Directional growth of quasi-2D Cu$_2$O monocrystals on rGO membranes in aqueous environments

Highlights

A new two-step method for the preparation of Cu$_2$O monocrystals is proposed

The quasi-2D (110)-Cu$_2$O monocrystals are showed for the first time

Assembly stems from pre-nucleation clusters aggregation and cation-π interactions

DFT calculation shows that (110)-Cu$_2$O crystals have well electrical conductivity
Directional growth of quasi-2D Cu$_2$O monocrystals on rGO membranes in aqueous environments

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SUMMARY
The preparation technology of unconventional low-dimensional Cu$_2$O monocrystals, which exhibit specific crystal planes and present significantly unique interfacial and physicochemical properties, is attracting increasing attention and interest. Herein, by integrating a high-temperature oxidation process under vacuum and a pure-water incubation process under ambient conditions, we propose the self-assembled growth and synthesis of quasi-two-dimensional Cu$_2$O monocrystals on reduced graphene oxide (rGO) membranes. The prepared Cu$_2$O crystals have a single (110) crystal plane, regular rectangular morphology, and potentially well conductivity. Experimental and theoretical results suggest that this assembly is attributed to the pre-nucleation clusters aggregation and directional attachment of Cu and O on the rGO membranes in aqueous environment and cation-π interactions between the (110) crystal plane of Cu$_2$O and rGO surface. Our findings offer a potential avenue for the discovery and design of advanced low-dimensional single-crystal materials with specific interfacial properties in a pure aqueous environment.

INTRODUCTION
The precise synthesis and processing of nanostructured metal oxides, represented by Cu$_2$O, play a key role in myriad fields such as electronics, energy, sensors, catalysts, quantum information, and bio-medicine.1–8 As the earliest known environmentally friendly p-type semiconductor material,9–11 Cu$_2$O has been one of the most intensively studied metal oxide crystals in the past decades.12,13 Besides the advantages of being cheap and non-toxic, Cu$_2$O crystals with specific structures have aroused great research interest due to their physicochemical properties for enabling various functions such as sensing and catalysis,14–16 which strongly stimulates the rapid development of Cu$_2$O crystals with tailored structures.17–19 However, important issues still remain, such as current studies on Cu$_2$O crystals are mainly focusing on 3D bulk structures, while related experimental researches on quasi-two-dimensional (quasi-2D) single-crystal systems20–23 with a single crystal plane and large specific surface area have not been reported, such as the low-dimensional Cu$_2$O monocrystals exhibiting conventionally unstable (110) plane,24,25 although a series of recent studies have shown that low-dimensional crystals that break the 3D symmetry always exhibit specific physicochemical properties different from the bulk structure.26–30 The (110) crystal plane of Cu$_2$O has been reported to have specific properties such as electrical conductivity,31,32 ferromagnetism,33 better photocatalysis,34–36 better sensing,37 and excellent electrochemical energy storage properties and carrier mobility,38 and the quasi-2D (110)-Cu$_2$O monocrystals can significantly increase the unit volume (110) area of Cu$_2$O while achieving single crystallinity, which will facilitate the enhancement of any specific physicochemical properties and the formation of unique properties that can be anisotropically enhanced by the (110) plane of Cu$_2$O. Therefore, the study of quasi-2D (110)-Cu$_2$O monocrystals will greatly promote the progress of Cu$_2$O crystals, enrich the research field of Cu$_2$O crystals, and facilitate the discovery of unusual Cu$_2$O conformations with special properties.

The control of low-dimensional nanostructure morphology (both size and shape) is important in materials chemistry because it can modulate the intrinsic physicochemical properties, which has led to an increasing demand for the design and synthesis of low-dimensional nanostructures with precise morphological characteristics,35 well-tailored surface properties, and functional attributes.36 And as a common phenomenon in synthetic, biological, and geochemical systems,36–40 the diffusive migration, pre-nucleation clusters...
aggregation, and directional attachment growth of ions and crystals in aqueous environments are of great importance in nanoscience and materials science.41,42 The aqueous environment not only affects the surface properties of nanostructured materials43–46 but also can modify their behavior, such as mobility in reactions, chemical activity, and structural morphology,47–51 which undoubtedly creates opportunities for the synthesis of nanomaterials with unusual crystallographic surface morphology and specific properties. Moreover, the self-assembled growth and regular alignment of advanced nanomaterials on graphite substrates, based on lattice matching and epitaxial growth, effectively facilitated the discovery of specific structural phases and the development of nanocomposites and their functional improvement.52–55 Combining the effects of aqueous environments and graphite substrates for modulating the structure and physicochemical properties of substances, promises progress in the design and synthesis of nanomaterials for various applications, creating low-dimensional materials with enhanced or unique properties while retaining the dimensional properties of nanoscale building blocks.56

