



Full Length Article

One-pot size-controlled growth of graphene-encapsulated germanium nanocrystals



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ABSTRACT

To realize graphene-encapsulated semiconductor nanocrystals (NCs), an additional graphene coating process, which causes shape destruction and chemical contamination, has so far been inevitable. We report herein one-pot growth of uniform graphene-germanium core-shell nanocrystals (Ge@G NCs) in gram scale by the addition of methane as a carbon source during the thermal pyrolysis of germane. The methane plays a critical role in the growth of the graphene shell, as well as in the determination of the nucleation density and diameter of the NCs, similar to a surfactant in the liquid-phase growth of monodisperse NCs. By adjusting the gas ratio of precursors, a mixture of germane and methane, we can control the size of the Ge@G NCs in the range of ~5–180 nm. The Ge@G NCs were characterized by various microscopic and spectroscopic tools, which indicated that the Ge core is single crystalline, and is completely covered by the graphene shell. We further investigated the merits of the graphene shell, which can enhance the electrical conductivity of nanocrystalline materials.

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1. Introduction

The incorporation of graphene with a semiconductor have been intensively studied over the past decade, because the superb physical and unique chemical properties of graphene generate synergistic effects in various areas [1–5]. For example, new types of transistors and high-speed optical modulators for next generation electronics have been invented by the integration of graphene with typical Si-based complementary metal oxide semiconductor (CMOS) technology [3,4]. These convergence systems are particularly required for nanocrystals (NCs) research to surmount the NCs weaknesses, such as their instability, low current density, and poor reliability [6–11]. Wrapping NCs with graphene can be considered an effective route, because the sp^2 -hybridized carbon network improves their physical and chemical properties. Encapsulation of NCs in a graphene cage is used for anode materials in

the lithium-ion battery, to achieve long-life cycles and high capacity [6,7]. In addition, the graphene shell improved the electrical conductivity, as well as the chemical stability of the NCs for conductive ink [8]. In either case, an additional graphene coating process to realize graphene-covered NCs cannot be avoided. Chemical vapor deposition (CVD) is a widely used method for the direct growth of a graphene shell on the surface of NCs [6–8]. However, after the synthetic process, the shape of the NCs becomes irregular and the size gets poly-disperse, owing to the melting point depression effects at the high graphene growth temperature. Alternatively, solution-based approaches have been reported; however, they also suffer from low crystallinity and chemical contamination issues [12,13]. Therefore, these approaches are not suitable for electronic devices that require high crystallinity, narrow size distribution, and a clean interface. Recently, Wang et al. and Sengar et al. introduced one-step growth methods for metal-graphene core shell NCs using organometallic precursor [14,15]. Although these techniques can satisfy the aforementioned requirements, they are so far only available for metal NCs.

The germanium (Ge) NCs, the group IV semiconductor, have been extensively explored for various types of electronic

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applications, such as transistor, battery, thermoelectric, and photo-voltaics [16–19]. In particular, compared to other semiconductor materials, Ge shows a good catalytic activity for the sp^2 hybridization of carbon atoms [20–22]. In this paper, taking advantage of catalytic behavior of Ge, we demonstrate one-pot growth of graphene-coated uniform Ge NCs (Ge@G NCs) in gram scale via the conventional CVD method. The diameter of the Ge@G NCs is controlled by the precursor ratio of methane and germane. Microscopic and spectroscopic analysis confirmed that the Ge core is single crystalline, and is completely covered by the graphene shell. In addition, based on the experimental results, we describe the growth mechanism of the Ge@G NCs; the role of methane is critical for determination of the density and diameter of the NCs.

2. Experimental

2.1. Characterization

The morphology and size of the Ge@G NCs were measured by JEOL JSM-7401F field emission scanning electron microscopy, operating with an accelerating voltage of 10 kV (FE-SEM). The crystallinity and composition of the NCs were characterized by JEOL JEM-2100F field emission transmission electron microscopy (FE-TEM). For TEM measurement, the Ge@G NCs were suspended in ethanol, dispersed onto a Cu grid with a thin lacey carbon support film, and imaged at an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) measurements were performed on a D8 ADVANCE (Bruker) using $\text{Cu K}\alpha$ radiation ($k = 1.5406 \text{ \AA}$), and a step size of 0.04° . X-ray photo-electron spectroscopy (XPS) analysis was carried out by ESCA2000 spectrometry using monochromatic $\text{Al K}\alpha$ radiation (1468.6 eV). The peak energies were calibrated to the C

1s peak at 284.6 eV. Raman spectroscopy (Renishaw, RM-1000 Invia) with excitation energy of 2.41 eV (514 nm; Ar ion laser) was used to characterize NCs. For both XPS and Raman measurement, the Ge@G NCs were dispersed on thin gold film (50 nm) deposited Si substrates.

