Electronic Supplementary Information (ESI) for Nanoscale
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Supplementary Information for

"One-atom-thick 2D copper oxide on graphene"

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S1. Stability of pure Cu and carbide clusters

Zhao *et al.*[1] observed 2D metal clusters with a square lattice by TEM, and claimed that the 2D clusters consisted of pure Fe. However, theoretical study[2] pointed out that pure 2D Fe with square lattice is not energetically stable and proposed that the observed 2D cluster was not pure Fe but FeC. In the same way, our calculation suggest that pure Cu cluster with a square lattice is energetically unstable, and it transforms into a hexagonal lattice. Yang *et al.* reported that the hexagonal lattice is the most stable structure for the infinite 2D Ag or Au sheet,[3,4] whereas it should be take into account the edge instability for the 2D metal sheets with finite size. The edges of the hexagonal 2D Cu clusters are strained and chemically active; therefore, they bind with the graphene surface, which result in the distortion of the 2D structure and transformation into a 3D Cu cluster.

We simulated a copper carbide cluster with a similar atomic structure to the 2D copper oxide cluster on graphene discussed in the main text, and found that the 2D copper carbide with a square lattice is energetically unstable. Carbon atoms are initially set in the same plane with the square Cu lattice (Fig. S1a), and during optimization process, carbon atoms tends to move out from the Cu plane, form the dimers or clusters, and bind with graphene (Fig. S1b). Such movements resulted in destroying of the initial 2D lattice. Cu-C bonds have lower polarity than Cu-O bonds due to their small electronegativity difference, therefore, CuC prefers to form tetrahedral structures. Cu-O bonds are more flexible due to the polar covalent nature and can be uniformly arranged in a square lattice. From these calculation, we can exclude CuC from the consideration and conclude that only oxygen can stabilize square 2D Cu lattice.

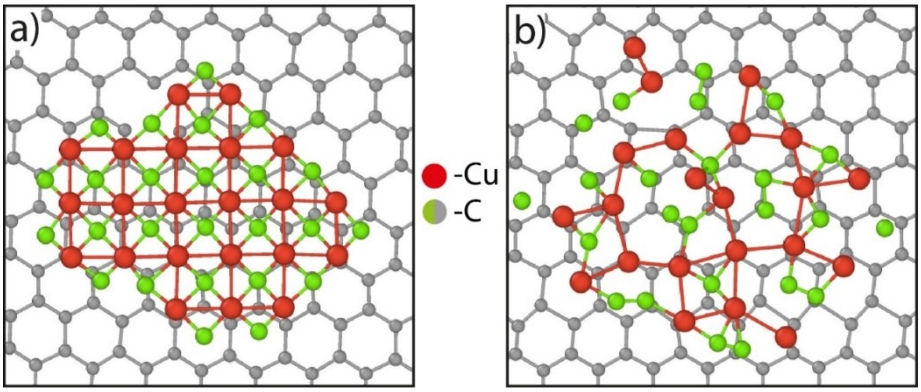

Fig. S1 Carbide cluster on graphene. Atomic structure of the 2D copper carbide cluster (a) before and (b) after the DFT relaxation at 0 K. Copper atoms are depicted by red circles. Carbon atoms in the graphene sheet and in the cluster are depicted by grey and green colours, respectively.

S2. Stability of 2D copper oxide

Fig. S2 shows the energy diagram of the simplified transformation between infinite square 2D CuO (1) and hexagonal 2D Cu with physisorbed O_2 molecules (3), including the transition state of 2D Cu_2O (2). The stability of each structure can be explained by the energy barrier height. During the present STEM experiment, a part of oxygen might be removed from the 2D CuO lattice by the strong electron irradiation, but other oxygen atoms can easily fill in the Cu lattice because there is no energy barrier for the dissociation and binding of the O_2 molecules. On the other hand, desorption of oxygen from 2D Cu_2O lattice requires huge energy penalty of ~6 eV/unit cell (the unit cell consisted of 4 copper and 4 oxygen atoms). Oxygen atoms are hardly removed from the square Cu lattice, therefore, both CuO and Cu_2O are stable.

