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Short Communication

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Production of single-crystal Cu plates by electrodeposition on high-index Cu foils

Xingguang Li¹, Zhihong Zhang^{2*}, Zhibin Zhang¹, Jinzong Kou^{3,4}, Muhong Wu^{3,5,6}, Mengze Zhao¹, Ruixi Qiao¹, Zhiqiang Ding³, Zhiqiang Zhang³, Fang Liu¹, Xiaonan Yang², Dingxin Zou⁷, Xinqiang Wang¹, Peng Gao⁵, Ying Fu³, Enge Wang^{3,5,8*}, Kaihui Liu^{1,3,5*}

¹ State Key Laboratory for Mesoscopic Physics, Frontiers Science Centre for Nano-optoelectronics, School of Physics, Peking University, Beijing 100871, China

² Beijing Advanced Innovation Center for Materials Genome Engineering, Beijing Key Laboratory for Magneto-Photoelectrical Composite and Interface Science, State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China

³ Songshan Lake Materials Laboratory, Dongguan 523808, China

⁴ Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

⁵ International Centre for Quantum Materials, Collaborative Innovation Centre of Quantum Matter, Peking University, Beijing 100871, China

⁶ Interdisciplinary Institute of Light-Element Quantum Materials and Research Centre for Light-Element Advanced Materials, Peking University, Beijing 100871, China

⁷ Shenzhen Institute for Quantum Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China

⁸ School of Physics, Liaoning University, Shenyang 110036, China

* Correspondence: zhzhang@ustb.edu.cn (Z. Zhang); egwang@pku.edu.cn (E. Wang); khliu@pku.edu.cn (K. Liu)

Massive production of single-crystal metals has been a long pursuit in materials science and engineering due to their superior electrical, thermal and mechanical performances compared with polycrystalline ones. Single-crystal metal ingots could be traditionally fabricated by the Czochralski technique, and large-size single-crystal metal foils (with thickness limited to several tens of micrometers) have been recently prepared by the designed thermal annealing of polycrystal

ones [1–4]. However, for the thicker single-crystal metal foils or plates, the economic and efficient preparation has yet been achieved. In principle, epitaxial electrodeposition of metal on single-crystal substrates provides an economic and efficient way to achieve highly ordered metal films [5–9]. However, as the electrodeposition goes on, the number of defects increases and lattice twinning occurs more easily, which leads to the structure transition to polycrystals [5,6]. Consequently, epitaxial electrodeposition on single-crystal substrate was reported to only reach several-micrometer-thick single-crystal films, even the epilayer and the substrate are of the same lattice structure [7–9]. Hence, a new strategy needs to be developed to regulate the electrodeposition process for the preparation of thick single crystals.

In this work, we demonstrated the electrodeposition of single-crystal Cu with thickness up to submillimeter on high-index single-crystal Cu foils. The electrodeposition was carried out with polycrystalline Cu plates as anodes and high-index single-crystal Cu foil ($\sim 25 \mu\text{m}$, obtained by the designed thermal annealing [4]) as cathode (Fig. 1a, see Method in Supplementary materials and Fig. S1 (online) for more details). Fig. 1b shows a $\sim 100 \mu\text{m}$ -thick electrodeposited Cu plate with single-crystal Cu(211) foil as cathode (the thickness of the deposition layer on each side, Δt , is $\sim 38 \mu\text{m}$). We first used X-ray diffraction (XRD) to characterize the crystal orientation of the deposition layer. The XRD 2θ -scan results show that the out-of-plane orientation of the deposition layer is the same as the Cu(211) substrate (Fig. 1c). In the XRD azimuthal off-axis ϕ scan, only one peak corresponding to Cu(200) was observed, indicating the single-crystal structure without in-plane rotation (inset in Fig. 1c). Electron back-scattered diffraction (EBSD) was also carried out and uniform colors of the inverse pole figure maps in the Z and Y directions (IPF Z and IPF Y) demonstrate the deposition layer is indeed a single crystal (Fig. 1d). The atomic resolved high angle annular dark field scanning transmission electron microscopy (STEM) image confirms the lattice structure of the Cu(211) (Fig. 1e). All above results have verified that the deposition layer on Cu(211) is single-crystal.