Herein, by innovatively integrating a high-temperature oxidation process under vacuum and a pure-water incubation process under ambient conditions, and in situ observation with cryo-electron microscopy (cryo-EM),57–59 for the first time we show that Cu2O can grow directly on the rGO membranes, align themselves along the (110) crystal plane of Cu2O, eventually form widely distributed quasi-2D Cu2O monocrystals with a single flat (110) crystal plane (referred to as “(110)-Cu2O” hereafter), which exhibits a non-classical nucleation behavior60 that distinguishes them from ordinary Cu2O crystallizing with (100) crystallographic planes.61 The (110)-Cu2O monocrystals are synthesized by a two-step method, i.e., a high-temperature oxidation process under vacuum followed by a pure-water incubation process under ambient conditions, indicating that this metal oxide can spontaneously bind to the rGO surface.52 Correlated atomic-resolution observation and density functional theory (DFT) calculations suggest that this assembly originates from the pre-nucleation clusters aggregation62–65 and directional attachment growth66,67 of Cu and O on the rGO membranes in aqueous environment and the lattice matching and cation-π interaction68–70 between the (110) crystal plane of Cu2O and rGO surface. In addition, the potential electrical properties of these quasi-2D (110)-Cu2O monocrystals have also been theoretically analyzed.

RESULTS AND DISCUSSION

The (110)-Cu2O monocrystals were synthesized by simultaneously incubating Cu-grids and rGO membranes loaded on them (Figure S1) in ultrapure water for over 12 h under ambient conditions (25°C, 1 atm) (Figure 1A). The rGO membranes were obtained by vacuum reduction of GO membranes loaded
on Cu-grids at 180°C for 3 h, accompanied by partial oxidation of copper to cuprous ion.53 And the GO membranes loaded on Cu-grids were simply prepared from a GO suspension via the drop casting method (details in Method Details section).52

To study the formation process of Cu₂O crystals, conventional TEM observations were performed on the samples, which were prepared at different incubation time following by a drying process in a vacuum oven at 70°C for 2 h (Figure S2). As seen in the TEM images, after incubating the samples in ultrapure water for 1 h, some shadows representing denser matter were formed on rGO membranes due to the enrichment of Cu and O elements; corresponding FFT image shows that only diffraction pattern of rGO is in the shadow, indicating that other crystalline state, composed of Cu and O elements, has not yet been formed (Figure S2A). However, with the prolonged incubation time (12 h), a crystalline phase, with an atomic ratio of 1.93:1 (~2:1) (Figures S2B and 1B), appeared on the rGO membranes by self-assembled growth of Cu and O elements that enriched on the rGO surface (Figure S2A). These experimental results revealed the pre-nucleation clusters aggregation and directional attachment of Cu and O on the rGO membranes in aqueous environment, which eventually led to the formation of Cu₂O crystals. To avoid the effect of relaxation processes such as drying during conventional TEM sample preparation on crystal formation and to improve the resistance of the samples to electron irradiation, samples for cryo-EM observation were also prepared by plunge-freezing method57,71,72 without the drying process in vacuum oven. The atomic-resolution image (Figure 1B) and corresponding FFT image (Figure 1B) obtained by cryo-EM show that the crystal structure of this phase is consistent with the (110) crystal plane of Cu₂O. We note that due to the relatively small sizes of these formed (110)-Cu₂O monocrystals and the interference of signals from Cu grids and rGO membranes, conventional X-ray diffraction and powder X-ray diffraction experiments could not be performed to analyze the structure of such monocrystals. Therefore, we improved the experimental scheme and performed cryo-electron tomography (cryo-ET) imaging53 of such crystals by tilting the frozen samples to different angles. It is found that no matter if the sample was tilted at 20° (Figures 1C and 1D) or 40° (Figures S3A–S3C), only some diffraction spots of the (110) plane disappeared while no diffraction spots of other crystal planes appeared. These results were consistent with the changes of diffraction spots of single-crystal rGO membranes (Figures S3D–S3F), indicating that the Cu₂O crystals are low-dimensional monocrystals with only (110) plane. In a word, cryo-ET imaging further demonstrates that the crystals formed on rGO membranes are flake-like Cu₂O monocrystals with only a flat (110) plane and a finite number of layers (Video S1). Hereafter, we refer to these experimentally observed Cu₂O monocrystals as quasi-2D (110)-Cu₂O monocrystals in view of the current research on low-dimensional materials (Figure S4).20–23,74

