DC atmospheric pressure plasma for the synthesis of gold nanoparticle/carbon nanotube hybrids for photothermal conversion

[1]Daye Sun, [2,3]James McLaughlan, [4]Li Zhang, [1]Brian G. Falzon, [5]Davide Mariotti, [5]Paul Maguire, [1]Dan Sun

[1]*Advanced Composites Research Group (ACRG), School of Mechanical and Aerospace Engineering, Queen's University, Belfast, UK*

[2]*School of Electronic and Electrical Engineering, University of Leeds, UK*

[3]*Leeds Institute of Cancer and Pathology, University of Leeds, UK*

[4]*Research Center for Nano-Biomaterials, Analytical & Testing Center, Sichuan University, Chengdu, China*

[5]*Nanotechnology and Integrated Bioengineering Centre, Ulster University, UK*

Abstract: We demonstrated a direct current atmospheric pressure plasma-based synthesis approach for the fabrication of gold nanoparticle decorated carbon nanotube (AuNP/CNT hybrids). The multiple potential reaction pathways induced by the plasma-chemistry have been elucidated in detail by ultraviolet-visible spectroscopy, ζ-potential and X-ray photoelectron spectroscopy. The resulting hybrids presented enhanced Raman scattering (SERS) and enhanced photothermal conversion efficiency, hence holding great promise for future multi-modal cancer therapy.

Keywords: Gold Nanoparticles, CNTs, Plasma, Photothermal Conversion, SERS

1. Introduction

Non-equilibrium atmospheric pressure plasma (AMP) has emerged as a new platform for the synthesis of nanomaterials. Its flexible setup allows for room temperature operation and eliminates the need of vacuum equipment as required in conventional plasma processing. In addition, nanomaterial synthesis through AMP/ liquid interaction could eliminate the use of harsh chemicals as seen in most of the wet chemistry approaches. The highly energetic electrons and free radicals generated at the plasma/water interface trigger a series of cascading reactions and complicated plasma chemistry, which contribute to the formation of various well dispersed nanostructures even without the use of surfactants [1]. To date, the AMP process has been deployed for the surface functionalization and synthesis of various nanomaterials an nanoparticles (NPs), including silicon nanocrystals, TiO_2, BN, Au NPs, Ag NPs, Fe_3O_4 NPs, alloyed Au_xAg_{1-x} NPs, and Cu_2O NPs etc. [2].

Amongst various metallic nanomaterials synthesised via the AMP process, gold NPs (AuNPs) are of particular interest especially in the biomedical field, due to their unique physical/chemical properties and exceptional biocompatibility [3]. To date, AuNPs have been widely exploited in the area of drug delivery, cancer theranostics, bioimaging and biosensing, etc.

Carbon nanotubes (CNTs), on the other hand, also demonstrated promising properties desirable for biomedical applications such as hyperthermia, drug vehicles and tissue scaffold [4]. In recent years, AuNP/CNT hybrids have received increasing attention. These unique structures combine the multi-functional properties of the two constituents, offering enhanced theranostic functions for many applications such as surface enhanced Raman scattering (SERS) for cellular imaging/detection, enhanced photothermal transduction capability for photothermal therapy (PTT), and drug delivery [5].

2. Method

In this work, a direct current (DC) room temperature atmospheric pressure microplasma (AMP) has been employed (Fig. 1) for the synthesis of AuNP/functionalized -CNTs (AuNPs/f-CNTs) hybrids. Commercial available –COOH groups f-CNTs purchased from Sigma-Aldrich were chosen. The AMP was ignited at the gas (helium, 25 standard cubic centimetre per minute) / liquid interface 1 mm above the aqueous mixture of f-CNTs (~ 50 µg/mL) and gold salt precursor (0.1 mM $HAuCl_4$ in this case). AuNPs were also prepared for reference under the same plasma processing conditions in the absence of f-CNTs. The AMP processing time for all samples is constant at 10 min.

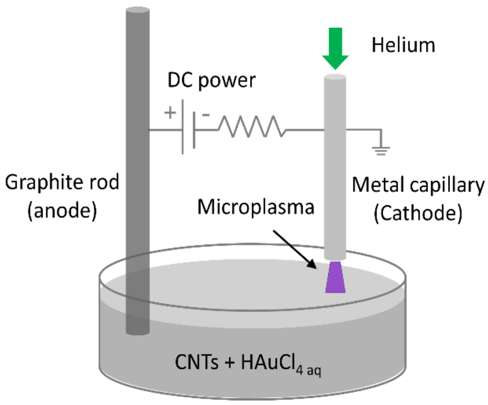

Fig. 1. Schematic of AMP set-up.

3. Results and discussion

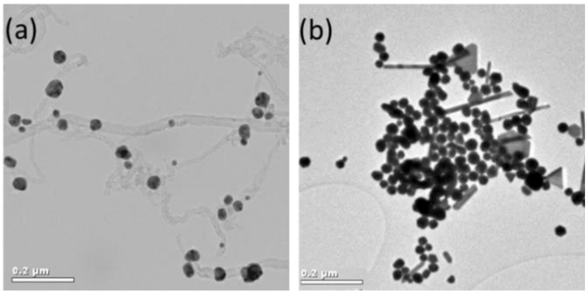

Fig. 2. TEM images of (a) 0.1 mM AuNP/f-CNT (b) 0.1 mM AuNPs under the same AMP processing parameter.

Transmission electron microscopy (TEM) image of 0.1 mM AuNP/f-CNT hybrid (Fig. 2a) shows that AuNPs (mostly spherical) are uniformly distributed on the CNTs surface. In contrast, pure AuNPs synthesized under the same plasma conditions without f-CNTs are more aggregated and exhibit more diverse geometries (e.g. nanorods, triangles, pentagons, hexagons, etc.). It is suggested that the –COOH moieties have immobilized AuNPs on the CNT surface and could also potentially control the crystal growth kinetics [6]. Ultraviolet-visible (UV-Vis) spectroscopy, X-ray photoelectron spectroscopy (XPS), and zeta potential measurements were deployed to gain more insight into the reduction and growth mechanisms of AuNPs on the surface of f-CNTs. Results (not shown here) indicate that the formation of AuNP/f-CNT hybrids can be accomplished through multiple reaction pathways induced by the APP process, where the -COOH groups acted as preferential sites for the reduction and growth of AuNPs. The solvated electrons as well as the plasma activated liquid chemistry at the plasma liquid interface can both contribute to the reduction and further growth of AuNPs [7]; a third possible reaction pathway is determined by the CNT electron affinity and high conductivity. Negative charges are captured and transported to the CNT surface CNT-AuNP binding sites, contributing to the surface reduction [8].

We also investigated the important properties of our AuNP/f-CNT hybrid. The Raman analysis shows that the resulting AuNP/CNT hybrid structures demonstrated enhanced Raman scattering, comparing to pure f-CNT samples. The photothermal effect of the hybrids has been investigated using a near-infrared region (NIR) continuous wavelength (CW) laser (852 nm, 1.5 W), commonly used in cancer treatment [9]. AuNP/CNT hybrid demonstrated a significantly enhanced photothermal conversion efficiency ($\Delta T \sim 50$ °C) in 240 s as compared to that of the pure AuNPs ($\Delta T \sim 10.5$ °C) or untreated CNTs ($\Delta T \sim 23.9$ °C). These enhanced properties suggest a synergistic effect between AuNPs and CNTs, which may enable the potential application of our hybrid materials in the next generation multi-modal cancer treatment combining photo-thermal therapy, sensing, drug delivery and bio-imaging.

4. References

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