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Supplementary Information

Multi-Scale Materials Synthesis via Ultrafast Thermal Radiative Vapor Deposition

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Materials and Methods

Materials preparation

All chemicals used in this study were of analytical grade and utilized without further purification. Cu foam was initially cleaned by washing with a diluted hydrochloric acid solution, followed by thorough rinsing with deionized water to eliminate surface impurities. The cleaned Cu foam was then immersed in a 2 wt% ammonia solution for 6 hours, resulting in the formation of a $Cu(OH)_2$ layer on its surface. After immersion, the Cu foam with $Cu(OH)_2$ was rinsed with deionized water and dried at 60 °C. Subsequently, the dried foam underwent heating at 160 °C for 2 hours to achieve dehydration. Finally, the foam was subjected to reduction at 400 °C for 3 hours in a mixed flow of hydrogen and argon (5% H_2 by volume) to obtain the desired rough-surfaced Cu foam. Additionally, carbon black (Ketjen/Vulcan-72) was treated to introduce surface defects. This was achieved by activating the carbon black at 1023 K in a flow of CO_2 for 6 hours.

Ultrafast TRVD set up and process

The reaction setup consisted of a quartz container, which was sealed tightly to ensure a vacuum environment. Electrical leads were extended from both ends of the quartz container to connect it to a home-made Joule-heating power source. For the sample setup, graphite paper was utilized as the heating substrate. The carbon paper was securely connected to the electrical leads using conductive clips, ensuring efficient and uniform heating throughout the experiment. Following the completion of the setup, electrical pulses of differing durations were applied to the carbon substrate. These pulses generated the precise temperatures and heating times necessary for the synthesis of a series of materials.

ICP-MS measurement

We measured the metal concentration of the dispersed metal atoms by ICP-MS (PerkinElmer NexION 300D ICP Mass Spectrometer with autosampler). The solutions were prepared by digesting the samples in nitric acid (≥ 65 to < 70%) followed by 100 dilution times with 2% hydrochloric acid. The resultant solutions were analyzed directly by ICP-MS.

Raman characterization

Raman spectroscopy measurements were conducted using an in Via-Reflex laser confocal micro-Raman spectrometer (Renishaw, UK) acquired in January 2012. The excitation wavelength of 532 nm was employed for all measurements, with the spectral acquisition range set between 1000 cm^{-1} and 2000 cm^{-1}. The laser power was maintained at 50% of maximum intensity to minimize sample heating effects. Spectra were collected with a step size of 1.3 cm^{-1} and a spectral resolution of 2 cm^{-1}. The instrument features scanning capabilities across ranges of 15-600 cm^{-1} and 100-4000 cm^{-1}, with a wavenumber accuracy of ±0.2 cm^{-1} and scanning reproducibility of ±0.2 cm^{-1}. The system is equipped with a variable temperature sample stage (77 K-873 K, 15 K-room temperature) and provides spatial resolution of 0.5 μm laterally and 2 μm vertically. The spectrometer is fitted with three laser sources (325 nm, 532 nm, and 785 nm) and includes a high-precision three-dimensional automated stage capable of point-by-point scanning for Raman mapping applications.

Structural characterization

SEM was conducted on a Hitachi S-4800. TEM was performed on high-resolution TEM (JEOL JEM-2100F) at an accelerating voltage of 200 kV. The HAADF-STEM images were acquired with a Hitachi HD2700C dedicated STEM with a probe Cs corrector. X-ray diffraction (XRD) patterns of different samples were obtained using a Rigaku D/max 2200 pc diffractometer with Cu *K*α radiation. The X-ray photoelectron spectroscopy (XPS) was carried out with an Axis Supra X-ray photoelectron spectrometer.

Environmental and economic analysis

Calculation model based on PVD, ALD, CVD, and ultrafast TRVD processes.[1-3] The energy consumption, water consumption, greenhouse gas (GHG) emissions, atmospheric pollutant emissions, and energy costs of the process were calculated separately. Detailed calculations and data sources can be found in Table S1.