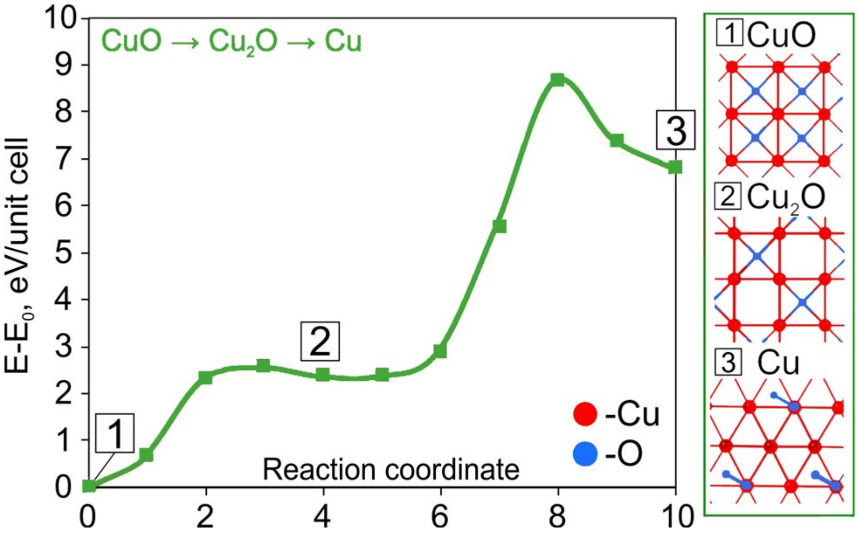

Fig. S2 Energy diagram of simplified transformation between square CuO and hexagonal Cu. We plot the total energy of each structure during the transformation. The energetically minimum structures of infinite 2D CuO, Cu_2O and Cu (with adsorbed oxygen atoms) are presented on the right panel.

S3. Electronic properties of 2D CuO

We investigated the electronic properties of the infinite 2D CuO sheet by the calculation of the band structure (Fig. S3). We used DFT+U approach proposed by Dudarev et al.[5] Firstly we defined the parameters U-J for the correct description of electronic properties, in particular the value of the band gap, of bulk (3D) CuO (Fig.S3a) by taking into account the intra-atomic Coulomb and exchange interactions. The U-J parameter was found to be 8.5 eV (Fig.S3a) to obtain the band gap about 1.5 eV.[6] Figure S3a shows the calculated density of states (DOS) for all applied values of U-J parameter (from 0 to 10). Figure S3b shows the band structure of infinite 2D CuO monolayer. Unlike 3D case, 2D CuO has a wider band gap ~2.7 eV, which formed by copper orbitals in conduction band and oxygen orbitals in the valence band.