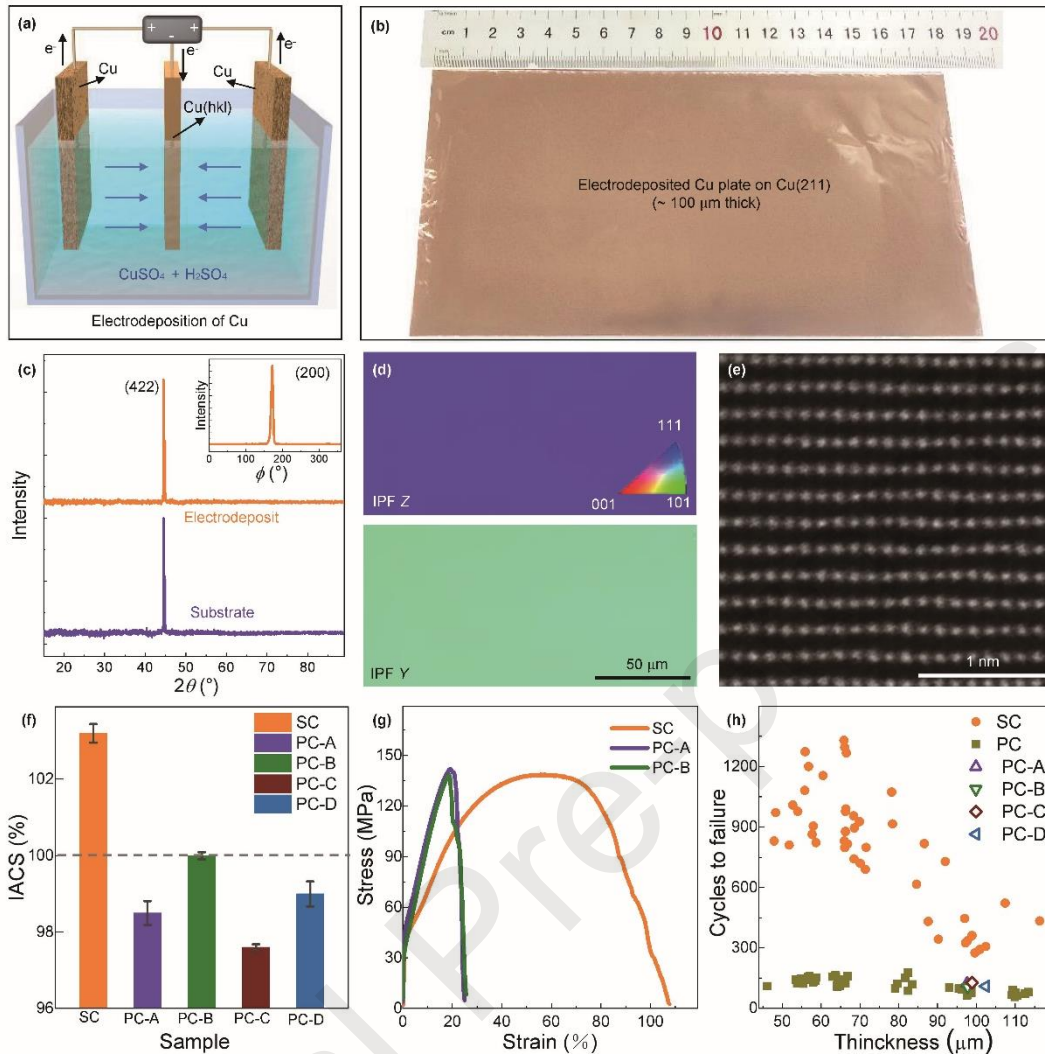


Fig. 1. (Color online) Electrodeposition of single-crystal Cu plates and their structural and properties characterizations. (a) Schematics of electrodeposition on single-crystal Cu foil, where the polycrystalline Cu plates are used as anodes and high-index single-crystal Cu foil as cathode. (b) Photograph of the electrodeposited Cu plate. (c) XRD 2θ scan spectra for the Cu(211) substrate and the electrodeposited Cu plate, respectively. Inset, azimuthal off-axis ϕ scan spectrum for the electrodeposited Cu plate with only one peak corresponding to Cu(200). (d) Representative EBSD IPF maps of the electrodeposited plate in the Z (top, along the thickness direction) and Y (bottom) directions, respectively. (e) Atomically resolved STEM image of the electrodeposited plate. (f) Room temperature electrical conductivity of single-crystal Cu plates and four kinds of commercial electrolytic polycrystalline products. (g) Typical tensile stress-strain curves for the single-crystal Cu plate and two kinds of commercial electrolytic polycrystalline products. The thickness of the all specimens in (f, g) is of $\sim 100 \mu\text{m}$. (h) Fatigue performance for our electrodeposited single-crystal and polycrystalline Cu with different thicknesses, and four kinds of commercial electrolytic polycrystalline Cu products ($\sim 100 \mu\text{m}$ thick).