Table S1 Environmental–economic analysis data of this work and other deposition techniques

Technology	Energy/dosage (kJ/g)	Coal (g/g)	Water (kg/g)	GHG (CO_2 g/g)	NO_x (mg/g)	SO_x (mg/g)	PM_{10} (mg/g)	Cost (US$/kg)
Ultrafast-TRVD	27.648	2.46	0.08	6.53	1.23	6.61	1.25	0.6
PVD [1]	1890	168	5.78	446.25	84	451.92	85.68	40
ALD [2]	3900	346.67	11.92	920.83	173.34	932.54	176.8	82
CVD [3]	8640	768	26.4	2040	384	2065.92	391.68	182

Note: Coal consumption for thermal power generation is 320g/kWh. Data source: Ministry of Ecology and Environment of the People’s Republic of China (mee.gov.cn).
Thermal power generation water consumption is 0.011m^3/kWh. Data source: DOI: 10.19760/j.ncwu.zk.2 021026.
Baseline emission factor of 0.85 kg/kWh for China’s power grid in 2024. Data source: Ministry of Ecology and Environment of the People's Republic of China (mee.gov.cn).
Standard coal atmospheric pollutant emission factor: NO_x: 0.5g/kg, SO_x: 0.69 g/kg, PM_{10}: 0.51g/kg. Data source: DOI: 10.16389/j.cnki.cn42-1737/n.2019.06.005.
The price of electricity is 0.076 US$/kWh. Data source: State Grid (www.js.sgcc.com.cn)

References

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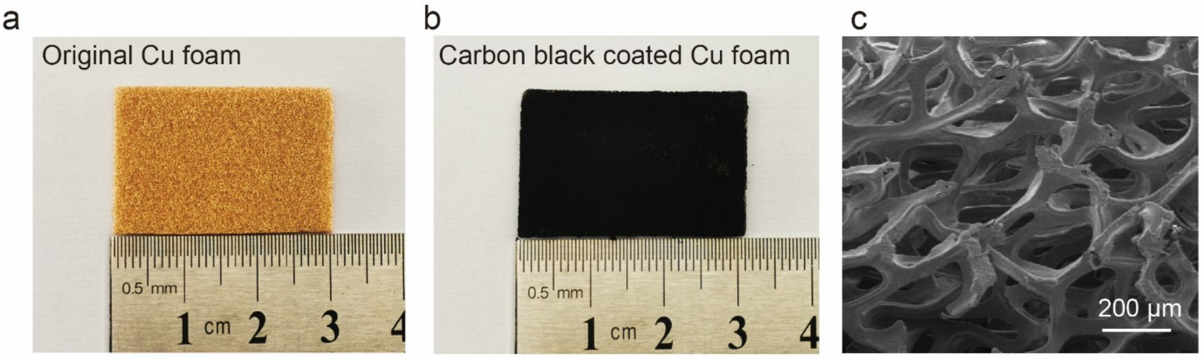

Figure S1. Schematic diagram and images of the ultrafast TRVD process and products. Digital images of the Cu foam target (a) and the carbon black powder sprayed onto the Cu foam as the substrate (b). SEM images of the sprayed carbon black on the Cu foam are shown in (c) and (d), with (c) being the low-magnification image.

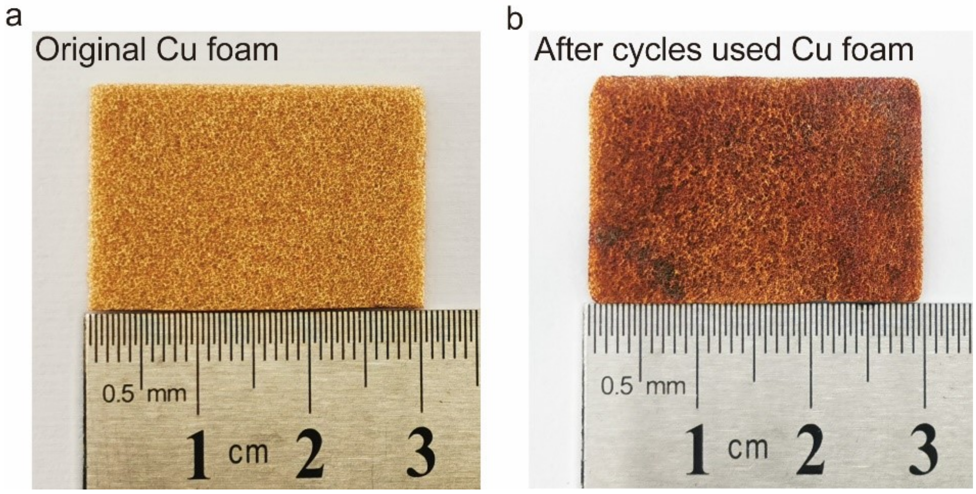

Figure S2. Digital images of the original Cu foam and after cycles ultrafast TRVD process. It demonstrates that the Cu foam after ultrafast TRVD can be reused.

