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Atmospheric Pressure Plasma Synthesized Gold Nanoparticle/Carbon Nanotube Hybrids for Photo-thermal Conversion

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KEYWORDS: Gold Nanoparticles, Carbon Nanotubes, Atmospheric Pressure Plasma, Surface Enhanced Raman Scattering, Photothermal Conversion

ABSTRACT: In this work, a room temperature atmospheric pressure direct-current plasma has been deployed for the one-step synthesis of gold nanoparticle/carboxyl group functionalized carbon nanotube (AuNP/CNT-COOH) nanohybrids in aqueous solution for the first time. Uniformly distributed AuNPs are formed on the surface of CNT-COOH, without the use of reducing agents or surfactants. The size of the AuNP can be tuned by changing the gold salt precursor concentration. UV-Vis, ζ-potential and X-ray photoelectron spectroscopy suggest that carboxyl surface functional groups on CNTs served as nucleation and growth sites for AuNPs and the multiple potential reaction pathways induced by the plasma-chemistry have been elucidated in detail. The nanohybrids exhibit significantly enhanced Raman scattering and photothermal conversion efficiency, properties that are essential for potential multi-modal cancer treatment applications.

INTRODUCTION

AuNPs are currently approved by the Food and Drug Administration (FDA) for non-invasive biomedical applications and have been widely explored in cancer treatment for drug delivery, bio-imaging, diagnose and photothermal therapy (PTT) due to their unique physical/chemical properties and high biocompatibility. Nanocarbon based materials, such as graphene, graphene oxide and carbon nanotubes (CNTs), on the other hand, have also been explored for a wide range of healthcare applications including cancer diagnostics, treatment, and sensing. CNTs, in particular, have gained increasing attention in cancer therapies for the delivery of anti-cancer drugs, hyperthermia, and bio-imaging in virtue of their unique structural, thermal, and chemical properties. For instance, CNTs can effectively accumulate in tumour cells/tissues due to their enhanced permeability and retention effects induced by the defectiveness, leakage and abnormalities in tumour cells/tissues. Although the toxicity issue of CNTs remains controversial, it is believed to be closely related to the dosage used as well as the structure/properties of the CNTs (such as length, diameter, alignment, degree of entanglement surface functionalities) and therefore cannot be generalized. For these reasons, further efforts are still required to control the dosage-related toxicity of CNTs and to improve the tumour-targeting efficiency of AuNPs in cancer applications. The creation of AuNP/CNT hybrid nano-systems with enhanced opto-thermic properties may offer the opportunity to address these specific challenges, for instance by reducing the dosage. In this sense, fundamental opto-thermic properties of AuNP/CNT hybrids are very important and can be used to optimize the nano-systems and assess initial viability. This approach avoids carrying out full and extensive toxicity studies on a very large range of morphologies, chemical compositions, configurations etc. Such hybrid may also potentially serve as a new nanomedicine platform providing multi-theranostic functions including cellular imaging/detection, photothermal therapy, and cancer drug delivery.

Several strategies have been attempted for the synthesis of AuNP/CNT nanohybrids. Wet chemistry based synthesis is one of the most common approaches, where harsh/hazardous reducing chemicals (such as sodium borohydride) are normally required. Although greener reducing agents (such as gallic acid) has been proposed, wet chemistry based synthesis still remain laborious and mostly require elevated temperature, long processing time, and cumbersome cleansing processes. Raghunee et al. proposed microwave assisted chemical reduction routines which could markedly reduce the reaction time, however, harsh reducing agents and potentially hazardous radiation source are inevitable. Alternative methods, such as solid-state thermal evaporation or sputtering require more sophisticated facilities and AuNPs that formed randomly on the CNT surfaces are often aggregated. The hybridising of CNTs with
AuNPs can also be achieved via electrochemical or electroless deposition, however, in both cases CNTs need to be immobilized on a substrate.\textsuperscript{32,33}

The application of AuNP/CNT hybrids specifically for cancer treatments has favoured other and more recent synthesis techniques. Layer-by-layer (LBL) assembly has been the main technique deployed to date.\textsuperscript{23–27} The LBL technique involves multiple steps which normally starts with functionalization of CNTs surfaces with polymers, biomacromolecule, or thiols to form an intermediated layer. The surface modified CNTs are then either hybridized with pre-synthesized AuNPs through electrostatic interaction\textsuperscript{23,25,26} or AuNPs formed in situ via conventional chemical reduction method\textsuperscript{24,27}. Many of these hybrid structures feature heavily aggregated AuNP (with varying size and morphology) coated on the CNT surface. The effects of AuNP size and the process-structure-property relationship with respect to the synthesis of such hybrid structures have not been well established in the context of cancer treatment.