This is an intriguing discovery since the favorable crystal plane for Cu₂O crystals is usually the (100) plane,19 but not the (110) plane. Recent studies have shown that copper oxidation is associated with stepped Cu surfaces: Cu atoms detached from the steps, and then diffused and crossed the terraces, which finally led to the growth of Cu₂O on the plane.75,76 To explore the nucleation and growth mechanism of the quasi-2D (110)-Cu₂O monocrystals formed on rGO membranes, we further investigated the Cu₂O crystals distributed on the same rGO membrane but in different growth states. As illustrated in Figures 2A and 2B, the (110)-Cu₂O crystals in the growing stage exhibited distinct “steps” from the edges (P point in Figure 2A) to the center (Q point in Figure 2A) of the crystal domain due to the increase in crystal thickness. In contrast, the (110)-Cu₂O crystals at another growth stage exhibited uniform thickness with clearly neat grain boundaries (Figure 2C). These results indicate that the crystals grow on the rGO substrate in a layer-by-layer fashion, which resembles the Stranski–Krastanov (S–K) growth mode.55,61,77 Moreover, we also observed a certain degree of lattice matching between the rGO substrate and the (110)-Cu₂O crystals (Figure 2D) on the thin areas of the rGO membranes (diffraction spots rather than rings), which indicates that the substrate has dominating effect on the formation of crystals, suggesting the growth mode that resembles Frank–van der Merwe (F–M) mechanism61 also plays a key role in the nucleation and crystallization of (110)-Cu₂O crystals on the rGO membranes. Overall, we found that this growth mechanism of such (110)-Cu₂O crystals on rGO membranes in aqueous environment is similar to the recent studies on the growth mechanism of epitaxial oxide islands during Cu oxidation.61

Furthermore, we found that nucleation of (110)-Cu₂O monocrystals with different in-plane rotational orientations occurred even at the same site on the rGO membranes (Figures 2E and 2F). With further crystal growth, these crystal domains exhibited obviously competitive relationships during the growth process, leading to significantly different growth thicknesses and areas of the crystals (Figures 2G and 2H, and
Figure S5. Considering that the rGO substrates were obtained by simply dropping slightly diluted GO suspensions onto untreated TEM-carrier Cu-grids, we believe that the “multi-directional coexistence” phenomena of the (110)-Cu₂O crystals arise for the following reason. (i) The rGO membranes as substrates are formed by stacking multiple rGO monolayer structures. Such rGO monolayers have different in-plane rotation angles, resulting in (110)-Cu₂O crystals grown under the effect of different monolayers with different in-plane orientations. (ii) There are inevitably wrinkles and undulations on the rGO membranes prepared by simple drop casting method. These factors result in the formation of (110)-Cu₂O single crystals with different growth rates and in-plane rotation orientations even if Cu₂O crystals nucleate at the same site on the rGO surface.

To further elucidate the effect of rGO substrate on Cu₂O crystallization, we improved the preparation method of the substrate: By pretreating the Cu-grids with glow discharge to greatly enhance the hydrophobicity of the Cu-grids and the surface tension of the GO suspensions on them, and diluting the GO suspensions for drop casting to very dilute concentrations (≤6.25 × 10⁻³ mg/mL), we successfully obtained very flat, uniform multilayer, few-layer, and monolayer rGO membranes loaded on Cu-grids (Figure S6). By selecting the freshly prepared rGO membranes as the substrate for crystal growth and adopting the same ultrapure-water incubation scheme as mentioned above, we finally observed the freshly formed (110)-Cu₂O monocrystals on the rGO membranes. Unlike the previously observed “multi-directional-coexistence” Cu₂O crystals, these freshly prepared (110)-Cu₂O monocrystals have regular rectangular morphology and single in-plane orientation at the same site (Figures 3 and S7). With the reduction of the number of rGO layers, especially on monolayer rGO membranes, (110)-Cu₂O monocrystals show obvious lattice matching with the rGO substrate (Figures 3 and S8). In contrast, the Cu₂O crystals formed on pure Cu-grids without rGO membranes, as control experiments, randomly present irregular morphologies and other crystal planes (such as (100) and (111) crystal surfaces) (Figure S9). These results reveal the key role of rGO substrates for the formation of quasi-2D (110)-Cu₂O monocrystals with sub-micrometer scale and regular rectangular crystal morphology, demonstrating that such improved sample preparation method could improve the quality of crystals grown by self-assembly.

