SELF-ASSEMBLED NANOWIRES ON GRAPHENE IN MICROFLUIDIC CHANNELS
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ABSTRACT
This work presents a nanoscale assembly process to synthesize nanowires that are aligned to molecular directions of graphene. The nanowires are synthesized from simple incubation in an aqueous solution, thus this process can be easily performed inside of microfluidic channels. In the experimental study, we analyze the nanoscale geometrical characteristics, material compositions, and reduction phenomenon of the synthesized nanowires. We envision that it can be an important building-block for bottom-up nanofabrications, even in microfluidic environments.

KEYWORDS: nanowire, graphene, self-assembly, epitaxial alignment

INTRODUCTION
Graphene has high anisotropy in its electrical and physical properties [1-4], thus aligning nanostructures to its crystal directions is important to realize graphene-based nanodevices. Previously, various nanostructures were synthesized on graphene derivatives (graphene, graphene oxide, and/or reduced graphene oxide) using liquid-phase and vapor-phase techniques. (reviewed in [5]) However, it has been challenging to fabricate nanostructures aligned to the graphene lattice directions. With the liquid-phase synthesis techniques, all of inorganic materials formed only randomly-distributed nanostructures on graphene [5] and a few organic materials generated epitaxially-aligned nanopatterns only on thick graphite [6,7]. The vapor-phase synthesis techniques could align edges of deposited nanostructures to the graphene lattice directions [8-10], but it’s still far from the realization of nanodevice fabrications. Thus, this work presents a liquid-based synthesis method that can align inorganic nanowires to the crystal directions of graphene. In addition, the synthesis process can be easily applied to microfluidic environments (Fig.1) since the process is based on simple incubation of an aqueous solution.

The key part of the nanowire synthesis process is to incubate graphene and gold (source material for nanowires) in the aqueous reaction solution (118mM ammonium persulfate, \((\text{NH}_4)_2\text{SO}_4\)) for 10-17h. This incubation grows nanowires on graphene surfaces along the molecular directions of graphene. Figure 2 shows detailed processes in this study. Single-layered graphene synthesized by CVD is transferred using PMMA to two kinds of substrates – Si x/Si substrates and TEM grids. The first prototypes – graphene covered Si x/Si substrates – can form microchannels using a PDMS cover, and the reaction solution in the microchannel generates the nanowires on graphene. The Si x/Si substrates have a 100nm-thick Si x window for the TEM analysis. In the second prototypes – graphene covered TEM grids, the nanowires are synthesized from the reaction solution in petri-dishes. The second prototypes include free-standing membranes of single-layered graphene for further nanoscale analyses.

Figure 1: Perspective view to show the concept of the present work. Nanowires are synthesized on the graphene coated surfaces of microchannel walls. The synthesized nanowires are aligned to the molecular directions of graphene.

Figure 2: Graphene transfer and nanowire synthesis processes.
RESULTS AND DISCUSSION

First, the alignment of the synthesized nanowires and graphene is experimentally verified using TEM. Figure 3A shows that the synthesized nanowires make equilateral triangular patterns since they are mainly aligned to one of three directions on graphene. The inset in Fig.3A shows the SAED (selected area electron diffraction) pattern of the bottom graphene, which indicates the molecular directions of graphene. The nanowire image and the SAED pattern clearly show that the nanowires are aligned to (1-210) directions of graphene, as illustrated in Fig.3B. The histogram of nanowire directions (Fig.3C) verifies this alignment quantitatively. In addition to the outer nanowire directions, inner molecular structures of the nanowires are also aligned: Figure 4 indicates that lattice lines in every nanowire have the same directions (perpendicular to nanowire lengths) and have the uniform spacing of ~5Å. We also perform the AFM analysis to measure nanowire geometries. The typical nanowires have the length of ~100nm, the width of ~10nm, and the thickness of ~3nm, which means the nanowires actually form ‘nanoribbon’ shapes.

In order to analyze nanowire materials, the EDX (Energy-dispersive X-ray spectroscopy) analysis is performed as shown in Fig.5. The peaks in Fig.5 indicate that the nanowires may contain Au, O, and C and don’t contain Cu, S, or N. Al and Si are impurities commonly shown in EDX analysis. From this EDX results and chemicals used in the synthesis reaction, elements that may form the nanowires are Au, O, C, and H. Since ammonium persulfate, (NH₄)₂SO₄, is a strong oxidizer, we may be able to expect that the nanowires are made out of gold oxide or one of hydrated forms of gold oxide. Further analysis should be performed for the detailed analysis of materials.

We additionally characterize the reduction phenomenon of the nanowires inside of TEM. One of important aspects of the nanowires is that we can generate epitaxially aligned Au nanoparticles on graphene from the nanowires. The irradiation of electron beams in TEM can cause a reduction reaction of the nanowires to form Au nanoparticle chains as shown in Figure 6.
CONCLUSION
This work presents the self-assembly process of aligned nanowires on graphene. The nanowires are synthesized on graphene using the aqueous reaction solution, and the synthesized nanowires are aligned to molecular directions (one of three (1-210) directions) of graphene. We also study nanoscale characteristics and material compositions of the nanowires. Finally, we analyze the reduction phenomenon of the nanowires, which can be used to form Au nanoparticle chains aligned to graphene molecular directions. We envision that this method can be useful for bottom-up fabrication of graphene-based nanodevices, even in microfluidic components.

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REFERENCES

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