Non-equilibrium atmospheric pressure plasma (APP) and in particular APP-liquid interactions, have demonstrated exceptional versatility in the synthesis and surface engineering of nanomaterials.\textsuperscript{34–39} When interacting with water, a high density of gas phase plasma electrons become solvated in the liquid, creating a rapid cascade of transient non-linear chemical reactions and highly reactive radicals (e.g., H· and OH·).\textsuperscript{40,41} Solvated electrons and/or reactive species are responsible for the successful synthesis of various nanomaterials, such as AuNPs, AgNPs, Fe₃O₄ NPs, Cu₂O NPs, and alloyed NPs such as Au₄Ag₁₋₄ in aqueous solutions.\textsuperscript{42–46}

In this work, we report the proof-of-concept of using of a facile and rapid direct current (DC), room temperature APP technique for the one-step synthesis of AuNP/CNT nanohybrids in aqueous solution. Stable and uniformly dispersed hybrid samples can be achieved unhindered by the use of solvents and surfactants. Great insight has been developed for the interfacial interaction between AuNPs and CNTs with different surface functionality, enabling the identification of the underlying mechanisms of different photothermal conversion capabilities seen in AuNP/CNT hybrid systems. The study also helps to establish the "process-structure-property relationship", which may provide important guidance for optimizing the future fabrication process of a wide range of nanocomposite/hybrid materials for healthcare applications and beyond.

**EXPERIMENTAL SECTION**

**Materials.** Three different types of surface functionalized multiwall carbon nanotubes (CNTs) were purchased from Cheap Tubes Inc., including carboxyl (-COOH) functionalized CNT with higher (1.2 %) -COOH density (namely CNT-COOH-H, purity > 95 wt%, length 10-30 μm, diameter 20-30 nm, according to manufacturer's data sheet), carboxyl (-COOH) functionalized CNT with lower (0.73 %) -COOH density (namely CNT-COOH-L, purity > 95 wt%, length 0.5-2.0 μm, diameter 30-50 nm), and hydroxyl (-OH) functionalized CNT with 1.0 % OH density (namely, CNT-OH, purity > 95 wt%, length 0.5-2.0 μm, diameter 30-50 nm). HAuCl₄ (Sigma Aldrich) aqueous solutions (2.5 μM, 0.1 mM, and 0.2 mM) were prepared by mixing chloroauric acid trihydrate (HAuCl₄·3H₂O, > 99.9%, Sigma-Aldrich) with appropriate amount of deionized water (Millipore Milli-Q machine (18.2 MΩ· cm⁻¹).

**APP set-up.** The APP set-up deployed in this work, as shown in Scheme 1, consists of a graphite rod as anode and a stainless-steel capillary (250 μm inner diameter) as cathode. The graphite rod was immersed in the aqueous solution, while the stainless steel capillary was placed approx. 1 mm above the liquid surface. The approximate distance between the anode and cathode was 2 cm. Helium (He) gas (25 sccm flow rate) was supplied through the capillary and the plasma can be triggered and maintained at ~2 kV voltage and 5 mA current. All samples mentioned in this work were treated for 10 min under a static condition.

**Synthesis of AuNP/CNT hybrids.** 0.1 mg/ mL CNTs/ water mixture was sonicated (140 W) for 6 hours and centrifuged at 5000 rpm for 4 hours, and the supernatant with dispersed CNTs was collected. The supernatants were diluted by adding appro-

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### Table 1. Nomenclatures of samples and their preparation methods

<table>
<thead>
<tr>
<th>Samples</th>
<th>CNTs used</th>
<th>Precursor used</th>
<th>APP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT-COOH-H</td>
<td>As purchased, 1.2 % -COOH density</td>
<td>None</td>
<td>No</td>
</tr>
<tr>
<td>2.5 μM AuNP/CNT-COOH-H</td>
<td>CNT-COOH-H</td>
<td>2.5 μM HAuCl₄</td>
<td>Yes</td>
</tr>
<tr>
<td>0.1 mM AuNP/CNT-COOH-H</td>
<td>CNT-COOH-H</td>
<td>0.1 mM HAuCl₄</td>
<td>Yes</td>
</tr>
<tr>
<td>0.2 mM AuNP/CNT-COOH-H</td>
<td>CNT-COOH-H</td>
<td>0.2 mM HAuCl₄</td>
<td>Yes</td>
</tr>
</tbody>
</table>

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Scheme 1. Diagram of the APP set-up
Appropriate amount of deionized water to obtain dispersed CNT solutions with a concentration of 50 ± 3 μg/mL. Appropriate amount of concentrated (5 mM) HAuCl₄ solution was added to different CNTs dispersion samples, to obtain aqueous mixtures of CNT with different HAuCl₄ concentrations (2.5 μM, 0.1 mM, and 0.2 mM were used in this work). The resultant mixtures were settled for 0.5 hour prior to APP processing.

The samples were named after the type of CNT functional groups and the HAuCl₄ precursor concentration used (see Table 1) and all samples were stored in glass vials (see Figure S1 in SI); For comparison and to provide further details for the discussion and analysis, a range of other samples were considered and these are summarized in Table 2.