We also characterized the electrical and mechanical properties of the single-crystal Cu plates

to demonstrate their single-crystal nature and evaluate their quality. As shown in Fig. 1f, our prepared single-crystal samples have the highest electrical conductivity up to 103.2% of international annealed copper standard (IACS) compared with those of the commercial polycrystalline ones (typically 98%~100% IACS). The electrical conductivity enhancement originates from the absence of grain boundaries in single crystals, which reduces the electrons scattering by disordering and surface roughness [10].

We then compared the mechanical properties of the electrodeposited single-crystal Cu to the commercial polycrystalline ones. Before testing, all samples (~100 μm) were subjected to the same thermal annealing process. The microstructures of 4 kinds of polycrystalline Cu after thermal annealing were characterized by EBSD, showing coarse grains with the size of several hundred micrometers and various crystallographic orientations (Fig. S2 online). Tensile tests were first carried out and representative tensile stress-strain curves for different samples are shown in Fig. 1g. The tensile test of the electrodeposited single-crystal sample was conducted along its $\langle 112 \rangle$ direction (the crystallographic direction was determined by EBSD characterization, as shown in Fig. S3 online), and it exhibited excellent ductility that the elongation-to-fracture was as high as 108%, about 4 times of those of commercial ones. This is because in coarse-grain metal polycrystals, the uneven deformation between grains is difficult to coordinate, and cracks may form at the grain boundaries and lead to fracture easily, displaying inferior plasticity compared to the single crystal.

In terms of yield strength and ultimate tensile strength, there is no obvious difference between our prepared single-crystal samples and commercial ones for little grain boundary strengthening in coarse-grains polycrystalline Cu foils [11]. As for elasticity, due to the small specimens and small elastic strain of Cu ($< 5\%$), it is extremely difficult to measure the displacement accurately in the elastic deformation region in the tensile test, leading to large error in calculating Young's modulus. But under the same test conditions, the obtained Young's modulus of single crystal is smaller than that of polycrystals, which can be ascribed to the anisotropy of single crystal [12].

The fatigue performances of our prepared samples were also evaluated (see Methods section in Supplementary materials (online) for more details). As shown in Fig. 1h, the numbers of cycles to failure follow similar trends for both the single-crystal and polycrystalline samples as their thickness increases, where they first climb up and then decline with the reflection point at the thickness of 60–70 μm . Thinner samples have better flexibility, while their fracture strength is also lower. Thus when the thickness of the sample is small enough, their folding endurance performance starts to degrade [13]. Obviously the single-crystal samples have much better fatigue performance than the polycrystalline ones in the whole thickness range. In addition, we tested the fatigue performance of commercial samples (~100 μm) and obtained similar results to our prepared polycrystalline samples.

To illustrate the mechanism of epitaxial electrodeposition of single-crystal Cu, we compare the different deposition behaviors on Cu(111) and Cu(211) in Fig. 2a. The surface of Cu(111) can be considered to have atomic flatness and the epitaxial deposition occurs by the two-dimensional (2D) nucleation and three-dimensional island growth [14]. During the process, the nuclei with parallel and anti-parallel orientations may form due to the small energy difference on (111) plane (Fig. S4 online) [5]. Meantime when the islands meet, they cannot always merge together perfectly,

leading to faults formation, which may further induce the lattice twinning and lead to twin crystal formation (Fig. 2a, upper panel). On the other hand, the deposited Cu atoms could directly diffuse to the atomic step edges on Cu(211) and attach on them and there is no nucleation stage during the electrodeposition on Cu(211) [15]. The interaction between Cu atoms and the step edges are much stronger, under which the Cu atoms could order themselves to duplicate the lattice arrangement of the substrate completely, which is the most energetically favorable. Although under our electrodeposition condition, the deposited Cu also follows the island growth, faults formation is less possible in such step-guided island growth mode (Fig. 2a, lower panel). The distinct island morphologies and growth behaviors on Cu(111) and Cu(211) at early deposition stage shown in scanning electron microscopy (SEM) images (Fig. S5 online) confirm this step-guided island growth and the advantageous effects of Cu(211) surface atomic steps on the epitaxial electrodeposition. Furthermore, SEM images taken when the samples were tilted by 70° show that the deposition layer on Cu(211) has a smoother surface compared to that on Cu(111) (Fig. 2b), which may also benefit from the step-guided deposition. The detailed mechanism needs further theoretical exploration and it should provide a new direction to produce low-profile electrolytic copper foil.