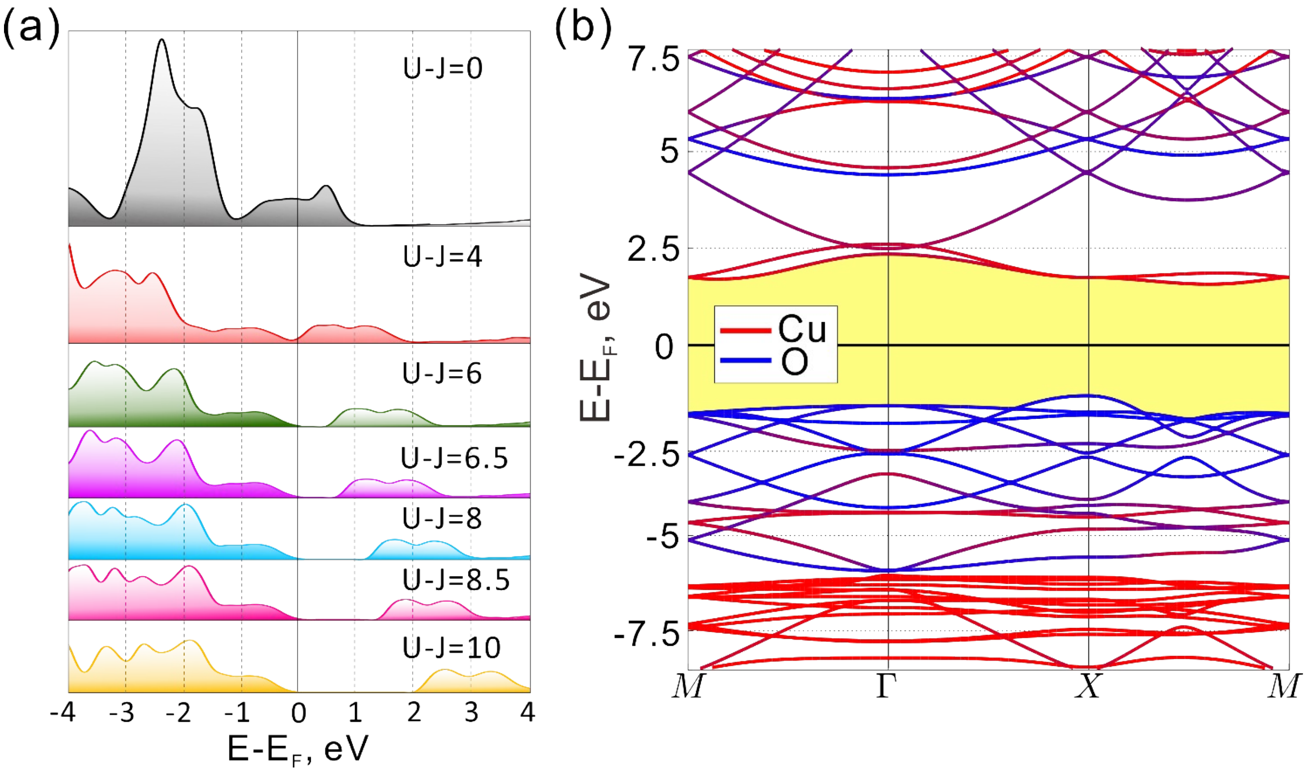

Fig. S3 Electronic properties of CuO nanostructures. (a) Density of states of 3D bulk CuO calculated with various U-J values. The top of valence band (E_v) is taken as zero. (b) Band structure of 2D CuO. The red and blue curves represent energy bands derived from Cu and O orbitals, respectively. The band gap is depicted by a yellow area. The Fermi level energy (E_F) is taken as zero.

S4. Magnetic properties of 2D CuO

To investigate magnetic properties of 2D CuO, we considered paramagnetic (PM), antiferromagnetic (AFM) and ferromagnetic (FM) states. Fig. S4 shows the schematic illustration of each spin configuration of 2D CuO. Since the computational costs increase with the decreasing the symmetry for each structure, only two AFM spin configuration were considered for 2D CuO. For comparison, the various spin configurations of 3D CuO were also considered. The unit cell of both 2D and 3D CuO consisted of 4 Cu and 4 O atoms.

It was found that 2D CuO has an antiferromagnetic ground state, while the 3D CuO displays paramagnetic properties. The energy difference between the PM and AFM state of 3D CuO was about 6.23 meV per unit cell, which is much higher than that in 2D CuO (about -0.14 meV per unit cell). This lower energy difference comes from the spin configuration with alternation of the spin-up and spin-down in the neighbouring rows of the Cu atoms. These data allow us to suppose that spin direction of 2D CuO can be easily controlled by the variation of the external electric and magnetic field.

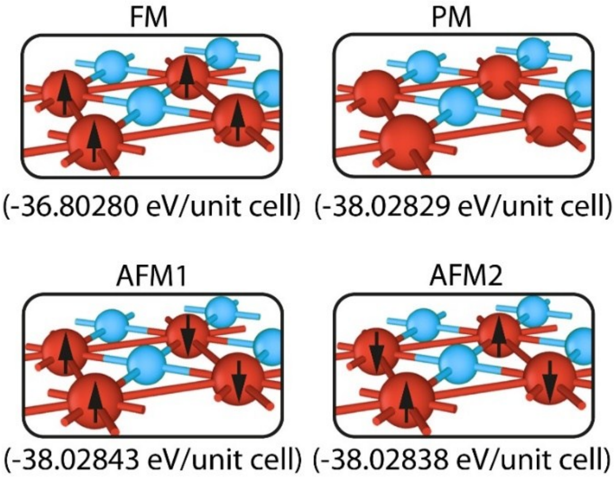

Fig. S4 Schematic illustration of different spin configurations of 2D CuO. Copper and oxygen atoms are depicted by red and blue colours, respectively. The black arrows indicate the spin orientation. The total energy was calculated for each spin configuration and presented in the brackets under the illustrations.