**Characterization.** Ultraviolet-visible (UV-Vis) absorption spectra of the solutions were recorded using an Agilent spectrometer (Cary 60 UV-Vis, Agilent Technologies). The morphologies and sizes of the nanostructures were investigated by transmission electron microscopy (TEM; Philips Tecnai F20D), along with ImageJ software for the particle size analysis (more than 100 particles were analyzed). Samples for TEM characterization were all prepared by depositing a 25 μL droplet of sample solution onto a TEM sample grid. ζ-potential measurements were carried out using a Zeta Potential Analyser (Omni, Brookhaven). X-ray photoelectron spectroscopy (XPS) results were obtained from a Kratos Axis Ultra XPS system (monochromatic Al Kα X-rays, 1486 eV) which was run at a current of 10 mA and a voltage of 15 kV, respectively. The conducting environment base pressure was 1 × 10⁻⁹ mbar. The samples were prepared by drop casting aqueous solutions on neat and intrinsic silicon wafer and thoroughly dried under room temperature. High-resolution (0.05 eV) XPS spectra including C 1s and Au 4f peaks were performed at a pass energy of 40 eV. The C 1s peak located at 284.5 eV was used for the calibration of the obtained spectra. An open source software (CasaXPS) was deployed for the data analysis. Samples for Raman analysis were prepared by drop casting 100 μL of liquid sample on neat and intrinsic silicon wafer with a pre-fabricated 6 mm × 6 mm square well. After completely drying under room temperature, Raman scattering spectra of all samples were measured under ambient conditions by Raman spectroscopy (LabRAM 300, Horiba, UK with a 632 nm N₂-H₂ laser excitation source). The output of the laser box was 3.7 kV and 7 mA, and 1 % of the output was chosen for characterization. Each scan was divided into three segments with a total illumination time of 45 s.

**Photothermal conversion tests.** The photothermal effect of the hybrids was tested under the irradiation of an 852 nm continuous wavelength (CW) diode laser source with a power of 1.5 W (B4-852-1500-15C, Sheumann Laser Inc). 100 μL of each solution was placed in a 96-well plated container, which was irradiated by the laser and the temperature of the solution was monitored by an IR temperature sensor (CSL-CF2 High performance pyrometer, Micro-Epsilon).

**RESULTS AND DISCUSSION**

The optical properties of all samples were analysed by UV-Vis spectroscopy, see Figure 1. The APP treatment had no influence on the absorption spectra of the CNT-COOH-H when they were processed without added HAuCl₄. However, for samples containing HAuCl₄, APP treatment had led to a well dispersed colloid solution with changed colour (Figure S1, SI), indicating the formation of AuNP with different particle sizes. The emergence of peaks at 531 nm for 0.1 mM AuNP/CNT-COOH-H and 554 nm for 0.2 mM AuNP/CNT-COOH-H shown in Figure 1 can be attributed to the typical localized surface plasmon resonance (LSPR) effects of AuNPs. The red shift of LSPR peak can be related to the increase of the NP size as a result of greater...
HAuCl₄ concentration. However, the LSPR peak for 2.5 μM AuNP/CNT-COOH-H hybrid is not visible. With very low gold precursor concentration (2.5 μM), the plasmonic absorption may be very low due to the very low concentration of the synthesized AuNPs.

The morphologies of the AuNP/CNT-COOH-H hybrids have been investigated by TEM, see Figure 2. CNT-COOH-H after plasma treatment do not show any morphological changes (e.g. length; see also Figure S2 in SI for TEM of untreated CNT-COOH-H). However, AuNPs are found to attach on CNTs surfaces without obvious agglomerations, demonstrating that the plasma induced liquid chemistry is effective in producing AuNP/CNT-COOH-H hybrids. As it is shown in Figure 2a-c, the AuNPs within all the nanohybrids are mostly spherical (the shape projections of AuNP within AuNP/CNT-COOH hybrids can be found in Figure S3, SI), though NPs in the 0.2 mM AuNP/CNT-COOH-H hybrids start to show signs of heterogeneous growth (e.g. triangles, rods, etc., also see Figure S3 in SI). In contrast, pure AuNPs synthesized under the same plasma conditions (i.e., without the presence of CNT-COOH-H and using the respective HAuCl₄ concentrations) tend to exhibit more irregular shapes (e.g. triangles, hexagons, and rods) (See the shape projections of AuNPs in Figure S4 a-c, SI). Detailed examination of each sample (Figure 2a-c insets) suggests some form of interactions between AuNPs and CNT-COOH-H interface as, for all samples, there is no evidence of any AuNP remaining un-attached. Particle sizes and distributions are analysed by “ImageJ”, and more than 100 NPs were studied for each sample. The size of spherical NPs is determined by diameter, while that of other shapes are determined by the longest length; the average size and distribution is fitted with a Gaussian function. As can be seen from Figure 2d, the average NP size (corresponding size distribution can be seen in Figure S3) increases with increasing HAuCl₄ concentration, which is consistent with the UV-Vis results discussed earlier (Figure 1).