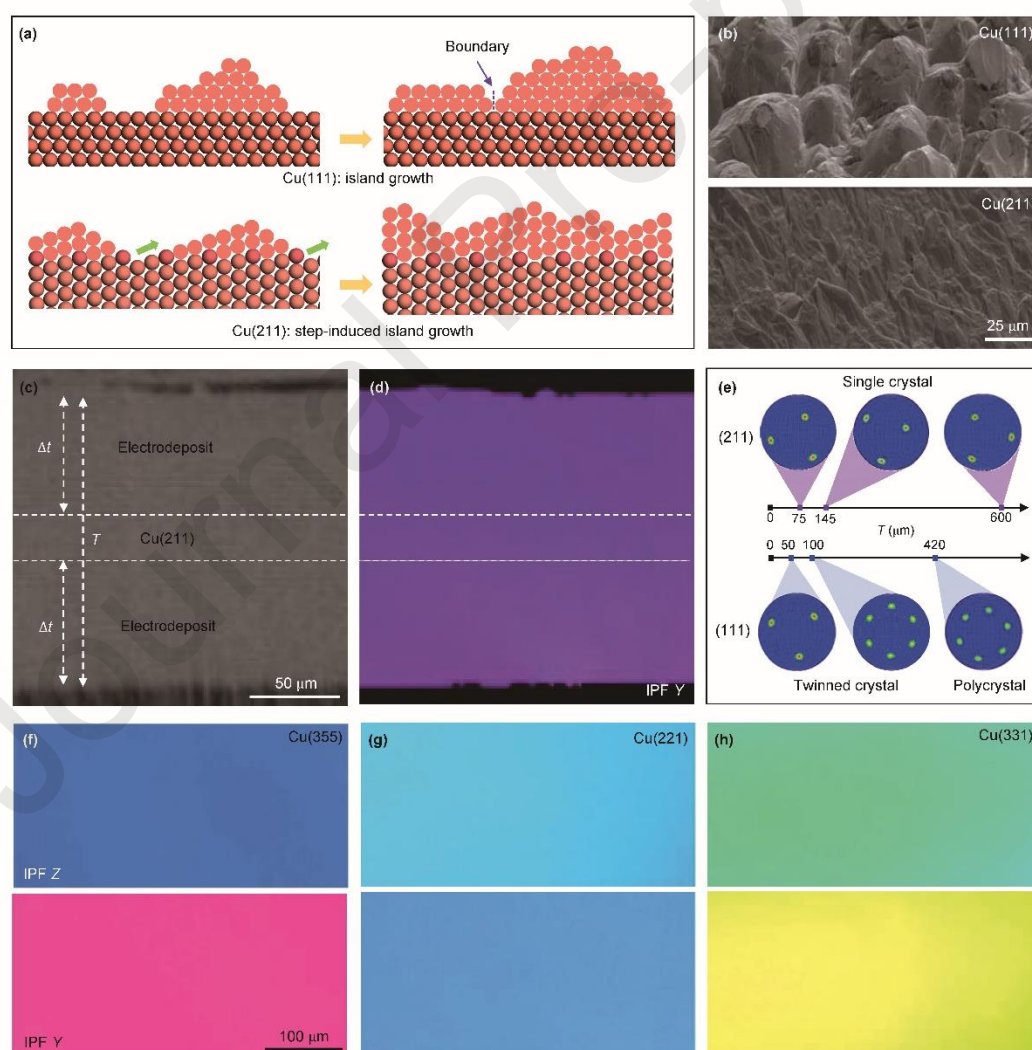


Fig. 2. (Color online) Step-guided single-crystal duplication on high-index single-crystal Cu

substrate. (a) Schematics of the different deposition behaviors on Cu(111) and Cu(211). (b) The distinct surface morphologies of electrodeposited Cu on Cu(111) (top, ~120 μm -thick) and Cu(211) (bottom, ~130 μm -thick) substrates, respectively. The cross-sectional SEM (c) and corresponding EBSD IPF Y map (d) of the electrodeposited Cu(211) plate (~145 μm -thick). The normal direction of the IPF Y map is the same as the thickness direction of the electrodeposited foils. (e) Crystal structure evolution of the electrodeposited layers on Cu(211) and Cu(111) substrates as the electrodeposit thickness increases. (f)–(h) EBSD IPF maps in the Z (top, along the thickness direction) and Y (bottom) directions of the electrodeposited Cu single-crystal plates (~100 μm -thick) with the facet indices of (355), (221), and (331), respectively.