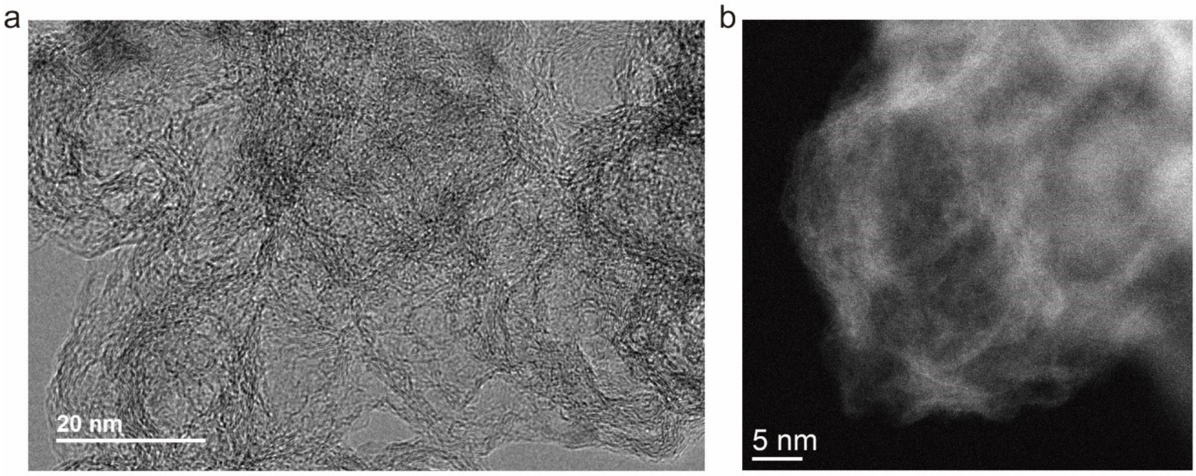

Figure S3. Characterization of the carbon black before ultrafast TRVD process. (a) TEM image. (b) HAADF-STEM images. Images indicate that there are no nanoparticles, cluster, or dispersed Cu atom on the carbon black before ultrafast TRVD process.

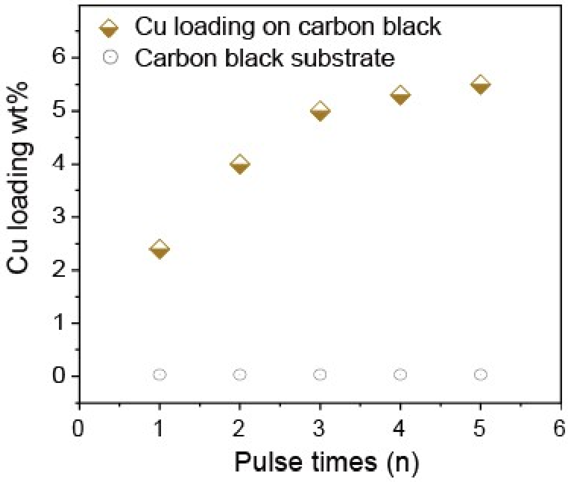

Figure S4. The highly dispersive metal atom/cluster/nanoparticle catalyst synthesized by ultrafast TRVD and its application in electrocatalysis. (a) ICP-MS results of the Cu with different loadings on the carbon black substrate. According to Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis, the mass loading of Cu varies from 2.3 to 5.0 wt% with increasing pulse cycles. At these loadings, Cu maintains its highly dispersed state (Figure 3b).