Based on the experimentally observed lattice parameter of the crystals, we tried to build a theoretical model of the crystals for theoretical analysis. By modeling (110)-Cu₂O crystals with different number of
layers (Figure S10), we noted that the diffraction pattern of such crystals observed experimentally was always the same as that of the even-layer (two or four layers) (110)-Cu$_2$O crystal models, which implies that such (110)-Cu$_2$O crystals formed on rGO membranes are likely to follow a layer-by-layer growth mode of simultaneous bilayer growth, as recently reported for NaCl and MoS$_2$ films. Furthermore, based on the experimentally observed lattice matching relationship between (110)-Cu$_2$O monocrystals and rGO membranes, we established a lattice matching model between (110)-Cu$_2$O and rGO. As shown in Figure 3G, the distance between adjacent Cu atoms in the same horizontal direction (4.27 Å) is nearly the same as the triple C–C bond length of rGO (4.26 Å). This should be the main reason for the directional growth on rGO membranes of Cu$_2$O crystals along the (110) crystal plane, rather than the (100) or (111) plane as widely reported. We also analyzed the interaction energies of different crystal planes of Cu$_2$O with rGO. In Figure 4A we can see that, no matter whether the total number of Cu and O atoms is large or small, the (110) crystal plane of Cu$_2$O always interacts more strongly with rGO than the (100) or (111) planes, which further confirms that the nucleation and growth of Cu$_2$O crystals along the (110) plane on rGO is most favorable on energetic grounds. The charge density difference (Figure 4B) shows that the π orbitals of rGO donate electrons to Cu in Cu$_2$O, similar to previous reports that the transition metals–graphene interaction is mainly attributed to electron transfer. Furthermore, to investigate the electronic properties of such quasi-2D (110)-Cu$_2$O monocrystals, we calculated their projected electron band structure and density of states (DOS) based on the crystal structure models with different number of layers. The results showed that both for bilayer (110)-Cu$_2$O crystals combined with rGO and for bilayer (110)-Cu$_2$O crystals alone, these crystals exhibited electrical conductivity distinct from that of bulk Cu$_2$O crystals (Figures 4C and S11). In addition, the four- and six-layer (110)-Cu$_2$O crystals combined with rGO also exhibited well conductivity (Figure S12), suggesting that these quasi-2D (110)-Cu$_2$O monocrystals are likely to have unusual but well conductive properties.

To explore the universality of the formation of the (110)-Cu$_2$O monocrystals on graphene-based materials, we also tried different experimental methods such as using pure graphene instead of rGO as the substrate, preparing conventional Cu$_2$O nanoparticles on the surfaces of rGO membranes, and using ammonium persulphate to oxidize the TEM-carrier metal grids in an aqueous environment (Method Details section, Figure S13). All of them fabricated (110)-Cu$_2$O monocrystals, further elucidating the effect of graphene-related templates on the formation of quasi-2D (110)-Cu$_2$O monocrystals. We note that the high-resolution electron microscope images of (110)-Cu$_2$O monocrystals (Figure 1) and the analysis of their

