis of the Au and Pd nanoparticle solutions, an equal volume of an aqueous solution of MWCNT was added to the reaction vessel. The resulting mixture was then laser-irradiated using the same procedure employed for reducing the $AuCl_4^-$ solutions. In addition to irradiating the mixed solutions, the ef-

fect of the UV irradiation procedure on the initial MWCNT solution was also investigated, also employing the same range of pulse energies.

The nanostructure of the resulting nanoparticle:MWCNT hybrid materials was investigated using a Philips CM200 transmission electron microscope (TEM) Drops of the solutions were placed onto carbon grids and allowed to dry in air. The optical absorption of the resulting solutions was measured in a Cary 5000 UV-Vis-NIR spectrometer.

3 Results and Discussion

Before investigating the attachment of Au to the MWCNT, the size distribution of the initial nanoparticle solutions was examined. Histograms showing the size distributions of the Au nanoparticles produced by (a) PLA of a gold target underwater and (b) Photo-reduction of an $AuCl_4^-$ solution are shown in figure 1. Inset in each of the histograms is a TEM image of the nanoparticles. The PLA method produced smaller nanoparticles (mean diameter 6 ± 0.2nm), with a narrow size distribution. The nanoparticles produced by the photo-reduction method were larger (mean diameter 22 ± 0.8nm), with a wider size distribution, than those produced by PLA. As the solution produced by this method has the same colouration initially as the PLA produced solution, this larger nanoparticle diameter is likely a result of aggregation of smaller particles. A detailed discussion of the size distributions produced by this irradiation method can be found elsewhere [12].

As we are irradiating our MWCNT solutions with pulses at 248 nm, it was important to determine the effect of our laser pulses on the MWCNT in the solution. Structural damage has been observed by Kim et al. for MWCNT irradiated in air with nanosecond pulses, with a wavelength of 355 nm, at fluences in the range 254-527 mJ/cm^2 [13]. Here, the laser wavelength is closer to the absorption maximum of the MWCNT, so a lower threshold for damage would be expected.

Figure 2a shows plots of the optical absorption spectra from a series of MWCNT solutions laser treated at fluences in range 0 mJ/cm^2 (i. e. untreated) to 250 mJ/cm^2. The untreated solution has an absorption peak at around 251 nm. Laser irradiation at fluences below 63 mJ/cm^2 has little effect on the absorption of the solution. However, above this value the absorption in this wavelength range dropped dramatically, and indeed by 250 mJ/cm^2 the solution changed from dark to clear and colorless to the naked eye, indicating that the MWCNT had been significantly damaged or destroyed. Inset in figure 2a is an enlargement of the absorption spectrum from the MWCNT solution irradiated at 250 mJ/cm^2. Additional peaks, not observed in the spectrum from the untreated MWCNT, are observed and are likely the signature of organic decomposition products.

This irradiation series was then repeated for the mixtures of MWCNT and Au nanoparticle solutions synthesized by PLA. The optical absorption spectra for these mixtures are shown in figure 2b. Inset in this figure is the spectrum from a Au nanoparticle solution, without the MWCNT. The

surface plasmon resonance (SPR) absorption peak of the Au nanoparticles can be detected at 518 nm. In all cases, the reduction in the strength of the MWCNT absorption peak, with increasing laser fluence was less when Au nanoparticles were present. This indicates that the nanoparticles were absorbing at the laser wavelength, shielding the nanotubes from the full laser intensity. The Au SPR peak was also modified by the laser irradiation. A slight red-shift of the peak, a broadening and a reduction in absorption strength, were all observed with increasing laser fluence. For these small diameter particles (< 20nm), these modifications are consistent with a decrease in particle size, which has been observed experimentally [14] and predicted from electron mean-free path corrections to Mie theory [15].

By comparing the absorption plots in figure 2, it was determined that irradiation at fluences of around 63 mJ/cm^2 was optimal for this application, as higher fluences would cause unwanted damage to the nanotubes. Thus, mixtures of MWCNT and Au nanoparticle solutions produced by both PLA and photo-decomposition were irradiated at this fluence. Figure 3 shows TEM images of the resultant hybrid materials. In the case of the PLA grown gold nanoparticles (figure 3a), after irradiation the MWCNT can be seen to be decorated by Au nanoparticles, with diameters slightly smaller than the initial nanoparticle solution (mean diameter 4.2 ± 0.3nm), but with a broader size distribution. The resultant hybrid materials produced from Au nanoparticles synthesied by photo-decomposition, which started with a initially larger modal diameter, are shown in figure 3b. Here, the