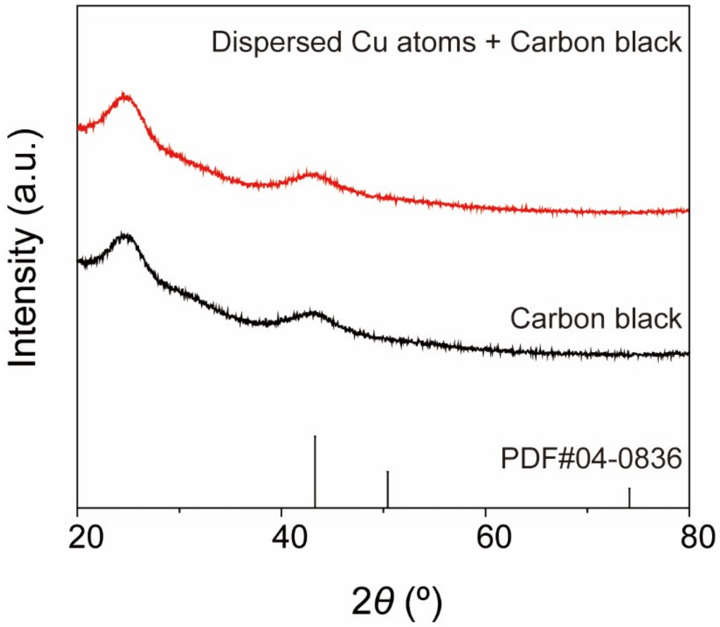

Figure S5. The XRD pattern of the dispersed Cu atom-loaded carbon black powders.

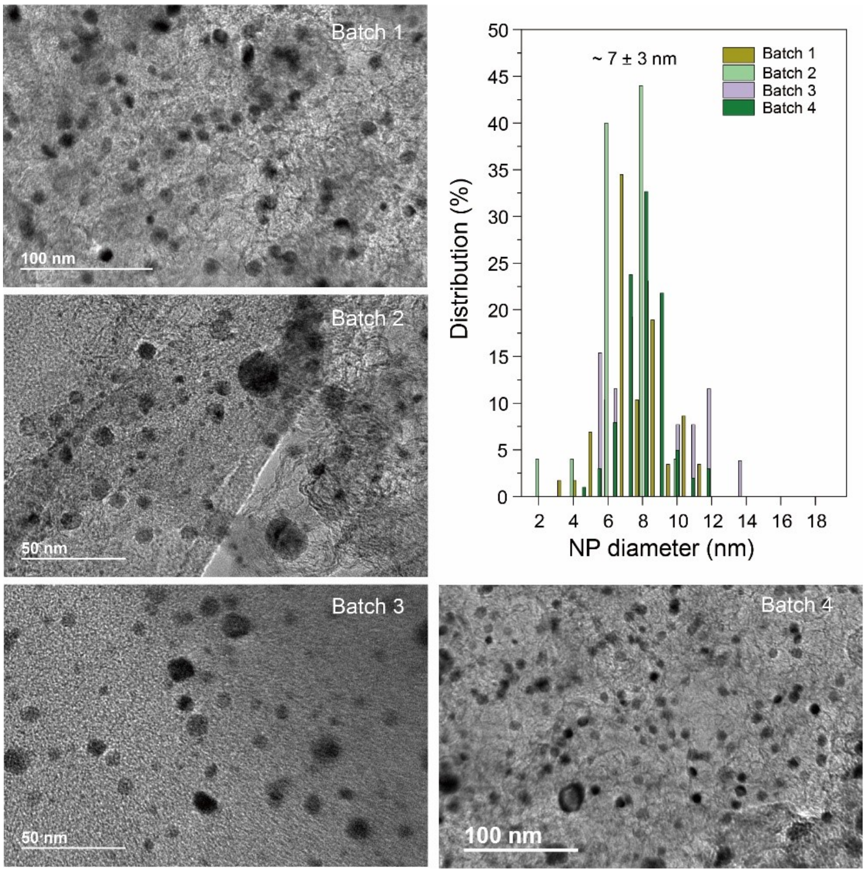

Figure S6. Batch-to-batch reproducibility of Cu-nanoparticle size distributions obtained by ultrafast thermal radiative vapor deposition method. TEM-derived size-distribution histograms for Cu nanoparticles from four independent syntheses under identical ten-pulse protocol, demonstrating the high precision and reproducibility of our method. In each panel, the diameter of particles was measured per batch (Batch 1–4), and the resulting histograms are overlaid to show the reproducibility of both the mean size and distribution shape across four separate runs.