Figure 3. Formation of (110)-Cu$_2$O monocrystals with regular rectangular morphology and lattice matching with rGO (A–F) Cryo-EM images of Cu$_2$O monocrystals with regular rectangular morphology formed on multilayer (A), few-layer (C), and monolayer (E) rGO membranes, and the corresponding FFT images (B, D, and F), respectively. (G) Theoretical lattice matching model between (110)-Cu$_2$O and rGO established by experimental results. The Cu, O, and C atoms are shown as yellow, green, and brown spheres, respectively. See also Figures S6–S10.
thickness contrast (Figure 2) show that the prepared (110)-Cu2O monocrystals exhibit very limited surface undulations and have homogeneous morphology, indicating that such crystals have relatively good homogeneity. Moreover, we found that the limiting incubation time of the quasi-2D (110)-Cu2O monocrystals was about 3 days, when the thickness of the crystals was about 140 nm (Figure S14). We further measured the macroscopic area of the quasi-2D (110)-Cu2O monocrystals with regular rectangular morphology and 3-day incubation time (Figure S15), and selected the areas of 8 typical Cu2O crystals for statistical analysis. The result shows that the macroscopic area of (110)-Cu2O monocrystals is 0.87 ± 0.07 μm². With further extension of the incubation time, the macroscopic area of the Cu2O crystals continued to exhibit a slight increase (~1.03 μm²), but the (110)-Cu2O crystals started to grow along other favorable crystal plane directions and tended to exhibit a multifaceted three-dimensional morphology (Figure S16). We further explored the stability of the Cu2O monocrystals, TEM imaging, and EDS analysis show that the Cu2O monocrystals, after two weeks of exposure in air, still exhibited a clear (110) crystallographic structure and a stable elemental composition of Cu:O = ~2:1 (Figure S17), indicating that the (110)-Cu2O monocrystals were not observably oxidized and relatively remained stable in air. Considering that DFT calculations have demonstrated that there is electron transfer between the rGO membranes and Cu2O monocrystals (Figure 4B), we believe that the rGO membranes improve the stability of Cu2O monocrystals in air, which is consistent with the recent report that graphene materials can be used as a general platform for single crystal growth.56 Furthermore, the presence of few other impurity phases on the rGO membranes, such as the (100) and (111) crystalline phases of Cu2O, was also observed especially on the dried samples for conventional (non-cryogenic) TEM imaging (Figure S18). We attribute the formation of these impurity phases to the defects present on the rGO membranes and the natural crystallization of Cu and O in the solution during the drying process.

Conclusions

In summary, we unprecedentedly report the directional synthesis of quasi-2D (110)-Cu2O monocrystals at the rGO interface in an aqueous environment by an innovative two-step method. We note that such (110)-Cu2O monocrystals are successfully prepared for the first time. The growth pattern followed by such crystals and the nucleation and stabilization mechanisms under the influence of aqueous environment and rGO substrate, as well as the potential conductive properties possessed by such crystals, are further investigated and discussed. Correlated in situ observation and theoretical calculations show that such quasi-2D...
Cu$_2$O monocrystals are formed under the synergistic effects of pre-nucleation clusters aggregation and directional attachment of Cu and O on rGO membranes in the aqueous environment and lattice matching and cation-$\pi$ interactions between the (110) crystal plane of Cu$_2$O and the rGO surface. They grow under the influence of S–K and F–M growth modes consistent with recent reports$^{61}$ and possess potential conductive properties to distinguish from those of conventional bulk structures. This work demonstrates a unique approach to the growth of metal oxides with specific interfaces and properties by using graphite-based materials in a pure water environment under ambient conditions.

With the rapidly raising tendency that the heterogeneous integration of graphene-based single-crystal materials$^{56}$ can provide great opportunities for advanced device platforms and functional systems, combining the modulating effects of the aqueous environment and rGO substrates on the structure and physicochemical properties of matter promises progress in designing and synthesizing nanomaterials for various applications. The latest research advances$^{81,82}$ have demonstrated that atomically engineered interfaces can break the property limits of existing materials and open a potential avenue for the design and manipulation of functional and device materials with extraordinary physical or chemical properties. The (110)-Cu$_2$O monocrystals we synthesized significantly increases the (110) area per unit volume of Cu$_2$O while achieving single crystallinity. Considering that the (110) crystal plane of Cu$_2$O has specific physicochemical properties such as electrical conductivity, ferromagnetism, stronger photocatalysis, and sensing, and excellent electrochemical energy storage properties,$^{1-8,31-34}$ the remarkable performance of such unusual (110)-Cu$_2$O monocrystals in the fields of physics, energy, catalysis, sensing, and biology, is also worthy of expectation.

Limitations of the study
The focus of this work is to study the directional self-assembly and non-classical nucleation of quasi-2D (110)-Cu$_2$O monocrystals on rGO membranes. Due to the relatively small size (<1 $\mu$m) of the (110)-Cu$_2$O crystals synthesized during the study, strong experimental evidences for the potentially specific physicochemical properties of such unconventional low-dimensional crystals are still lacking, and the preparation of high-quality (homogeneous) large-area quasi-2D (110)-Cu$_2$O monocrystals and their potential applications in different fields such as catalysis and sensing are also being explored.

STAR METHODS
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Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105472.

