

**Plasma-Assisted Synthesis of MWCNT-Based Nanostructures and Nanofluids**

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**Abstract:** In this contribution, we report on the successful development and integration of dry unit operations for the synthesis of novel nanostructures and nanofluids featuring multiwall carbon nanotubes (MWCNTs) as supporting structure over which immobilized nanoparticles (NPs) add localized, chemistry-dependent properties such as enhanced and tunable spectral absorptivity, catalytic properties and reacting sites. We present two examples: Ni NP-decorated MWCNT electrocatalysts for H₂ production and Au NP-decorated MWCNT nanofluids for direct volumetric energy absorption.

**Keywords:** MWCNTs, nanoparticles, plasma functionalization, nanofluid, nanostructure

1. Introduction

Due to their unique and tunable properties, metallic and semiconductor nanoparticles (NPs) are of considerable interest in various fields of application such as renewable energy harvesting and fuel production, catalysis, cancer therapy and imaging. In a number of applications, the NPs must be supported on a nanostructure that is firmly attached to a surface so as to provide heat and electrical conductivity to a base substrate, or uniformly suspended in a fluid (nanofluid) to provide enhanced volumetric absorption and transport (heat and mass) properties.

Wet chemistry approaches are commonly used for the synthesis of nanomaterials. They often make use of hazardous reagents, lengthy and complex protocols, and generate large amounts of waste chemicals. Furthermore, the produced nanomaterials are often not "dry" and must be separated from the synthesis solution. Processing plasmas offer, in many ways, advantages over wet-chemistry routes for the synthesis of nanomaterials and arguably, the only practical routes for complex heterogeneous nanostructures. The unique features of the processing plasmas are:

- Dry processing conditions;
- Use of simple, often environmentally-benign precursor gases, liquids and solids;
- A wide range of volumetric power densities and surface heat fluxes, covering ranges of \(-10^3\) to \(-10^6\) W/cm², respectively;
- *in-situ* surface charging by plasma electrons of the nanoparticles being formed, thus providing natural inter-nanoparticle repulsion;
- High temperature and species concentration gradients providing extreme quenching conditions and species separation and/or localization of the nanoparticle formation zones;
- In-flight stabilization of the nanoparticles;
- Ease of functionalization/coating of open 3D nanostructures;
- Relative ease of integration of various plasma-based processes.

Over the last ten years, our group has developed a number of unit operation systems that, individually, produce nanomaterials or add functionalities to existing structures and once combined, in various ways, enable a better control of the synthesis conditions and the production of wide array of complex heterogeneous nanostructures. In this contribution, two complex structures produced through the integration of various unit operations are highlighted and the resulting unique properties revealed.

2. Method

Fig. 1 presents an overview of the unit operations and some of the nanomaterials and heterogeneous nanostructures produced to date. The support material for all structures is the multiwall carbon nanotube (MWCNT). Dense yet open 3-dimensional MWCNT forests are grown directly on stainless steel meshes by thermal chemical vapour deposition using a protocol developed by Hordy et al [1] which uses C₂H₂ as the feed gas and a growth temperature of 700 °C. The as-produced structure is hydrophobic with a contact angle of ~153° [2]. The produced MWCNTs are typically 15-50 nm in diameter and 3-10 µm in length.
If surface functionalization is needed to render the MWCNTs dispersible in a host medium, a low-pressure RF (13.56 MHz, CW) glow discharge plasma is used to add functional groups [1,2] such as COOH, CO, OH, NH and NH₂ onto the MWCNT thus enabling a control of its surface energy and rendering its surface compatible with various host fluids (for nanofluid applications). We have recently observed that the functional groups covalently bound to the MWCNTs are stable at very high temperatures (up to 450 °C in air [3]), thus opening new application horizons, and in particular, in the area of high-temperature stable nanofluids (see section 3.2.).

Nanoparticles (NPs) are produced and transported to the MWCNTs by three means: i) Thermal evaporation/inert gas condensation for the low-vaporization point metals such as Zn and Al [4]; ii) pulsed cathodic arc erosion/inert gas condensation works with all metals [5]; and iii) pulsed laser ablation (PLA) [6]. PLA offers the additional advantage of producing NPs with non-electrically conducting target material. NP synthesis approaches ii) and iii) are very similar in nature, but PLA allows a much tighter control of the nanoparticle mean size and size distribution while avoiding the synthesis of macroparticles, an undesirable by-product of synthesis technique ii). It is believed that NPs are formed at the interface defined by the expanding plasma plume and the background gas that slows down the expansion. The NPs produced by techniques ii) and iii) appear to be transported ballistically and/or to acquire a negative surface charge since they disperse quite uniformly on the collection surfaces. Agglomerated NPs are observed only for large deposition times, as stacking becomes significant. The thermal evaporation-based process i) requires an additional in-flight NP charging device, otherwise the NPs heavily agglomerate in-flight. A mild inert glow discharge is an ideal tool for that [4].

Upon exposure to the NPs stream, the MWCNTs are initially decorated and ultimately coated with a granular coating at long deposition times. MWCNT decoration (or more technically-speaking, sparse coating) adds localized, NP chemistry-dependent sites onto the surface thus providing additional flexibility in the MWCNT compatibilization with external hosts.

Ultrasonication of the MWCNT-covered stainless steel mesh in the liquid host medium breaks them off from the growth surface - i.e. the MWCNTs are not uprooted [1] - and if correctly plasma functionalized beforehand, the MWCNTs...
will uniformly disperse in the liquid, thus forming a nanofluid, and stay stable over extended periods of time.

