Multifunctional Hybrid Structures for Energy and Environmental Applications

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Abstract

A large variety of elegant and multifunctional structures seen in nature have hierarchical architectures incorporating dendrites, capillaries and nano-attachments on larger substrates. If similar structures are adopted in synthetic materials, an immediate advantage will be orders of magnitude increase in surface area. This increased surface can be functionalized in a controlled way for a large variety of advanced applications ranging from nano-catalysts, sensors, and charge storage devices to heat exchangers, biomaterials, and nano-composites. This paper touches upon one such family of applications involving nano-metals tethered on these structures. Metals discussed here are palladium and silver. Nano-palladium clusters supported on this type of multi-scale hierarchical porous substrate can lead to unprecedented miniaturization since a very small amount of precious metal can result in a high level of surface activity. Palladium is a powerful catalyst suitable for water or gas purification and for fuel cell electrodes. Potential devices include sensors, water purification systems, fuel cell electrodes and hydrogen storage devices. Silver nanoparticles are useful for antimicrobial properties, and as plasmonic sensors. Fabrication issues of these structures have been successfully addressed, and collaboration with several research groups is currently underway to test device-specific properties In this paper, microstructure and spectroscopic analysis of nano-cluster distribution and possible ways of controlling them will be presented.

Introduction & Background:

This paper focuses on the creation of strongly tethered carbon nanotubes on larger substrates that are subsequently functionalized with metallic nanoparticles. It has been published earlier (1) by this group that it is possible to create hierarchical surfaces consisting of carbon nanotubes attached to substartes of all sizes and shapes, including porous uneven structures. The base substrates selected are microcellular carbon foam (2), and highly oriented Pyrolytic Graphite (HOPG). Foams used here have about 80% porosity, and therefore a high surface to volume ratio which is further increased by several orders of magnitude by grafting carbon nanotubes (CNT). The flat HOPG graphite is suitable for some device-related applications. Moreover it can serve as a model substrate for quantitative investigation of composition, chemistry and growth mechanisms.

There are several reports of growing metal nanoparticles on various surfaces (3-4) including on isolated or free-standing nanotubes. However, this is the first time that these are being grown on hierarchical substrates consisting of nanotubes attached to larger surfaces. The multi-scale surface profile, variations of surface activity and wettability of these morphologies provide unique challenges (5-6), and the process needs to be optimized for different substrate geometries.

Experiment:

Carbon Foam and HOPG samples were obtained from commercial providers. Carbon nanotubes (CNT) were grown on these susbtrtes using a 2-step process: growing a thin coating of amorphous silica nanolayer, followed by chemical vapor deposition (CVD) using the floating catalyst approach (1). A typical morphology is shown in Figure 1 (a).

Palladium nanoparticles were synthesized by liquid phase infiltration of TAPN precursor followed by thermal reduction in the presence of hydrogen. Silver particles were synthesized by reduction of silver nitrate solution by heated DMSO in the presence of a capping agent. The particles size, density and dispersion can be fine tuned by optimizing various process parameters These parameters usually vary with the substrate geometry (3,4) and typically include concentration of precursor solution, reducing temperatures, and activities of reducing and capping agents.

Surface morphology of metallic nanoparticles and hierarchical architectures were observed using JEOL 7401F Field Emission Scanning Electron Microscope (FE-SEM). Energy Dispersive Spectroscopy (EDS) was performed for elemental data analysis. X-ray Photoelectron Spectroscopy (XPS) was performed using Kratos (Axis Ultra) system with mono-chromatized Al *Kα* x-rays to obtain chemical states of the fabricated palladium nanoparticles. Quantitative analysis was carried out to determine particles size and distribution per unit area using Scandium SEM imaging software.

Results and Discussions:

Figure 1(a) shows the microstructure of nanotubes attached on the substrate. Figure 1 (b) shows growth of Pd particles on the nanotubes. Figure 1 (c) shows CNT attached surfaces with silver nanoparticles grown on them.

Density of nanoparticles can be changed with precursor concentrations etc., but control of particle size distributions was important for this study. Figure 2 (a)

and (b) shows particle size distributions of Pd and Ag nanoparticles for various process conditions. It can be seen from this that it is possible to obtain a stringent particle size distribution around 6-8 nm for Pd and 2-4 nm for Ag. Since the catalytic and anti-bacterial activities of these metals are dependent on particle size, this may be an important parameter to control for future applications.

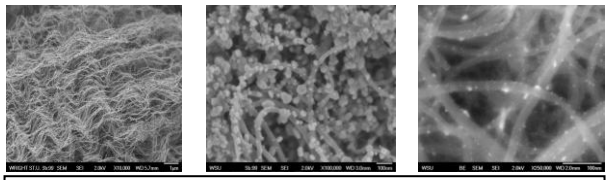

Figure 1: SEM images of (a) carbon nanotube (CNT) (b) Pd-CNT and (Aa-CNT structures.

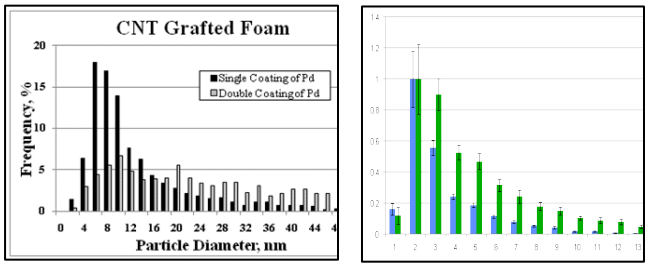

Figure 2: Particle Size distributions of (b) Pd on CNT and (b) Aa on CNT.

Figure 3 shows the XPS peak shape of Pd nanoparticles. Pd 3d peak clearly indicates fully reduced zero-valent Pd. For Ag 3d, XPS is not included here because oxides and nitrides of Ag have peaks that are very close to that of metallic Ag. Therefore XPS data alone would be inconclusive. Relative concentrations of surface elements as seen by XPS and EDAX are used to monitor average compositions of these materials.

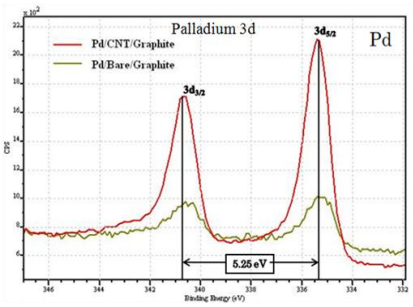

Figure 3: Pd 3d XPS peak from Pd-nanoparticles showing zero-valency reduced state.

The Pd-deposited structure has been tested for removal of CCl_4 from water and seen to be very successful (6). This structure also shows enhanced electrochemical activity in cyclic Voltammetry tests. Those results will be published in details elsewhere. The Ag-deposited structure was found to be toxic to some cells, but its optical plasmonic behavior is yet to be tested.

Both Pd and Ag nano-metallic particles were seen to be strongly attached to the nanotubes which were in turn strongly attached to the substrate. Scratch tests indicate that failure occurs by delamination of graphitic layers inside the substrate, rather than removal of individual CNT or the metallic nanoparticles from CNT. This observation bodes well for future use of this architecture in robust structures and devices.

Conclusions:

In this research, Pd-carbon based structures having multi-scale architecture have been successfully developed. Well-dispersed Pd and Ag nano-particles of various sizes and dispersion have been attached to nanotubes grown on micro-porous carbon foam, as well as graphite. Particle size distribution and surface spectroscopy data for these have been analyzed. Major advantages of attaching nanotubes to hierarchical structures is that very low amount of metal can provide extremely high surface activity for cheaper, smaller, and lighter components

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