In order to gain more insight into the chemical composition and bonding arrangements, a comparison of the element chemical states between the untreated CNTs and 0.1 mM AuNP/CNT-COOH-H hybrid was investigated by XPS, and the mediate mixture 0.1 mM HAuCl₄/CNT-COOH-H was considered for comparison. Firstly, we looked at the difference between the survey spectra of CNT-COOH-H and 0.1 mM AuNP/CNT-COOH-H hybrid was investigated by XPS, and the mediate mixture 0.1 mM HAuCl₄/CNT-COOH-H was considered for comparison. Firstly, we looked at the difference between the survey spectra of CNT-COOH-H and 0.1 mM AuNP/CNT-COOH-H hybrid was investigated by XPS, and the mediate mixture 0.1 mM HAuCl₄/CNT-COOH-H was considered for comparison. Firstly, we looked at the difference between the survey spectra of CNT-COOH-H and 0.1 mM AuNP/CNT-COOH-H hybrid was investigated by XPS, and the mediate mixture 0.1 mM HAuCl₄/CNT-COOH-H was considered for comparison. Firstly, we looked at the difference between the survey spectra of CNT-COOH-H and 0.1 mM AuNP/CNT-COOH-H hybrid was investigated by XPS, and the mediate mixture 0.1 mM HAuCl₄/CNT-COOH-H was considered for comparison.

Figure 2. TEM images of AuNP/CNT-COOH-H synthesized from different HAuCl₄ precursor concentrations (a) 2.5 µM, (b) 0.1 mM, and (c) 0.2 mM AuNP/CNT-COOH-H hybrids, respectively; insets: corresponding higher magnification images; and (d) - (f) average AuNPs particle sizes within the three hybrids.
CNT-COOH-H as shown in the survey spectrum; the C 1s peak of pure CNT-COOH-H (Figure 3b) can be detected and de-convoluted into six components due to the different carbon elemental environments: the sp²-hybridized carbon (C=C), the sp³-hybridized carbon (C-C), the oxygen-containing functionalities including C=O, C=O, and O-C=O, and the satellite peak due to π-π interactions. When the CNT-COOH-H was mixed with HAuCl₄ prior to the APP, an Au 4f peak emerged as shown in Figure 3c; the spectrum can be clearly fitted into two doublets centred at the BE of 84.7/88.3 eV and 86.9/90.6 eV that correspond to the BE of ionic Au state, i.e., Au⁺ and Au³⁺ in the unreduced salt, respectively. After treated by APP, the Au 4f core spectrum of 0.1 mM AuNP/CNT-COOH-H presents two Au 4f½ and Au 4f½ core peaks centred at the binding energy (BE) of 84.0 eV and 87.7 eV, respectively; these two element states of Au 4f are in accordance with the profiles of reduced metallic Au⁰, respectively. The changes seen in the Au 4f states clearly indicate the formation of the AuNPs on CNT-COOH-H surfaces due to the reduction of ionic Au after the APP treatment. In addition, there are also some changes observed in the C 1s core peak of CNT-COOH-H following the

Figure 3. (a) Survey XPS spectra of untreated CNT and 0.1 mM AuNP/CNT-COOH-H hybrid; (b) C 1s core XPS spectrum of CNT-COOH-H; Au 4f core XPS spectrum of (c) 0.1 mM HAuCl₄/CNT-COOH-H mixture and (d) 0.1 mM AuNP/CNT-COOH-H hybrid; and C 1s core XPS spectrum of (e) 0.1 mM HAuCl₄/CNT-COOH-H mixture and (f) 0.1 mM AuNP/CNT-COOH-H hybrid.
mixing with HAuCl₄ as well as after the APP treatment. Specifically, the C 1s of the 0.1 mM HAuCl₄/CNT-COOH-H sample (Figure 3c) and the 0.1 mM AuNP/CNT-COOH-H sample (Figure 3f) can be both deconvoluted into six peaks, similar to that of the pure CNT-COOH-H sample; the detailed BE and percentage of each fitted peak for all samples are listed in Table 3. Compared to pure CNT-COOH-H, the fractions of oxygen-containing C-O, C=O and -O-C-O peaks all decreased significantly for both the 0.1 mM HAuCl₄/CNT-COOH-H mixture and the 0.1 mM AuNP/CNT-COOH-H hybrid C 1s peak. The result is consistent with the report by Suarez-Martinez et al., where AuNPs formed on the CNTs with -COOH terminations had led to a decreased fraction of oxygen-containing carbon species in the C 1s core XPS peak.⁵⁴ The formation mechanisms leading to reduction and growth of AuNPs can now be discussed. Firstly we should note that when the COOH-functionalized CNTs are dispersed in water, CNTs become negatively charged due to deprotonation and the surface terminations effectively become -COO⁻.⁵⁵ At this point, the CNT aqueous dispersion has pH of ~ 6.3 and the ζ-potential is -40 mV (Table 4), confirming the surface negative charge and stability of the colloid. Upon addition of the gold salt, the pH is immediately reduced to ~2.3 and also the ζ-potential decreases in absolute values (Table 4). HAuCl₄ in water is present in its ionic state (i.e. [AuCl₄]⁻ + H⁺), which justifies the acidity of the solution; here the solution was not buffered at any point of the process and therefore we did not use the pH to control or vary reaction paths. It has been shown that [AuCl₄]⁻ undergoes a partial reduction via ion exchange reaction on the CNT surface through chemical binding with de-protonated -COOH terminations⁵⁶⁻⁵⁷, in particular