MWCNT can be seen to be decorated with nanoparticles with diameters much smaller than those present in the starting solution (mean diameter 4.8 ± 0.2nm). A lower density of significantly larger particles is also present, but these appear to be distributed randomly, rather than decorating the surface of the nanotubes. It should be noted at this point, that simple mixing of the MWCNT with the two different Au nanoparticle solutions, resulted in no decoration. This can be observed in figure 3c, where a sample of PLA produced nanoparticles is mixed with a MWCNT solution. After a few days, this mixture is drop-cast onto a TEM grid and the solvent allowed to dry. The Au nanoparticles are observed to have a tendency to cluster together, rather than decorate the surface of the MWCNT as was observed with the annealed samples.

In addition to investigating Au particles, the decoration with Pd was also investigated. As reports of Pd nanoparticle growth by the PLA method are rare, it was important to determine the nature of the nanoparticles formed here. Inset in figure 4a is a selected area electron diffraction pattern from a large number of nanoparticles, confirming the formation of the *fcc* metal, rather than the oxide. Figure 4b&c show TEM images of the resultant hybrid material formed after irradiation of the mixed solution at a fluence of 63 mJ/cm^2. Again, Pd nanoparticles can be seen to decorate the surface of the MWCNT, which did not occur by simple mixing.

As the decoration of the MWCNT with metal nanoparticles only occurred after laser irradiation of the mixtures, a photo-thermally assisted

mechanism for decoration is suggested, whereby the laser-heating of the nanoparticles induces melting or boiling and subdivision into smaller clusters and atoms, which then attach to the MWCNT. The attachment mechanism is likely by a physical, rather than a chemical, process similar to the interaction that occurs when a carbon surface is exposed to a flux of metal atoms and clusters by evaporation coating. The interaction between metals and the surface of carbon nanotubes has been investigated previously, [11] where it was found that the binding energy between metal atoms and the carbon surface had a significant effect on the density of metal nanoparticles produced on the surface. In the results presented here, the nucleation density is relatively low, indicating weak interaction between the metal and the carbon surface, although the density is likely to be strongly affected by the presence of surface defects on the tube. Metal nanoparticles can interact strongly with light of the correct wavelength and can be readily heated to high temperatures when thermally isolated [16]. Photo-thermal size modification of gold and silver nanoparticles by laser irradiation for nanosecond and picosecond irradiation has been studied in detail previously [12,17], so a detailed discussion would not be appropriate here. However, for nanosecond irradiation nanoparticles that are larger than a certain threshold size can be heated by the laser irradiation to temperatures high enough to cause fragmentation and boiling, producing a distribution of hot, smaller clusters and atoms in solution. Particles that are smaller than this threshold cool rapidly due to their high surface-area to volume ratio, and are hence relatively un-

affected by the irradiation . Here, it is proposed that the MWCNT that are also present in the solution are exposed to a flux of these hot metal atoms, clusters and molten nanoparticles and are thereby decorated. Growth of these metal clusters in to metal nanoparticles decorating the tubes would also be expected, especially if the flux of atom species have significant mobility on the carbon surface. This hypothesized decoration mechanism is strongly supported by the observation that the nanoparticles decorating the tubes are smaller than those that were present in the solution initially. This is especially clear for the large initial nanoparticles produced by reduction of the $AuCl_4^-$ solution (see figure 3b.) As the attached nanoparticles are smaller in size than those present in the initial solution, they are likely to be more stable against photo-thermal modification (especially as they are attached to a heat sink in the form of the MWCNT). Hence, further irradiation of these particles should have little effect.

As this technique is readily scalable, simply by increasing the area of the vessel used to hold the solution, requires no specific chemical modification prior to attachment and involves no macroscopic heating of the solutions, it may be applicable to larger-scale synthesis of wider range of hybrid nanomaterial systems.

4 Conclusions

Hybrid nanomaterials consisting of multiwall carbon nanotubes decorated with gold and palladium nanoparticles were produced by irradiating aque-

ous mixed solutions of the separate components with nanosecond lasers pulses at 248 nm. No decoration of the MWCNT was observed by simple mixing with nanoparticle solutions. Hence, a photo-thermal mechanism is suggested, whereby the laser-heating of the nanoparticles induces melting, boiling and subdivision into smaller clusters and atoms, which then attach to the MWCNT. This hypothesis is supported by the observation that the nanoparticles attached to the tubes are smaller than those present in the initial solution. As the technique is readily scalable, requires no specific chemical modification prior to attachment and involves no macroscopic heating, it may be applicable in a wider range of nanomaterial systems.

