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Chemical vapor deposition growth of scalable monolayer polycrystalline graphene films with millimeter-sized domains

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ABSTRACT

The preparation of scalable graphene films has attracted an enormous attention due to its industrial importance for graphene applications. Here we present a synthesis method of high-quality continuous monolayer graphene films with millimeter-sized domains on ordinary Cu substrates using oxygen-assisted chemical vapor deposition. This method demonstrates a significantly improvement to the resultant graphene such as a largely decreased nucleation density from $\sim10^6$ to $\sim10^1$ nuclei/cm^2, an increased average domain size from ~0.004 to ~1.5 mm and a film coverage from 64% to 100%. We attributed the success of this growth to the surface layer formed by bonded oxygen in Cu, which provides a higher priority for catalyzing the nucleation and growth of graphene domains.

1. Introduction

Graphene has been attracting broad research interests because of its many excellent properties [1]. Chemical vapor deposition (CVD) method on Cu foils is considered as the most promising method for graphene synthesis [2], but its yield tends to be polycrystalline because of the domain nucleation with different in-plane orientations [3]. A hot topic for CVD synthesis of graphene is to produce large-scale single crystals, but it always requires either a time-consuming single-seed graphene growth [4,5] or a costly single-crystal Cu (1 1 1) surface [6,7]. Therefore, a scalable and economic way to synthesize polycrystalline graphene with relatively large domains is by far a best choice for graphene industry. The major challenge is to nucleate graphene domains with a suitable density so that their growth rates and coalescence probability are matched. Up to now the largest domain size reported for continuous polycrystalline graphene is still <1 mm [8], mainly due to that the nucleation density of graphene domains cannot be considerably reduced in a traditional CVD process.

Here we present a synthesis method of high-quality continuous monolayer graphene films with millimeter-sized domains on ordinary Cu substrate by low pressure (LP-) oxygen-assisted CVD process. This method demonstrates a significantly improvement to the resultant graphene such as a largely decreased nucleation density from $\sim10^6$ to $\sim10^1$ nuclei/cm^2, an increased average domain size from ~0.004 to ~1.5 mm and a film coverage from 64% to 100%. We attributed the success of this growth to the surface layer formed by bonded oxygen in Cu, which provides a higher priority for catalyzing the nucleation and growth of graphene domains.

2. Experimental

All the graphene films were synthesized in a quartz tube furnace (Thermo Scientific) on Cu foils (25 μm thick, 99.8% purity, Alfa Aesar). The tube was pumped to the base pressure <0.5 Pa and heated to 1060 °C under 300 sccm H_2. 1 sccm O_2 was introduced for 10 min prior to the growth by 300 sccm H_2 and 0.3 sccm CH_4. The pressure was kept at 350 Pa during the growth (Fig. S1). The as-grown graphene was heated in air for 5 min at 180 °C for direct optical visualization [9]. The characterizations were performed by scanning electron microscopy (SEM, S-3700 from Hitachi Co., Ltd.), transmission electron microscope (TEM, JEM2100 from JEOL Co., Ltd.), micro-Raman spectroscopy (LabRAM HR Evolution, Horiba Co., Ltd.), and Hall effect measurement system (Hall 8800 from SWIN Co., Ltd.).

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3. Results and discussion

Fig. 1a shows the optical photograph of a scalable graphene film on Cu. After direct optical visualization [9], no color contrast was observed, suggesting a complete graphene coverage of the Cu surface. With shorter growth time, graphene partially covers the Cu surface (~75.0%), in which most of the domains have achieved a considerable large domain size of >1 mm. The maximum domain size is approximately 2.8 mm, corresponding to an average growth rate of ~16 μm/min. Fig. 1c shows the OM image of a graphene film transferred on SiO_2 (300 nm)/Si substrate. The whole sample exhibits a light-violet color, indicating the high layer continuity and uniformity. Fig. 1d shows the selected-area-electron-diffraction (SAED) pattern of a graphene domain. The sharp diffraction from a set of six spots with a hexagonal symmetry can be observed, and the intensity profile along the yellow line reveals the characteristics of monolayer graphene. Fig. 1e shows the typical Raman spectrum of a graphene film, which only exhibits peaks at