3. Results & Discussion

3.1. Ni NP-Decorated MWCNTs as Electrocatalyst for H₂ Production

Hydrogen is considered a clean energy carrier and the efforts to develop cost-effective and safe production technologies have grown significantly over recent years. Alkaline electrolysis produces pure H₂ but it is costly due to the use of large electrolysis systems and high electrical energy demand due to the poor electrocatalytic properties of currently used cathodes [7]. These costs can be reduced by increasing the cathode's electrocatalytic activity, and one of the ways is by increasing the electrochemically-active specific surface area of the electrocatalyst. One could achieve this goal by stacking electrochemically-active NPs onto a surface thus forming a loose granular coating. This is doable using pulsed cathodic arc erosion/condensation and pulsed laser ablation, though the structural integrity and adhesion of the coating on to the surface would become the main issue. Rather, we deposited Ni nanoparticles onto MWCNTs forming an open 3D network on a stainless steel substrate.

Fig. 2 shows SEM and TEM images of a Ni NP-decorated MWCNT electrocatalyst obtained after 20 min of PLA. Ni NPs with an average diameter 5 nm and corresponding high specific surface area of 615 m²/g were consistently obtained.

A comparative study of the electrocatalytic activity of several Ni NP-MWCNT electrocatalysts relative to a 2D Ni plate at a fixed hydrogen reduction potential of -1.3 V (which represents an overpotential of -0.24 V) has been performed. Fig. 3 reveals a drastic increase in electrocatalytic activity as the NP production-deposition time is increased, reaching a 2 orders of magnitude higher electrocatalytic activity than the bulk Ni plate. The enhancement effect tends to a plateau as the deposition time increases most likely due to the loss of surface area associated with Ni NP stacking and formation of large agglomerates. Further tests are required to investigate the stability of such coating over time. Similar coatings were exposed to intense sonication and no noticeable sign of NP detachment from the MWCNT was observed. Rather, the MWCNTs break off the growth substrate. We will see in the next section that this is a key enabler for the synthesis of nanofluids with tunable properties.

3.2. Au NP-Decorated MWCNT Nanofluids as Volumetric Absorber

Nanofluids are engineered colloidal suspensions designed for specific purposes [8]. They have received a great deal of attention since the early 1990's mostly because of the hype they generated in the heat transfer community and unfortunately, the promises they couldn't meet. Recent work in our group helped resolve a number of stability issues and permitted to eliminate the need for foreign stabilizing agents (i.e. surfactants) through plasma functionalization of the NPs before dispersion (see MWCNT example in Fig. 1 and [1]). Recent work in the solar energy collector community highlighted a sound and realistic potential application: the direct volumetric absorption of solar energy [8,9]. A great majority of low-cost heat transfer fluids are transparent throughout the UV-vis range, making them very poor solar energy absorber. The addition of a dispersed solid phase drastically enhances the absorptivity of the fluid. Stable aqueous MWCNT nanofluids show a characteristic absorption curve which peaks in the UV and monotonically decreases in the UV and NIR range (See Fig. 4, lowest curve). Decorating the MWCNTs with NPs of various compositions permits to enhance the absorptivity of the nanofluid, as can be seen in Fig. 4. The lowest absorption curve was obtained with a nanofluid made up of Ar/C₆H₆/O₂...
plasma functionalized MWCNTs dispersed in water. The two other curves were obtained with similar nanofluids, but with the MWCNTs decorated with Au NPs produced by PLA (see Fig. 5 (left)). Gold NPs are strong NIR absorbers and thus, add absorptivity in this range. The absorption spectrum can be further tuned by combining various amounts of different NPs. Fig. 5 (right) shows a MWCNT coated with Ag and Ni NPs (absorption spectrum not shown).

![Absorbance spectrum](image)

Fig. 4 UV-vis-NIR absorption spectrum of aqueous Au NP-decorated MWCNT nanofluids. Lower to upper curves: PLA time = 0, 240 and 300 sec.

![STEM images](image)

Fig. 5 STEM image of Au NPs- (left) and Ni and Ag NPs-decorated (right) MWCNTs.

In order to illustrate the high absorbance and high-temperature stability of the produced Au NP-decorated MWCNT aqueous nanofluid, the output power of a solid state laser (808 nm, 2W, CW, 0.4 mm waist) aimed at a polyethylene tube (5 mm ID, 0.8 mm wall) containing the nanofluid was modulated to produce fast temperature ramps and cycles (Note that the temperature of water only would not respond due to its transparency at 808 nm). Fig. 6 reveals an excerpt of the temporal evolution of the nanofluid temperature near the laser absorption volume (~0.64 mm³) and accompanying laser power modulation. Heating ramps shorter than 10 sec are observed. It is particularly important to notice that the laser-exposed nanofluid volume is repetitively heated to temperatures exceeding by more than 25 °C the characteristic temperature above which surfactant-stabilized nanofluids are irreversibly degraded [10]. This result confirms again the superior qualities of the plasma-functionalization approach to achieve MWCNTs (and NPs) stabilization. Our recent results [3] further confirm this high-temperature stability with a number of heat transfer fluids.

![Temporal evolution](image)

Fig. 6 Heating cycles and accompanying laser power modulation (100% corresponds to 2 W).

4. Conclusions

We reported on the successful production of complex heterogeneous nanostructures and nanofluids making use of MWCNTs as the support structure through the development and integration of unit operations. Processing plasmas clearly demonstrate significant advantages over wet chemistry routes. Work is ongoing to expand the range of applicability of the produced structures to advanced catalysts, optically- and chemically-tunable nanofluids for gas absorption/separation/sequestration as well as optical therapeutic applications.

5. References