To consolidate the robust single-crystal duplication behavior during the whole electrodeposition process, we also conducted the EBSD characterization of the cross section of the electrodeposited Cu plate (145 μm) with Cu(211) as substrate. The uniform contrast in the vicinity of the Cu(211) surface and the purple color across the entire thickness in the IPF mapping along Y direction demonstrate that the deposition layers are single-crystal and have the same lattice orientation as the substrate (Fig.2c, d).

We further tried to prepare thicker Cu plates. Surprisingly, as the thickness is up to ~ 600 μm , the Cu plate still remains to be single-crystal, indicating by the single orientation in the (100) pole figures (Fig. 2e, upper panel) as well as the IPF mapping along Z and Y direction and the XRD results (Fig. S6a–c online). On the other hand, when using Cu(111) as substrate, as the total thickness of the Cu plate increases, twin crystals and polycrystals will appear sequentially in the structures of electrodeposited layers (Fig. 2e lower panel and Fig. S6d–i online). Actually, the twinning already occurs in the 50 μm -thick Cu(111) plate.

Lastly, we investigate what is the maximum thickness of the single crystals that can be prepared on single-crystal Cu substrates with atomic steps on the surface. The transition from single crystal to twin- or polycrystal can be ascribed to the cumulation of defects during the epitaxial electrodeposition [5,6]. Thus, reducing defects formation can effectively increase the thickness of single-crystal deposition. From this point, we speculate that the surface quality of single-crystal Cu substrate, current density and purity of plating solution may determine the maximum thickness. We conducted controlled experiments to show the effects of the substrate surface quality, current density and purity of electrolyte on the maximum thickness. The results demonstrate poorer substrate quality, higher current density and/or lower-purity electrolyte would lead to easier transition from single crystal to polycrystals, and largely reduced thickness of single crystal (Fig. S7 online). By consistent efforts to optimize these experimental conditions, currently we have obtained a single crystal with thickness of ~3.3 mm on a vicinal Cu(110) substrate, which also has the surface with atomic steps. This maximum thickness is determined by our current experimental conditions and might be much larger in a more suitable electrodeposition environment.

In principle, this step-guided single-crystal duplication should in principle be applicable to the electrodeposition of Cu on other high-index Cu single crystal as well. Here we present three

examples in Fig. 2f–h, with EBSD results verifying the single crystallinity of the Cu plates (each with thickness of $\sim 100\ \mu\text{m}$), proving the validity of our proposed robust single-crystal duplication mechanism.

In summary, we have demonstrated the step-guided single-crystal duplication on high-index Cu, where the step edges interact with electrodeposited Cu atoms and guide them to position at the intended sites, to prepare large-size thick single-crystal Cu plates by electrodeposition. The obtained single-crystal Cu plates exhibit obvious improvement in the electrical conductivity, ductility and fatigue performance compared with the commercial electrodeposited polycrystalline ones. With these superior properties, we anticipate that our prepared single-crystal Cu plates may have potentials in high-speed and high-power electric applications. More importantly, the proposed mechanism of step-guided single-crystal duplication may also be suitable to produce other metal single crystals.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

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Author contribution

Kaihui Liu, Zhihong Zhang, and Enge Wang conceived and supervised the project. Xingguang Li and Zhiqiang Zhang took the electrodeposition of Cu. Zhibin Zhang, Mengze Zhao, Muhong Wu, Ying Fu, and Dingxin Zou prepared the single-crystal Cu foils. Xingguang Li and Zhihong Zhang carried out the SEM and EBSD characterizations. Ruixi Qiao, Xiaonan Yang, and Peng Gao took the TEM characterization. Xingguang Li, Zhibin Zhang, Fang Liu, and Xinqiang Wang performed the XRD measurement. Xingguang Li, Jinzong Kou, and Zhiqiang Ding carried out the electrical and mechanical properties measurements. Zhihong Zhang, Xingguang Li, and Kaihui Liu performed the analysis and wrote the paper, and all the authors reviewed the paper.