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins | | |
| Graphene Oxide (GO) suspension | Professor Liang Chen of Ningbo University | Chen et al.1 |
| RGO | This paper | N/A |
| Ultrapure water | Sartorius | Anium 611 |
| (NH4)2S2O8 (99.99%) | Aladdin | CAS: 7727-54-0 |
| NaOH (95%) | Shanghai Macklin Biochemical Co., Ltd | CAS: 1310-73-2 |
| Cu(Ac)2 (99%) | Aladdin | CAS: 142-71-2 |
| Glucose (99%) | Shanghai Macklin Biochemical Co., Ltd | CAS: 50-99-7 |
| Software and algorithms | | |
| VESTA | Momma et al.2 | https://doi.org/10.1107/S0021889811038970 |
| CrystalMaker | CrystalMaker Software Ltd | http://www.crystalmaker.com/crystalmaker/index.html |
| SingleCrystal | CrystalMaker Software Ltd | http://www.crystalmaker.com/singlecrystal/index.html |
| TEM Imaging & Analysis | Thermo Fisher Scientific | Version 4.17 SP1 |
| Digital Micrograph Software | GATAN | https://www.gatan.com/products/tem-analysis/gatan-microscopy-suite-software |
| VASP | Kresse et al.3 | https://www.vasp.at/ |
| Origin Pro | Origin Lab | https://www.originlab.com/ |
| Microsoft Powerpoint 2019 | Microsoft Office | https://www.office.com/ |
| Other | | |
| Quantifoil R1.2/1.3 holey carbon Cu-grids | Quantifoil Micro Tools GmbH | No: 206,947 |
| Quantifoil R2/2 holey carbon Cu-grids | Quantifoil Micro Tools GmbH | No: 203,149 |
| Singe Lyr Graphene Support Film, 300M Cu | TED PELLA, INC. | No: 21,710-5 |
| eaisGlowTM 91000 | TED PELLA, INC. | Model No: 91,000 |
| Test tube | Coming | No: 430,828 |
| Filter papers | Whatman™ | Cat No:1005-090 |
| Vacuum drying oven | Shanghai bluepard instruments Co.,ltd. | Model No: BPZ-6063LC |
| Parafilm | Parafilm® M | Model No: PM-996 |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Prof. Lei Zhang (zhangleio@xjtu.edu.cn).

Materials availability
This study did not generate new unique reagents.

Data and code availability
- All data reported in this paper will be shared by the lead contact upon request.
- This paper does not report original code.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.
EXPERIMENTAL MODEL AND SUBJECT DETAILS

Our study does not use experimental models typical in the life sciences.

METHOD DETAILS

Sample preparation scheme for (110)-Cu₂O

The fabrication of rGO membranes loaded on Cu-grids and oxidation of Cu were performed as follows: The rGO membranes were fabricated by simply dropping 3.0 μL GO suspension on a holey carbon-film coated Cu-grid (Quantifoil R1.2/1.3 or R2/2). The GO suspension of original concentration (5 mg/mL) was prepared via a modified Hummer’s method⁸³–⁸⁵ and diluted 80 times (0.0625 mg/mL), and the Cu-grid has circular and orthogonal arranged holes with hole sizes of ~1.2 μm and center-to-center distances of ~2.5 μm (R1.2/1.3) or hole sizes of ~2.0 μm and center-to-center distances of ~4.0 μm (R2/2). The GO membranes loaded on Cu-grids were heated at 180°C for 3 h under vacuum in a vacuum drying oven to reduce the GO into rGO membranes, accompanied by partial oxidation of Cu to Cu⁺.

The (110)-Cu₂O monocrystals for TEM and EDS analysis were prepared by incubating the rGO membranes and Cu-grids simultaneously in ultrapure water (ρ > 18.25 MΩ·cm) inside a test tube for hours (1 h, 12 h, 24 h, 48 h...) under ambient conditions (25°C, 1 atm), where the test tube was kept in air and the inside of the test tube was isolated from the air with parafilm. The samples were then removed from the ultrapure water, wiped off with filter paper and dried at 70°C for 2 h in vacuum oven. Finally, the samples were stored at room temperature (25°C) under vacuum in the vacuum oven before experimental analysis. The entire transfer and handling process of the samples is performed in air.