S5. Mechanical stability of 2D CuO against bending

The bending property is as important as in-plane elastic constant to estimate the stability of 2D structures. In periodical boundary conditions, we cannot model the structure with a finite curvature; therefore, CuO nanotubes with various radii (0.25–1.42 nm) were considered to calculate the stability of 2D copper oxide against bending. Such analysis is useful to reveal the out-of-plane instability.[7] For example, Fig. S5a shows the top and side views of the atomic structure of the CuO nanotube with a radius of 0.69 nm. We calculated the total energy of each nanotube using DFT-PBE calculations. Fig. 5b shows the total energy difference between CuO nanotube (E_{NT}) and flat 2D CuO (E_{2D}) as a function of the inverse squared radius of the nanotube. It was found that the CuO nanotube with the radius of ~0.86 nm is the most stable structure, although the energy difference from 2D CuO is only 7.79 meV/CuO. We also performed molecular dynamics simulation, and found that the 2D copper oxide on graphene could maintain the square lattice structure at 300 K, but has a curved structure (Fig. S5c). The curvature radius agrees with the radius of the stable nanotube.

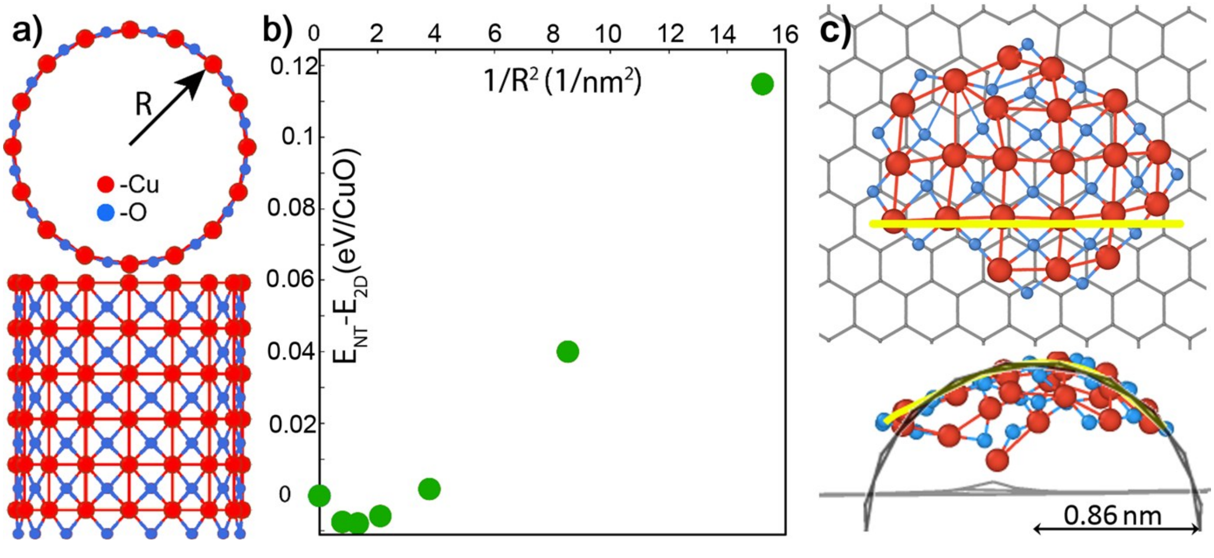

Fig. S5 Calculation of bending strain energy. (a) Atomic structure of CuO nanotube. (b) Total energy difference between the CuO nanotubes and flat 2D CuO plotted as a function of the inverse squared diameter of the nanotube. (c) Top and side views of the atomic structure of 2D copper oxide cluster on graphene after 0.45 ns simulated at 300 K.

Supplementary References

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