-\text{COO}⁻ + [AuCl₄]⁻ \rightarrow [-\text{COOAuCl₄}]⁻ + Cl⁻ \tag{1}

The reduction in the ζ-potential (in absolute values), as observed experimentally (Table 4), is the result of -COOH sites on the surface of CNTs that are now surrounded by Au⁵⁸. UV-Vis has been also used to support reaction (1), see Figure 4. For pure HAuCl₄ aqueous solution, two absorption bands are present at approximately 220 nm and 288 nm, corresponding to the p₅dₓ² and p₅dₓ²⁻σ² ligand-metal transition modes in the [AuCl₄]⁻ complex structures, respectively.⁵⁹ The absorption peaks of free [AuCl₄]⁻ (200 nm and 280 nm) both decreased and blue shifted when UV-Vis was taken from the 0.1 mM HAuCl₄/CNT-COOH-H solution prior to APP processing. This transition can be attributed to the interaction between the [AuCl₄]⁻ complex and the de-protonated carboxylic groups as per reaction (1).

Our results therefore corroborate surface reaction (1) whereby pH, ζ-potential, UV-Vis and also the reduction of the oxygen-containing carbon species in the C 1s core XPS peak (Table 3) are all in agreement with the literature.⁵４⁻⁵⁷ It follows that the aqueous samples subjected to the plasma treatment are therefore formed by CNTs with a hybrid surface functionalization (i.e. [-COOAuCl₄]) and with the remaining of the gold salt still in solution. The subsequent formation of the AuNP has taken place through APP induced chemistry, where we believe that [-COOAuCl₄]⁻ on the surface of the CNTs served as preferential sites for further reduction and growth. We should note that the mechanisms leading to particle growth in this type of plasma-assisted processes are different, but in some aspects closely related to nanoparticle formation using more standard methods (e.g. wet chemistry), which are still source of great debates; for instance, the formation mechanism of the so-called “Turkevich synthesis”⁶⁰—which was initially proposed in 1951, is still largely under investigation.⁶¹-⁶⁵ It is convenient at this point to discuss separately the reduction/supply of Au monomers and the AuNP growth.

The reduction and supply of Au monomer under plasma treatment can take place through different pathways (see Scheme 2). Solvated electrons (Scheme 2-I) and hydrogen peroxide

<table>
<thead>
<tr>
<th>Samples</th>
<th>C (sp²)</th>
<th>C (sp³)</th>
<th>C-O</th>
<th>C≡O</th>
<th>O-C≡O</th>
<th>π-π</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT-COOH-H</td>
<td>284.2</td>
<td>284.7</td>
<td>285.6</td>
<td>287.0</td>
<td>288.7</td>
<td>290.6</td>
</tr>
<tr>
<td></td>
<td>Fraction (%)</td>
<td>34.7</td>
<td>39.8</td>
<td>13.4</td>
<td>4.3</td>
<td>5.3</td>
</tr>
<tr>
<td>0.1 mM HAuCl₄/CNT-COOH-H</td>
<td>284.3</td>
<td>284.7</td>
<td>286.0</td>
<td>287.5</td>
<td>288.8</td>
<td>290.8</td>
</tr>
<tr>
<td></td>
<td>Fraction (%)</td>
<td>42.3</td>
<td>39.2</td>
<td>12.7</td>
<td>1.50</td>
<td>3.0</td>
</tr>
<tr>
<td>0.1 mM AuNP/CNT-COOH-H</td>
<td>284.4</td>
<td>284.7</td>
<td>288.3</td>
<td>287.6</td>
<td>288.8</td>
<td>290.8</td>
</tr>
<tr>
<td></td>
<td>Fraction (%)</td>
<td>42.6</td>
<td>36.6</td>
<td>8.7</td>
<td>3.5</td>
<td>3.4</td>
</tr>
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</table>

Table 4. ζ- potentials of the CNT-COOH-H solutions before and after the addition of HAuCl₄.