Acknowledgments

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Figure Captions

Fig. 1 Histograms showing the size distributions of the Au nanoparticles produced by (a) PLA of a gold target underwater and (b) Photo-reduction of an $AuCl_4^-$ solution. Inset in each histogram is a TEM image of the nanoparticles.

Fig. 2 Plots of the optical absorption spectra from a series of solutions. (a) MWCNT solutions laser treated with at fluences of (i) 0 mJ/cm^2 (i. e. untreated), (ii) 63 mJ/cm^2, (iii) 125 mJ/cm^2, and (iv) 250 mJ/cm^2. Inset in (a) is an enlargement of spectrum (iv). (b) PLA gold nanoparticles + MWCNT solutions laser treated at fluences of (v) 0 mJ/cm^2, (vi) 63 mJ/cm^2, (vii) 125 mJ/cm^2, and (viii) 250 mJ/cm^2. 9000 laser shots were used in all cases. Inset in (b) is the spectrum from a PLA gold nanoparticle solution.

Fig. 3 TEM images of (a) MWCNT decorated with Au after irradiation of a mixture of a Au nanoparticles (produced by PLA) and MWCNT. (b) MWCNT decorated with Au after irradiation of a mixture of a Au nanoparticle (produced by photo-reduction) and MWCNT. The laser fluence used in both cases was 63 mJ/cm^2. (c) MCWCNT mixed with Au nanoparticles, without laser treatment.

Fig. 4 TEM images of (a) Pd nanoparticles produced by PLA of a Pd target underwater. Inset in the image is a SAED pattern taken from a ensemble of these nanoparticles demonstrating the fcc crystal structure. (b)&(c) MWCNT decorated with Pd nanoparticles after irradiation of a mixed solution at 63 mJ/cm^2.

