Gold Nanoparticles Encapsulated within Graphene Shells and Decorated on Silicon Nanowires

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ABSTRACT

Graphene shells encapsulating gold nanoparticles could provide stability and multifunctionality to such hybrid nanoparticles. Integration of such nanoparticles with nanowires could be vital for their applications in biological/chemical sensors. Herein, we demonstrate a new approach to fabricate silicon nanowires decorated with graphene shells encapsulated gold nanowires. This approach utilized chemical etching method to achieve vertically standing silicon nanowires and then nucleate gold nanoparticles onto these nanowires in a wet-chemical metal-reduction process. These silicon nanowires decorated with gold nanoparticles were further utilized as a substrate to grow graphene shells selectively around gold nanoparticles in a chemical vapor deposition process. The complex nanowire-based heterostructures were characterized using electron microscopy and Raman spectroscopy method. Such unique nanowire and nanoparticle combination are highly warranted for developing advanced devices and sensors.

Keywords: graphene, gold nanoparticles, silicon nanowires, microscopy, Raman spectroscopy

1 INTRODUCTION

Noble metal nanoparticles are of interest due to their size-dependent chemical and optical properties [1,2]. In particular, gold nanoparticles due to their plasmonic properties [3] can enhance Raman signals of the absorbed molecules and render them useful for their applications in sensors [4]. However, nanoparticles have tendency to aggregate in concentrated ionic media and/or at high temperature [5,6], which can adversely affect their properties [7,8]. Passivating surface of gold nanoparticles with a shell can overcome the above challenges [9-11]. In this regard, graphitic or carbon shell encapsulating gold nanoparticles is a promising configuration [10,12]. Further decoration of such hybrid nanoparticles onto one-dimensional nanowires can lead to highly multifunctional architecture useful for selective and well-dispersed device geometries [13-17]. Herein, we demonstrate the fabrication of silicon nanowires coated with graphene shells encapsulated gold nanoparticles.

2 EXPERIMENTAL

Cleaned silicon wafer (<100> n-type with p-doping (IWS inc., Colfax, CA) was immersed in 10 mL etchant solution (0.02 M $AgNO_3$, 9.8 M HF, and 0.4 M H_2O_2 at 0 ^oC for 15 min [18]. The etched silicon wafer was cleaned by immersing in HNO_3 solution (10 mL, 67%). The wafer was ultrasonicated for 1 hour to remove the etched nanowires into 5 mL ethanol solution. The ethanolic solution of silicon nanowires was mixed with 100 µL $HAuCl_4$ (5×10^{-3} M) and 10 µL $NaBH_4$ (0.12 M). After the reaction, silicon nanowires coated with gold nanoparticles were cleaned. For the growth of graphene shells, with the fabricated nanowire heterostructures (silicon nanowires coated with gold nanoparticles) were dispersed on a substrate and dried in air. The heterostructures were plasma oxidized for 15 min [10,12]. Graphene shells growth was conducted in a chemical vapor deposition (CVD) process with H_2 balanced with Ar, and xylenes for 15 min. Finally, the reactor was cooled down in Ar flow. Samples were characterized using SEM, TEM, and Raman spectroscopy.

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3 RESULTS AND DISCUSSION

We report a new methodology for the growth of graphene shells encapsulated gold nanoparticles decorated on silicon nanowires. Figure 1 shows the silicon wafer etched with 9.8 M HF for 15 min and the resulting vertical arrays of silicon nanowires. Vertically standing nanowires were ~14.05 ± 1.08 µm long with diameter of ~100 ± 43 nm.

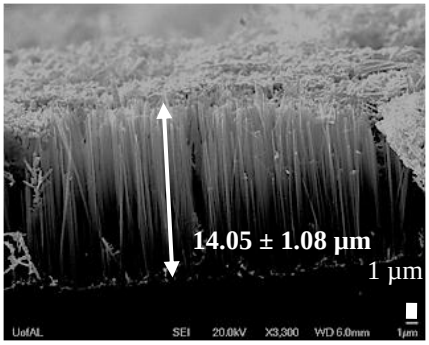

Figure 1. SEM image of vertically-standing silicon nanowires fabricated using the chemical etching approach.

Figures 2A-D shows gold nanoparticles with diameters of ~9.9±2.8 nm decorating silicon nanowires. High-resolution TEM image and FFT image showed that crystalline of silicon nanowires is preserved. HAADF image is shown in Figure 2D. Elemental contrast showed bright gold nanoparticles decorating silicon nanowires. Figures 3A-D shows the heterostructures after graphene shells growth in a CVD process. Due to the high temperature CVD process, diameter of nanoparticles increased to ~15.6±12.2 nm. This could be attributed to surface migration and Ostwald ripening effect. All gold nanoparticles were covered with a thin layer of graphitic layers (Figures 3E-F) with lattice spacing of ~0.37 nm, which consistently matches c-axis spacing of graphite [10]. Raman spectrum of the silicon nanowires decorated with graphene shells encapsulated gold nanoparticles confirmed the presence of graphene due to the presence of G band at ~1583 cm^{-1} and D band at ~1309 cm^{-1}[19]. A peak at ~520 cm^{-1} corresponds to silicon.