<table>
<thead>
<tr>
<th>Samples</th>
<th>ζ-potential (mV, 25 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT-COOH-H</td>
<td>-40.46 ± 0.74</td>
</tr>
<tr>
<td>2.5 µM HAuCl₄/CNT-COOH-H</td>
<td>-31.60 ± 1.76</td>
</tr>
<tr>
<td>0.1 mM HAuCl₄/CNT-COOH-H</td>
<td>-26.39 ± 1.03</td>
</tr>
<tr>
<td>0.2 mM HAuCl₄/CNT-COOH-H</td>
<td>-23.37 ± 0.68</td>
</tr>
</tbody>
</table>

Figure 4. The effect of UV–vis spectra of HAuCl₄ on the CNT-COOH-H UV-vis absorption profiles.
Scheme 2. Potential reaction pathways in APP synthesis of AuNP/CNT-COOH hybrids.

This qualitative description of the growth mechanisms is drawn from studies of AuNPs formation via standard wet chemical methods, however it is supported by our findings. For instance, growth by coalescence ensures that NPs are grown at the CNT hybrid sites; this is because, without coalescence, NPs would be present also in solution, which is not what we have observed. The synthesis of AuNPs without CNTs (see Figure S3 in SI) shows that, for the concentrations considered here, colloidal stability is reached during coalescence and before agglomeration; this confirms that surface growth continues until the monomer supply is halted. AuNPs produced on the CNTs, for the same initial salt concentration, are generally smaller and more spherical than NPs produced without CNTs (also see Figure S3 in SI). This shows that CNTs impact the aggregation stage and cluster formation and is because the presence of hybrid CNT-Au sites forces the formation of a higher number of clusters reducing the stability of a fraction of the gold salt precursor.

The main distinctive components of plasma-assisted synthesis are various: i) fast kinetics offered by electron-induced reduction, ii) on demand and localized production of the reducing agents (e.g. H2O2 and electrons), and iii) contained reaction volume with strong concentration gradients. These allow tailoring the reaction pathways and better controlling the time/impact of the growth mechanisms, e.g. the reduction of the reaction volume can preclude surface growth. In the context of this part of work, we believe that the reaction kinetics of electron-induced reduction contributes to prevent seed particle formation in the solution.

In the following step, to further prove the proposed mechanisms, CNTs with a lower surface -COOH density (0.73 %) (CNT-COOH-L, details see experiment section) and CNTs with –OH functional groups (CNT-OH, details see experiment section) were chosen for the synthesis of AuNP/CNT hybrids (see Table 2) following the same APP processing parameters.

The UV-Vis and TEM results of these 0.1 mM AuNP/CNT-COOH-L hybrid and 0.1 mM AuNP/CNT-OH hybrid are shown in Figure 5. The UV-Vis spectrum of 0.1 mM AuNP/CNT-COOH-L in Figure 5a shows that the LSPR peak wavelength of AuNP/CNT-COOH-L (552 nm) is red-shifted as compared to the 0.1 mM AuNP/CNT-COOH-H hybrid (531 nm). Similar to the 0.1 mM AuNP/CNT-COOH-H hybrid, the TEM image of 0.1 mM AuNP/CNT-COOH-L (Figure 5b) and corresponding shape projection analysis of AuNPs in this hybrid (See Figure S6, SI) also indicate that spherical AuNPs are uniformly attached to the surfaces of CNT-COOH-L. The average AuNPs size on CNT-COOH-L (95.1 ± 25.1 nm, see Figure S5 in SI) is much greater than that on CNT-COOH-H (28.7 ± 14.1 nm), which correlates to the red-shift of the LSPR peak. Observation from multiple TEM images of different magnifications (see Figure S6 in SI) also indicate there are less number of AuNPs formed on the surfaces of CNTs in 0.1 mM AuNP/CNT-COOH-L hybrid than in the 0.1 mM AuNP/CNT-COOH-H. As discussed earlier, AuCl3 on the surface of the CNT-COOH through ion exchange reaction with –COO- is believed to be preferential reduction and growth sites for AuNPs under such APP-assisted process. The much lower -COOH density of CNT-COOH-L provided much less sites compared to CNT-COOH-H, AuNPs with greater sizes could therefore be formed on the CNT-COOH-L surfaces by coalescence under the same...
initial HAuCl\textsubscript{4} concentration (same amount of monomers supplied to less CNT-Au sites).