References

- [1] Uecker R. The historical development of the czochralski method. *J Cryst Growth*, 2014, 401: 7-24
- [2] Xu X, Zhang Z, Dong J, et al. Ultrafast epitaxial growth of metre-sized single-crystal graphene on industrial cu foil. *Sci Bull*, 2017, 62: 1074-1080
- [3] Jin S, Huang M, Kwon Y, et al. Colossal grain growth yields single-crystal metal foils by contact-free annealing. *Science*, 2018, 362: 1021-1025
- [4] Wu M, Zhang Z, Xu X, et al. Seeded growth of large single-crystal copper foils with high-index facets. *Nature*, 2020, 581: 406-410
- [5] de Cusminsky JB. The role of stacking fault energy in metal electrodeposition. *Scripta Metallurgica*, 1976, 10: 1071-1073
- [6] Kozlov VM, Bicelli LP. Formation of structural defects during metal electrocrystallization. *J Cryst Growth*, 1996, 165: 421-428
- [7] de Cusminsky JB, Wilman H. Growth and structure of single-crystal electrodeposits of copper; a systematic electron-diffraction study. *Electrochim Acta*, 1972, 17: 237-246
- [8] Kelso MV, Tubbesing JZ, Chen Q, et al. Epitaxial electrodeposition of chiral metal surfaces on silicon(643). *J Am Chem Soc*, 2018, 140: 15812-15819
- [9] Brown DA, Morgan S, Peldzinski V, et al. Crystal growth patterns in dc and pulsed plated galvanic copper films on (1 1 1), (1 0 0) and (1 1 0) copper surfaces. *J Cryst Growth*, 2017, 478: 220-228
- [10] Mayadas AF, Shatzkes M. Electrical-resistivity model for polycrystalline films: The case of arbitrary reflection at external surfaces. *Phys Rev B*, 1970, 1: 1382-1389
- [11] Zhao YH, Bingert JE, Liao XZ, et al. Simultaneously increasing the ductility and strength of ultra-fine-grained pure copper. *Adv Mater*, 2006, 18: 2949-2953

- [12] Zhang L, Lu C, Tie AK. Nonlinear elastic response of single crystal cu under uniaxial loading by molecular dynamics study. *Mater Lett*, 2018, 227: 236-239
- [13] Hatano T, Kurosawa Y, Miyake J. Effect of material processing on fatigue of FPC rolled copper foil. *J Electron Mater*, 2000, 29: 611-616
- [14] Williamson MJ, Tromp RM, Vereecken PM, et al. Dynamic microscopy of nanoscale cluster growth at the solid-liquid interface. *Nat Mater*, 2003, 2: 532-536
- [15] Rynders RM, Alkire RC. Use of in situ atomic force microscopy to image copper electrodeposits on platinum. *J Electrochem Soc*, 1994, 141: 1166-1173



Xingguang Li received his B.S. degree from Jinan University in 2014, and his Master's degree from Department of Physics, Renmin University of China in 2019. Currently, he is pursuing a doctor degree in Condensed Matter Physics and Materials Physics at School of Physics, Peking University. His research interest includes electrochemistry and single-crystal metals.



Zhihong Zhang is currently an associate professor at the State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing. She received her Ph.D. degree from Peking University in 2019, followed by postdoctoral research at Peking University. Her main research interest is the controllable growth of

single-crystal metal and two-dimensional materials, focusing on surface and interface engineering and growth mechanism exploration.



Enge Wang is currently a chair professor at the International Center for Quantum Materials, School of Physics, Peking University. He received his Ph.D. degree from School of Physics, Peking University in 1990. His current research interest includes the exploration and physical properties of light-element nanomaterials, surface growth dynamics at atomic scale, and the behavior and properties of water in confined systems.



Kaihui Liu is currently a distinguished professor at the State Key Laboratory for Mesoscopic Physics, School of Physics, Peking University. He received his Ph.D. degree from the Institute of Physics, Chinese Academy of Sciences in 2009 and afterward worked as a postdoctoral research fellow at UC Berkeley. His current research interest is the growth, characterization, and applications of meter-scale single crystals including copper foils, graphene, and MoS₂.