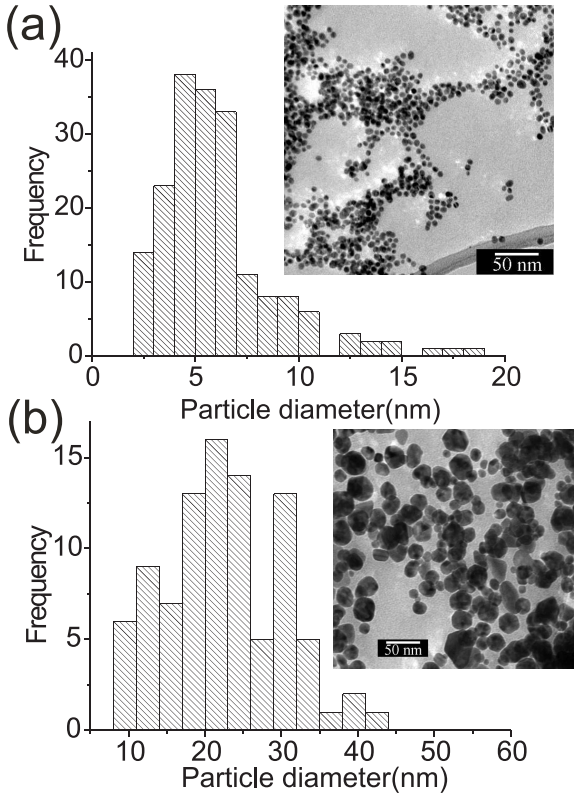

Figure 1. - Simon Henley

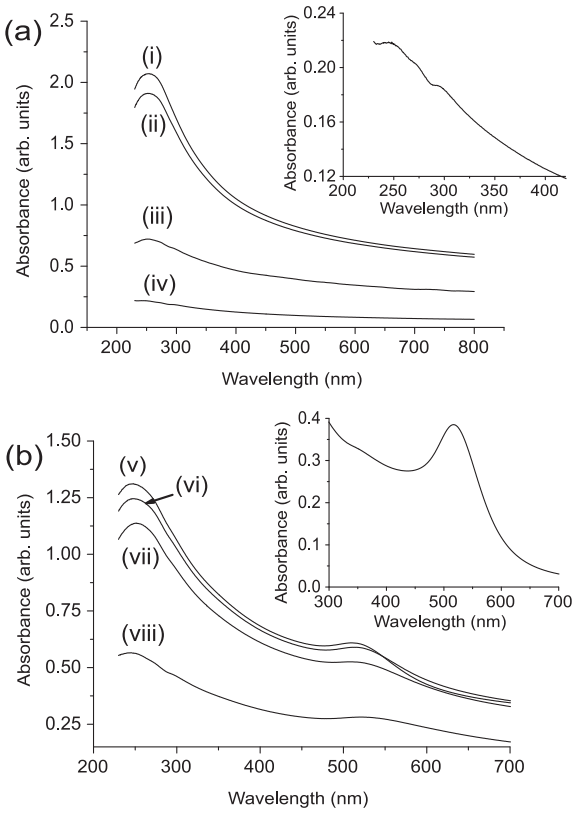

Figure 2. - Simon Henley

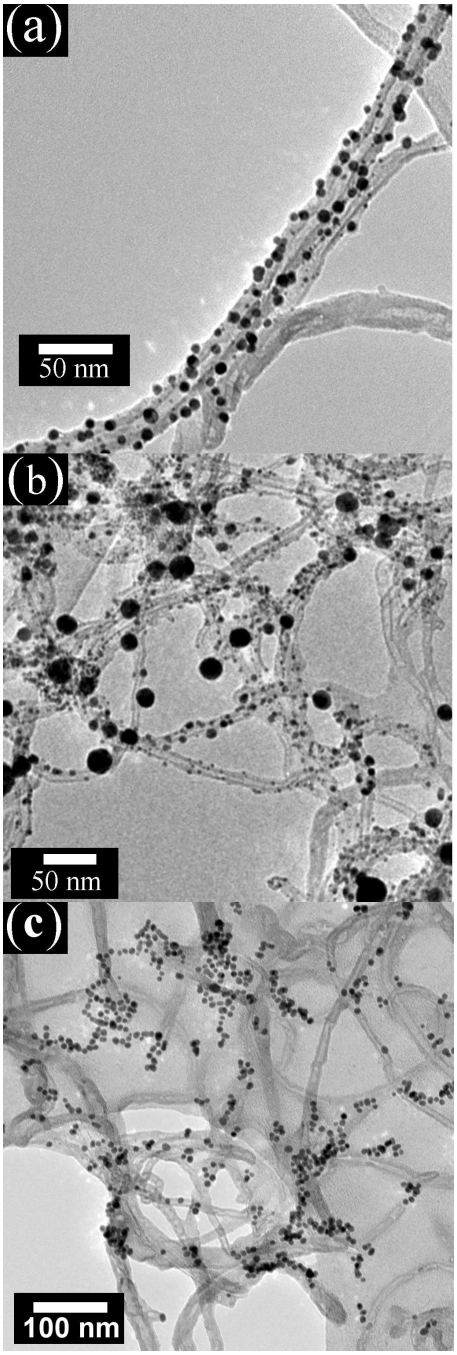

Figure 3. - Simon Henley

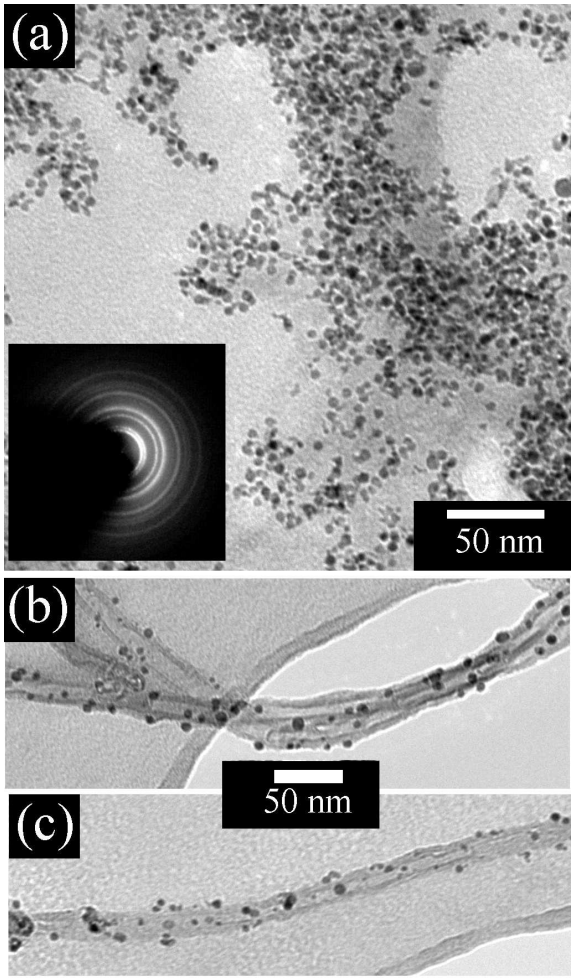

Figure 4. - Simon Henley