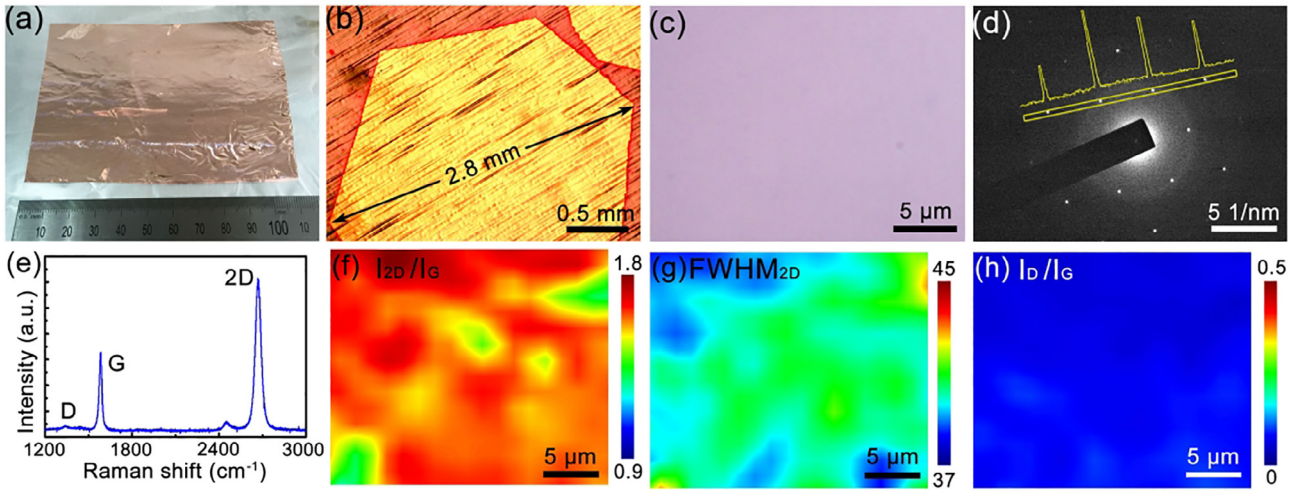

Fig. 1. (a) The optical photograph of a continuous graphene film on Cu. (b) The OM image of a graphene domain on Cu. (c) The OM image of a graphene film transferred on SiO_2/Si substrate. (d) The SAED pattern and intensity profile and (e) typical Raman spectrum of a graphene domain. (f–h) Scanning Raman maps of a continuous graphene film for I_{2D}/I_G, FWHM of the 2D-band, and I_D/I_G.

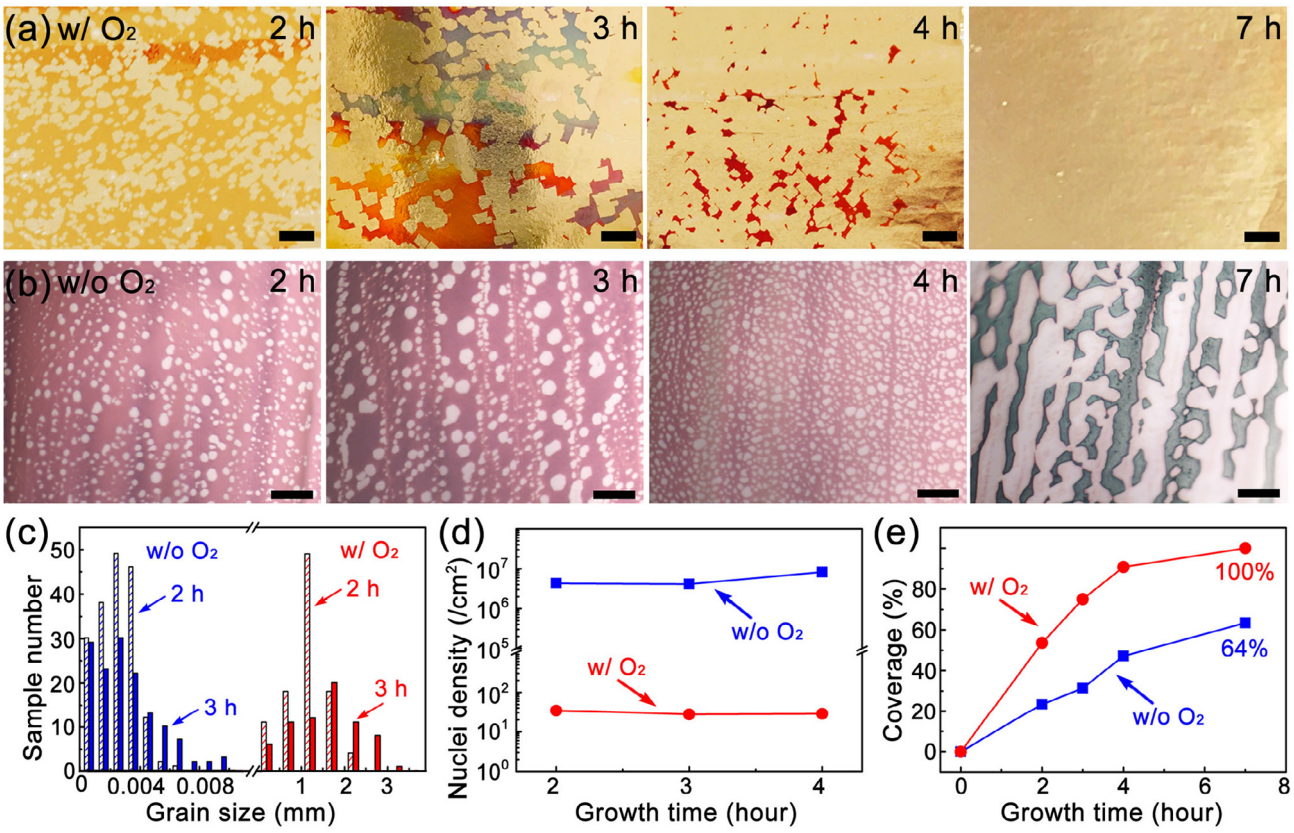

Fig. 2. (a and b) OM images of graphene on Cu with and without surface oxygen, respectively. Scale bars in (a) and (b) are 5 mm and 20 μm, respectively. (c–e) Size, nucleation density and film coverage of graphene grown with and without surface oxygen.