To avoid the influence of the sample drying process on the formation of Cu₂O, we also prepared cryo-EM samples. Similarly, the rGO membranes loaded on Cu-grids were immersed in ultrapure water for a long time under ambient conditions (25°C, 1 atm). After that, by using a FEI Vitrobot rapid-plunging device with conditions set at 100% humidity and room temperature (25°C) in the sample preparation cube, the wet membranes blotted with filter paper for 2 s in the sample preparation cube and then flash-frozen by rapidly insert the specimen into liquid ethane (ρ ~ 180°C). The frozen-hydrated specimen was then transferred to liquid nitrogen and placed onto a Gatan 626 cryo-TEM holder while immersed in liquid nitrogen and isolated from the environment by a tightly closed shutter. During insertion into the TEM column, temperatures did not increase above ~170°C.

Improved sample preparation scheme

To obtain flat, undulation-free and uniformly distributed monolayer rGO membranes, we improved the rGO preparation protocol: Before dropping the GO suspension, the Cu-grids were treated with glow discharge (10 mA, 0.38 mBar) for 30 s using a glow discharger (PELCO easiGlowTM 91000) to enhance the hydrophilicity. After diluting the GO suspension with the original concentration (5.0 mg/mL) 400, 800, 1000, and 1500 times with ultrapure water, 3 μL treated GO suspension was immediately dropped onto the Cu-grid pretreated by glow discharge with a pipette. After dried on Cu-grid under ambient conditions (25°C, 1 atm), the sample was transferred to a vacuum drying oven at 180°C for 3 h to reduce to rGO.

Subsequently, using the same pure-water-incubation method, we successfully observed quasi-2D (110)-Cu₂O monocrystals with a regular rectangular morphology on the freshly prepared rGO membranes. We found that the limiting incubation time for such crystals was about 3 days, at which time the crystals had a thickness of about 140 nm (Figure S14) and a macroscopic area of 0.87 ± 0.07 μm² (Figure S15). With further extension of the incubation time, the (110)-Cu₂O crystals started to grow along other favorable crystal plane directions and tended to exhibit a multifaceted three-dimensional morphology (Figure S16). We further observed that (110)-Cu₂O monocrystals are not significantly oxidized and remain relatively stable in air (Figure S17). In addition, we also observed the presence of few other impurity phases on the rGO membranes, such as the (100) and (111) crystalline phases of Cu₂O, especially on the dried samples for conventional (non-cryogenic) TEM imaging (Figure S18).

Other different sample preparation schemes

The preparation of (110)-Cu₂O monocrystals on rGO membranes using conventional methods for preparing Cu₂O nanoparticles⁸⁶–⁸⁸ were performed as follows: Under ambient conditions (25°C, 1 atm), 3 μL of 20%-concentration copper acetate (Cu(Ac)₂) solution was added dropwise to the rGO membranes loaded
on Cu-grids and maintained for 1 h to ensure the adsorption of copper precursors on the rGO surface, during which the concentration of the solution was maintained constant by continuous addition of ultrapure water. Subsequently, 3 μL of 40%-concentration NaOH solution was added dropwise and maintained for 2 min to form Cu(OH)₂. After slightly absorbing the excess solution from the surface with filter paper, the samples were immersed in 20%-concentration glucose solution and the solution cavity was sealed and heated in a vacuum oven at 90°C overnight. The samples were then removed from the glucose solution and the surface was slightly washed with ultrapure water to remove excess glucose. Finally, the samples were dried in a vacuum oven at 70°C for 2 h and set aside. The entire transfer and handling process of the samples is performed in air.

The preparation of (110)-Cu₂O monocrystals on commercial graphene instead of rGO membranes were performed as follows: This sample preparation process is similar to the experimental method in which Cu-grids and the rGO membranes loaded on them were simultaneously incubated in ultrapure water, except that the rGO membranes were replaced with purchased graphene coated on Cu-grids. Specifically, we first oxidize the Cu-grids loaded with commercial graphene in a drying oven for 3 h at 180°C. After the sample temperature dropped to room temperature (25°C), the sample was transferred to ultrapure water and incubated for 24 h. After the incubation was completed, the samples were removed from the ultrapure water and the water residue on the surface was blotted off with filter paper. Then the samples were dried in a vacuum drying oven set at 70°C for 2 h to obtain dried samples for TEM observations. Finally, the samples were stored in the vacuum oven before the experimental observations.