2.2. Spark plasma sintering

The Ge@G NCs were compacted into disk-shaped pellets with a diameter of 10 mm and a thickness of 3 mm using a spark plasma sintering (SPS) technique. Table S1 shows the SPS process conditions. The density (ρ_s) of the synthesized sample was calculated as 5.06–5.26 g/cm^3 , which is more than 95% of the theoretical value of Ge.

2.3. Thermoelectric measurement

The electrical conductivity (σ) was measured at 300–860 K using the ULVAC ZEM-3 equipment. The thermal conductivity (κ) was calculated using the equation $\kappa_{\text{tot}} = \rho_s C_p \lambda$. The heat capacity (C_p) value used in the equation is the C_p value (0.31 J/g K) of pure Ge at 300 K as the constant value [23]. Thermal diffusivity (λ) values were measured under vacuum by a laser flash method (TC-9000; ULVAC, Japan).

3. Results and discussion

3.1. Growth and characterization of the Ge@G NCs

Fig. 1(a) shows the schematic of the growth of Ge/graphene core/shell nanocrystals, which was demonstrated by conventional

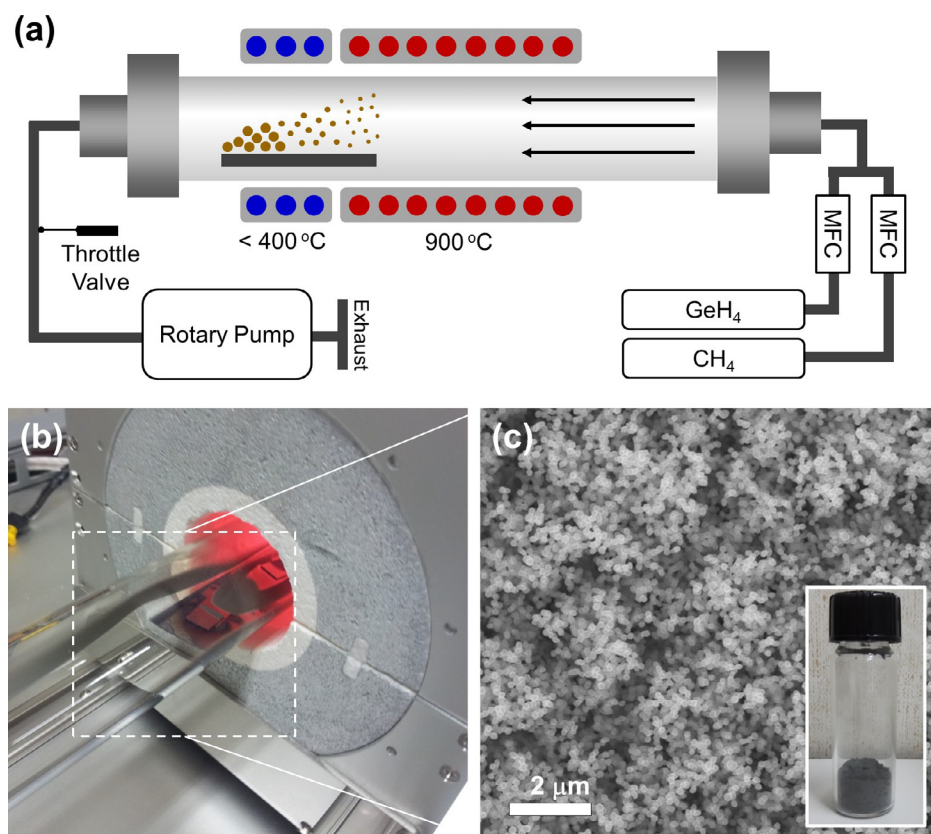


Fig. 1. (a) Schematic of the one-pot growth of the Ge@G NCs. (b) Photograph-, and (c) SEM- image of a large density of the Ge@G NCs on the collecting substrate. The inset in Fig. 1(c) shows a photograph-image of 80 mg of the Ge@G NCs in a vial.

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