However, when the surface functionalities of CNT was changed from –COOH to –OH groups, the formation mechanism of AuNP/CNT seems different from the results. Though a typical LSPR peak of AuNPs is still observed at 536 nm (Figure 5c), the AuNPs formed in the 0.1 mM AuNP/CNT-OH hybrid are presented in irregular shapes (hexagons, trapezoids, triangles, rods, etc.) with an average size of 50.3 ± 15.2 nm (see Figure S7 in SI) and some of them are loosely adsorbed/unattached to the CNT-OH (see NPs in red dash circles in Figure 5d). Figure 3 and literature have supported that [AuCl\textsubscript{4}]\textsuperscript{-} could react with CNT-COOH by ion exchanging reaction, due to the ionization of –COOH in water as –COO\textsuperscript{-} and H\textsuperscript{+}. While ion exchange is expected for CNT-COOH, no ion exchanging should in principle take place between CNT-OH and [AuCl\textsubscript{4}]\textsuperscript{-} because –OH cannot be ionized in water. This is confirmed by UV-Vis spectra in Figure 6 when compared with Figure 4. With the addition of CNT-OH into the 0.1 mM HAuCl\textsubscript{4} solution, both the 220 nm and 288 nm peaks remain constant in terms of the peak position and the intensity. The reduction and growth of AuNPs in this case mainly took place within the bulk solution, where the as-produced AuNPs then physically absorbed on the CNT-OH surfaces. This also explains AuNPs within 0.1 mM AuNP/CNT-OH hybrid shows similar morphologies (irregular shapes) to those produced without CNTs (Figure S4 in SI). Both the analysis of 0.1 mM AuNP/CNT-COOH-L hybrid and 0.1 mM AuNP/CNT-OH hybrid support our proposed formation mechanisms leading to reduction and growth of AuNP in the presence of –COOH functionalized CNTs.

We finally focus on the investigation of important properties of the AuNP/CNT hybrids. We firstly compared the Raman scattering of AuNP/CNT-COOH-H hybrids synthesized from different initial HAuCl\textsubscript{4} concentrations (Figure 7a). Typical disordered band (D band) (∼1332 cm\textsuperscript{-1}) and graphene-like band (G band) (∼1592 cm\textsuperscript{-1}) characteristic peaks are present for all sam-

![Figure 5. (a) and (c) UV-vis spectra of the 0.1 mM AuNP/CNT-COOH-L hybrid and 0.1 mM AuNP/CNT-OH hybrid; corresponding CNTs were used as references; (b) and (d) TEM images of 0.1 mM AuNP/CNT-COOH-L hybrid and 0.1 mM AuNP/CNT-OH hybrid.](image)

![Figure 6. The effect of UV–vis spectra of HAuCl\textsubscript{4} on the CNT-OH UV-vis absorption profiles.](image)
ples and the APP treatment did not induce any further defects/modifications to the CNT-COOH-H. After the AuNPs formed on the CNT-COOH-H, samples exhibit significantly enhanced electromagnetic surface enhanced Raman scattering (SERS), which can be essentially attributed to the LSPR oscillations of AuNPs under laser irradiation. The greater SERS signal associated with samples produced from higher HAuCl₄ concentration correlates well with sample’s greater particle size/number (also see Figure 2), as larger AuNPs normally possess higher SERS efficiency when the size of NPs falls in the range of 20 nm to 80 nm. The greater SERS signal associated with samples produced from higher HAuCl₄ concentration correlates well with sample’s greater particle size/number (also see Figure 2), as larger AuNPs normally possess higher SERS efficiency when the size of NPs falls in the range of 20 nm to 80 nm. Similar to the 0.1 mM AuNP/CNT-COOH-H hybrid sample, the 0.1 mM AuNP/CNT-COOH-L hybrid (Figure 7 b) and 0.1 mM AuNP/CNT-OH hybrid (Figure 7c) also demonstrated enhanced SERS properties comparing to corresponding pure CNT samples due to the presence of AuNPs on their surface after APP treatment. Raman spectroscopy is widely used for medical diagnostic applications, such as sensing and imaging. Due to their distinctive SERS signals, CNTs have attracted great research attention in the field of Raman spectrometric sensors. From our Raman scattering results, the AuNP/CNT hybrids herein demonstrated greatly enhanced SERS signal as compared to untreated CNTs, hence these hybrids would be promising materials to be used for medical diagnostic applications such as bio-imaging and sensing.

Another very important property of our AuNP/CNT hybrids is their photothermal effect. The photothermal conversion efficiency of our hybrids was assessed in their aqueous media under the irradiation of laser. An 852 nm CW diode laser was selected due to its skin-penetrating ability within the biological window. The photothermal conversion results of different AuNP/CNT-COOH-H hybrids are shown in Figure 8a, and corresponding pure AuNP colloids and CNT-COOH-H were used for comparison. The observed temperature increase represents the heat transfer from AuNP/CNT-COOH-H hybrids to the solution. All samples heated up from room temperature under the laser irradiation following the trend 0.1 mM AuNP/CNT-COOH-H > 0.2 mM AuNP/CNT-COOH-H > 2.5 μM AuNP/CNT-COOH-H > CNT-COOH-H > 0.2 mM AuNP > 0.1 mM AuNP > 2.5 μM AuNP. In particular, 0.1 mM and 0.2 mM AuNP/CNT-COOH-H hybrids heated up most rapidly (over 48 °C in 60 s), reaching the temperature range valid for photothermal cancer therapies. It can also be clearly seen that all AuNP/CNT-COOH-H hybrids demonstrated enhanced photothermal conversion when compared to pure AuNP and as-received CNT-COOH-H under all of the three HAuCl₄ concentrations.