Drawing on the recently reported sample preparation method for the formation of gold cyanide nanowires by oxidation of TEM Au-grids with ammonium persulfate solution, the preparation of (110)-Cu₂O monocrystals was also performed as follows: This sample preparation process is similar to the experimental method in which Cu-grids and the rGO membranes loaded on them were simultaneously incubated in ultrapure water, except that the ultrapure water was replaced with 20%-concentration ammonium persulphate ((NH₄)₂S₂O₈) solution. Specifically, the Cu-grids and the loaded rGO membranes were incubated in the ammonium persulfate solution for 24 h. Afterwards, the samples were removed from the ammonium persulfate solution, removed the solution residue by wiping with filter paper and centrifugal filtration (3000 rpm, 2 min), and then dried in a vacuum drying oven set at 70°C for 2 h to obtain dried samples for TEM observations. Finally, the samples were stored in the vacuum oven before the experimental observations.

**TEM data collection**

Conventional (non-cryogenic) TEM micrographs were acquired at room temperature by FEI F200C TEM operating at 200-kV. High-angle annular dark field scanning TEM (HADDF-STEM) and energy-dispersive X-ray spectroscopy (EDS) were performed at room temperature by a FEI Talos F200X TEM operating at 200-kV.

Cryo-EM micrographs were acquired at −180°C on a FEI CETA 4k x 4k CMOS camera by the same FEI F200C TEM operating at 200-kV and low-electron-dose conditions. Selected-area electron diffraction (SAED) images were taken with a ~350 nm diameter selected-area (SA) aperture. The exposure time was varied between 0.2 and 1 s.

**SEM data collection**

The rGO membranes loaded on Cu-grids and Cu₂O monocrystals were also characterized by Field Emission SEM GeminiSEM 500. The dried Cu₂O monocrystals were prepared by incubating the rGO membranes and Cu-grids simultaneously in ultrapure water for over 3 days and drying at 70°C for 2 hours in vacuum drying oven. And then the samples were quickly transferred to the vacuum chamber of Gemini-SEM 500 for scanning electron microscopy analysis (SEM).

**Theoretical computation methods**

First principles calculations based on the spin-polarized DFT were performed with the Vienna ab initio Simulation Package (VASP) code. In order to investigate the structural properties, the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) was used to treat the exchange-correlation interaction between electrons. A plane-wave basis set with a kinetic-energy cut-off of 520 eV was used to expand
the wave function of valence electrons (2s^22p^2 for C, 3d^{10}4s^1 for Cu and 2s^22p^4 for O). Three-dimensional periodic boundary conditions were applied to simulate the infinite systems. A 15 Å vacuum space between sheets was set to prevent the interaction between two layers. The structural relaxations were performed by computing the Hellmann-Feynman forces within total energy and force convergences of 10^{-5} eV and 5 \times 10^{-3} eV/Å, respectively. Gamma-centered Monkhorst-Pack grid of 9 \times 3 \times 1 and Gamma point were used in the full model (Figure 3G) and Cu_2O clusters with graphene (Figure 4A).

**Interaction energies of Cu_2O with graphene**

The interaction of Cu_2O clusters with graphene was calculated as

\[ E_{\text{int}} = \frac{(E_{\text{Gr} + \text{Cu}_2\text{O}} - E_{\text{Gr}} - E_{\text{Cu}_2\text{O}})}{N} \]

where \( E_{\text{Gr} + \text{Cu}_2\text{O}} \) is the total energy of the adsorbed system, \( E_{\text{Gr}} \) and \( E_{\text{Cu}_2\text{O}} \) is the total energy of the graphene and the Cu_2O cluster, and \( N \) is the total number of Cu and O atoms.

**Bader charge analysis**

Population analysis was performed using the Bader Charge Analysis code developed by Henkelman’s group. Most charge analysis methods such as Mulliken population analysis were based on electron wave functions and thus sensitive to the type and cutoff of basis sets. Bader analysis, on the other hand, makes use of zero flux surfaces and distinguish the ownership of electrons. The charge enclosed within the Bader volume is a good approximation to the total electronic charge of an atom and the analysis was merely dependent on charge density distribution. In this work, charge density distribution was calculated from VASP.

**QUANTIFICATION AND STATISTICAL ANALYSIS**

Experiments were repeated at least three times independently. The TEM images were collected and analyzed by TEM Imaging & Analysis (TIA) software; the thickness-contrast analysis was performed by DigitalMicrograph software; the model building was done by VESTA and CrystalMaker software; the simulation diffraction analysis of the crystal models was done by SingleCrystal software. Figures were produced in Origin from the raw data and combined in PowerPoint software.