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# Formation of Single-atom-thick Copper Oxide Monolayers

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Two-dimensional (2D) crystals display many intriguing physical and chemical properties that are distinctly different from their bulk parent counterparts. A well-known example is the transition from indirect to direct band gap in monolayer $MoS_2$ [1]. Among all 2D crystals, monolayer oxides are an interesting class of materials because of the coupled degrees of freedom (charge, spin, lattice) that are present in bulk oxides to which quantum confinement is now added. We can, therefore, expect a wide spectrum of electronic and magnetic properties with potential for applications. Many effects have been made to fabricate 2D oxides. However, as most of oxides are non-layered structures, the fabrication of 2D oxides has been limited [2-3]. Most published 2D oxide materials are either two to three atomic layers thick, as the exfoliated perovskites, or strongly bonded with the substrate. It is still elusive whether unsupported oxide monolayers can exist or not without the assistance of pore edge or substrate.

Bulk CuO and $Cu_2O$ have received a great deal of attention because of the similarity of Cu-O bonding to the planar Cu-O structures that give rise to high-temperature superconductivity in Cu-based oxides. In addition, these materials are widely studied because of their importance in the fabrication of supported catalysts, gas sensors, earth abundant solar cells, thin-film transistors, and so on. Recently, a superior visible-light-conversion efficiency has been achieved in a four-atom-thick $Cu_2O$ film photoelectrode [4]. However, single-atom-thick copper oxide layers in isolation have not yet been fabricated.

In this study, we fabricated the single-atom-thick copper oxide monolayers using electron beam irradiation (as shown in Figure 1). Small clusters of copper oxide can form monolayer nanosheets with a square Cu sub-lattice under a 60-keV electron beam irradiation, either spanning graphene pores to form unsupported monolayer oxide membranes or being supported on the graphene surface. Electron-energy-loss spectroscopy results confirmed the exclusive presence of Cu and O element. Both CuO and $Cu_2O$ square monolayer are possible while CuO is more stable than $Cu_2O$ in energy, as demonstrated by quantum mechanical calculations. As the Cu-Cu distance in the fabricated sample with a statistical analysis is more consistent with the calculated Cu-Cu distance with the latest hybrid functional, we deduce that the as-fabricated sample is CuO monolayer. Free-standing CuO and $Cu_2O$ monolayer are stable as proved by our calculations. Their bandgaps are ~ 3 eV. Moreover, CuO monolayer has an indirect bandgap while $Cu_2O$ monolayer has a direct one, which suggested that the electronic and optical properties of monolayer oxidized copper can be tuned by the oxygen content.

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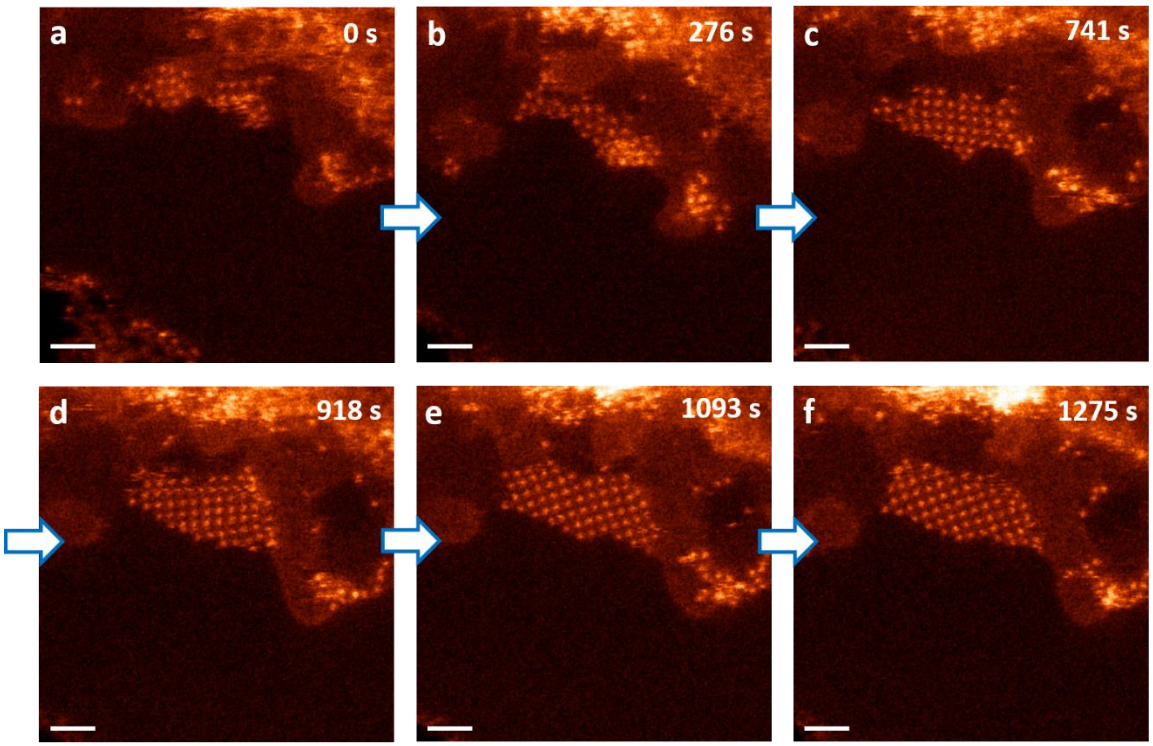


**Figure 1.** Formation process of a monolayer CuO on graphene substrate. (a)-(f) Time series of STEM-ADF images, showing the migration of CuO and the formation of ordered monolayer structure on graphene surface. Scale bars: 1 nm.

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