According to the TEM analysis (Figure 2), the presence of CNTs has a significant influence on the resultant AuNP shape and their distribution in the samples. Zedan et al. has shown that the photothermal effect of AuNP/nanocarbon hybrids can be affected by the shape and size of the AuNPs. A more uniform distribution of the AuNPs on the CNTs with a tighter spherical shape distribution can therefore contribute to a more enhanced photothermal effects. It is also worth noting that 0.2 mM AuNP/CNT-COOH-H hybrid shows a lower photothermal conversion efficiency as compared to the 0.1 mM AuNP/CNT-COOH-H hybrid. Due to the LSPR of AuNPs, the incident light irradiation on AuNPs could result in both light absorption and light scattering. According to El-Sayed’s calculation based on the Mie theory, larger AuNPs tend to have less light absorption but more scattering. The decreased photothermal efficiency of 0.2 mM AuNP/CNT-COOH-H hybrid might be caused by the enhanced light scattering due to the larger AuNP size within the sample. We also compared the photothermal effects of the 0.1 mM AuNP/CNT hybrid synthesized from different CNTs. In Figure 8a, the 0.1 mM AuNP/CNT-COOH-H hybrid shows a temperature rise (ΔT) as high as 52.5 °C, which is higher than the sum of the ΔT of pure CNT-COOH-H (23.4 °C) and the ΔT of 0.1 mM AuNP (10.6 °C). When CNT-COOH-H was changed to the CNT-COOH-L, the 0.1 mM AuNP/CNT-COOH-L hybrid also presents a reasonably high ΔT (~ 31.4 °C, see Figure 8b); but considering that pure CNT-COOH-L alone showed a ΔT of 26.3 °C, the contribution of AuNPs to the photothermal enhancement within the hybrid is 5.1 °C - much lower than for the 0.1 mM AuNP/CNT-COOH-H hybrid (19.1 °C). The observed trend appears to be again relevant to the size of AuNPs within these two hybrids; according to Figure 2 and Figure 6, the
AuNPs within 0.1 mM AuNP/CNT-COOH-L hybrid has a much greater size than within 0.1 mM AuNP/CNT-COOH-H hybrid and the enhanced light scattering of greater AuNPs could lead to decreased photothermal efficiency. When comparing to CNT-OH, the 0.1 mM AuNP/CNT-COOH-L hybrid only demonstrated a slight photothermal effect enhancement in the presence of AuNPs (∆T = 1.5 °C, see Figure 8c). AuNPs LSPR is reported to promote the photo-absorption of nanocarbon and induce their plasmons, therefore contributing to the overall enhanced photothermal effects. For –COOH functionalized CNTs, the surface binding sites facilitated the charge transfer between AuNPs and CNTs through these sites. However, for AuNPs physically adsorbed on the surface of CNT-OH, the chances for electrons transfer would be negligible.

CONCLUSION

In summary, we have successfully demonstrated a single-step preparation of AuNP/CNT hybrids through a facile and rapid APP processing technology. The complicated interaction between multi-phase materials (gas phase plasma, liquid and solid state nanomaterials) and the associated plasma-chemistry contributed to the formation of AuNP/CNT-COOH hybrids via multiple reaction pathways have been elucidated in detail. The [AuCl₄]⁻ and –COOH bindings serve as nucleation sites for the growth of AuNPs on the CNT-COOH surface and the resulting AuNP size increases with gold salt precursor concentration. The resulting hybrid structures, AuNP/CNT-COOH hybrids, demonstrated enhanced Raman scattering and high photothermal conversion efficiency, which are highly desirable for potential applications such as future multi-modal cancer theranostic.

ASSOCIATED CONTENT

Supporting Information

Photographs of CNT-COOH-H and AuNP/CNT-COOH-H hybrids solutions (Figure S1); TEM of pure CNT-COOH-H (Figure S2); shape project and size distribution of AuNPs within 2.5 µM, 0.1 mM, and 0.2 mM AuNP/CNT-COOH-H hybrids (Figure S3); TEM images of pure AuNP samples and corresponding size distribution (Figure S4); shape project and size distribution of AuNPs within 0.1 mM AuNP/CNT-COOH-L (Figure S5); additional TEM images of the 0.1 mM AuNP/CNT-COOH-H and 0.1 mM AuNP/CNT-COOH-L (Figure S6); shape project and size distribution of AuNPs within 0.1 mM AuNP/CNT-OH (Figure S7).

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Notes

The authors declare no competing financial interest.

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