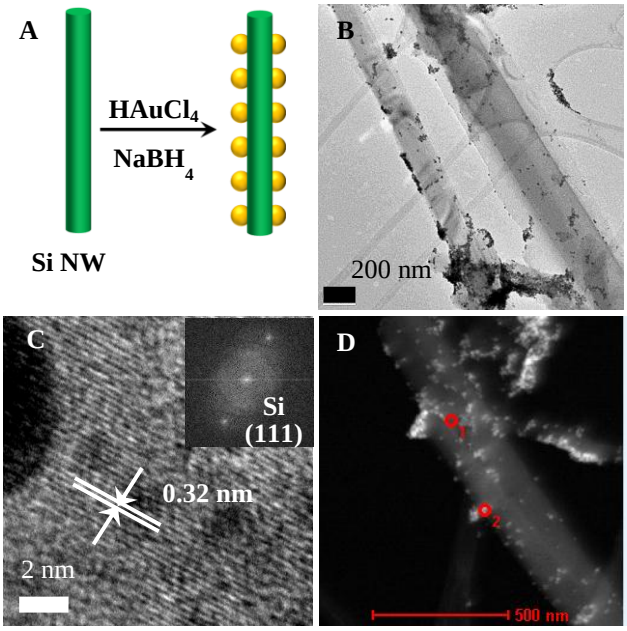

Figure 2. (A) Schematic showing nucleation of Au nanoparticles on silicon nanowires. (B and C) TEM images and (D) HAADF image of silicon nanowires decorated with gold nanoparticles. Inset in (C) shows FFT image.

4 CONCLUSION

Heterostructures comprised of graphene shells encapsulated gold nanoparticles decorated onto silicon nanowires were fabricated. The approach combined chemical etching with wet-chemical synthesis and CVD growth process to result in complex nanowire architectures as never derived before. Graphene shells were selectively grown around gold nanoparticles. Size of gold nanoparticles increased from ~9.9 nm to ~15.6 nm due to surface migration and Ostwald ripening at high temperature. Both TEM and Raman spectrum confirmed the formation of graphene shells on gold nanoparticles. This type of heterostructures could be useful for construction of nanowire-based sensor.

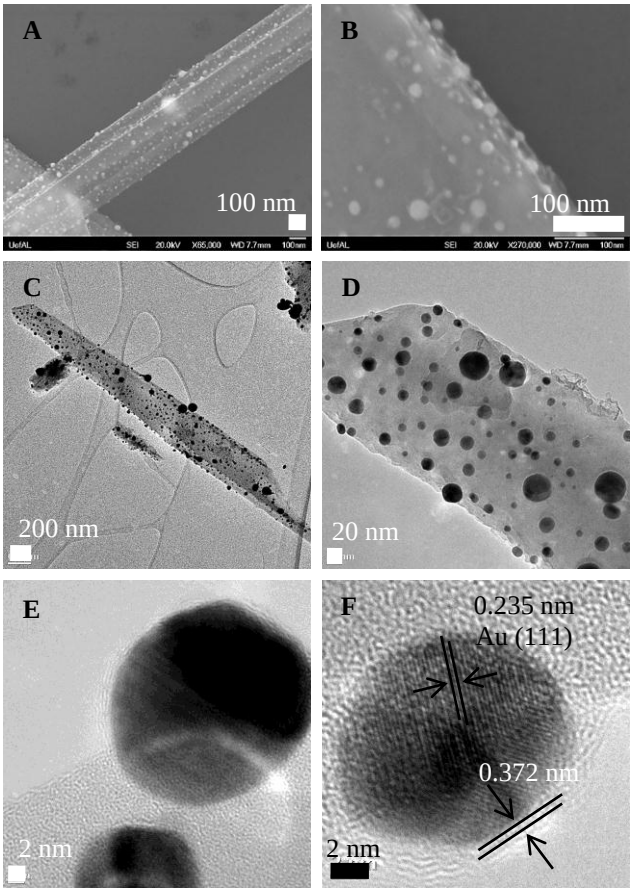

Figure 3. (A and B) SEM and (C-F) TEM images of silicon nanowire decorated graphene shells encapsulated gold nanoparticles.

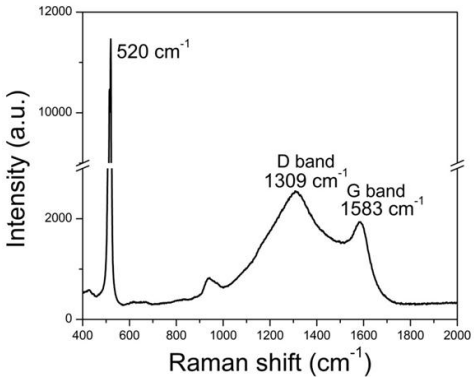

Figure 4. Raman spectrum of silicon nanowire-gold nanoparticles heterostructures coated with graphene.

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