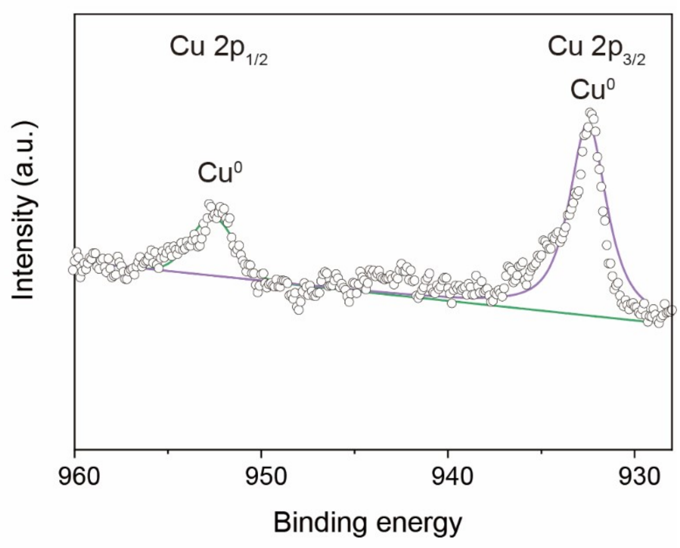

Figure S7. XPS fine spectrum of Cu nanoparticles. The results reveal that the Cu 2p3/2 spectrum exhibits sharp peak centered at 932.6 eV, aligning closely with reference values for metallic Cu form, with no detectable oxide peaks. This confirms that our treatment successfully maintains the metal in its reduced, metallic state without extensive oxidation.

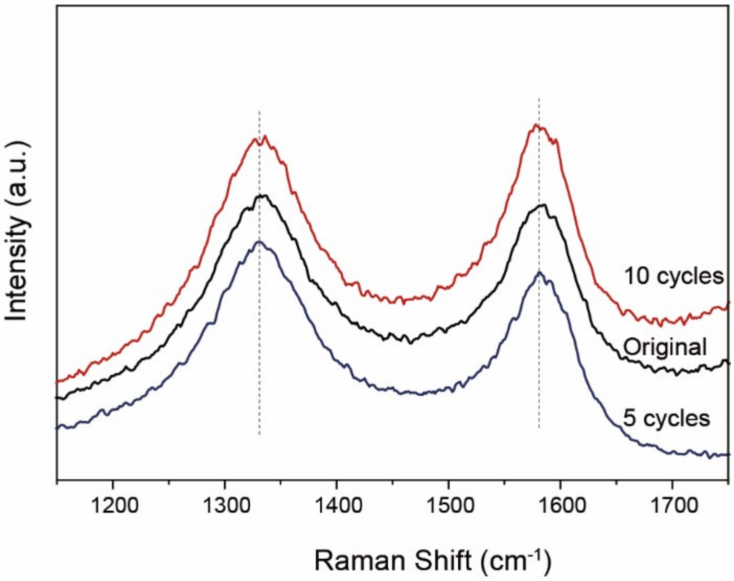

Figure S8. XPS fine spectrum of Cu nanoparticles. The results reveal that the Cu 2p3/2 spectrum exhibits sharp peak centered at 932.6 eV, aligning closely with reference values for metallic Cu form, with no detectable oxide peaks. This confirms that our treatment successfully maintains the metal in its reduced, metallic state without extensive oxidation.

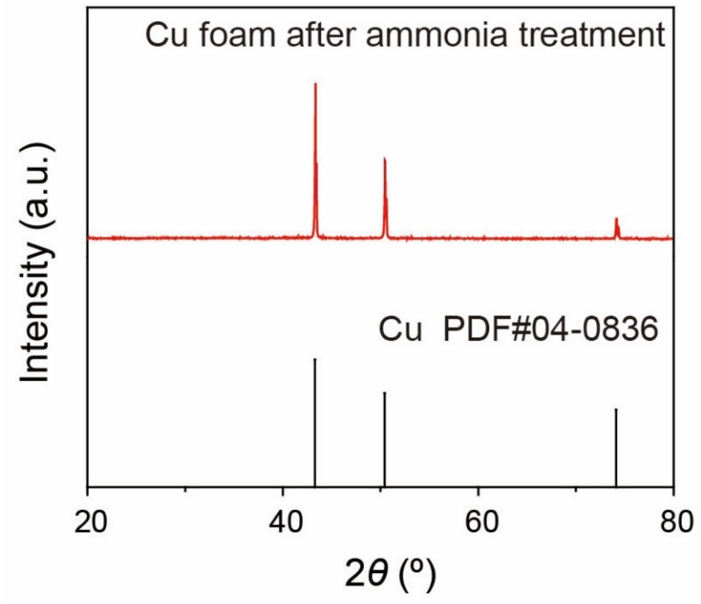

Figure S9. XRD pattern of the Cu foam after being treated with ammonia. PDF#04-0836 is the JCPDS (Joint Committee on Powder Diffraction Standards) card number of face-centered cubic Cu.

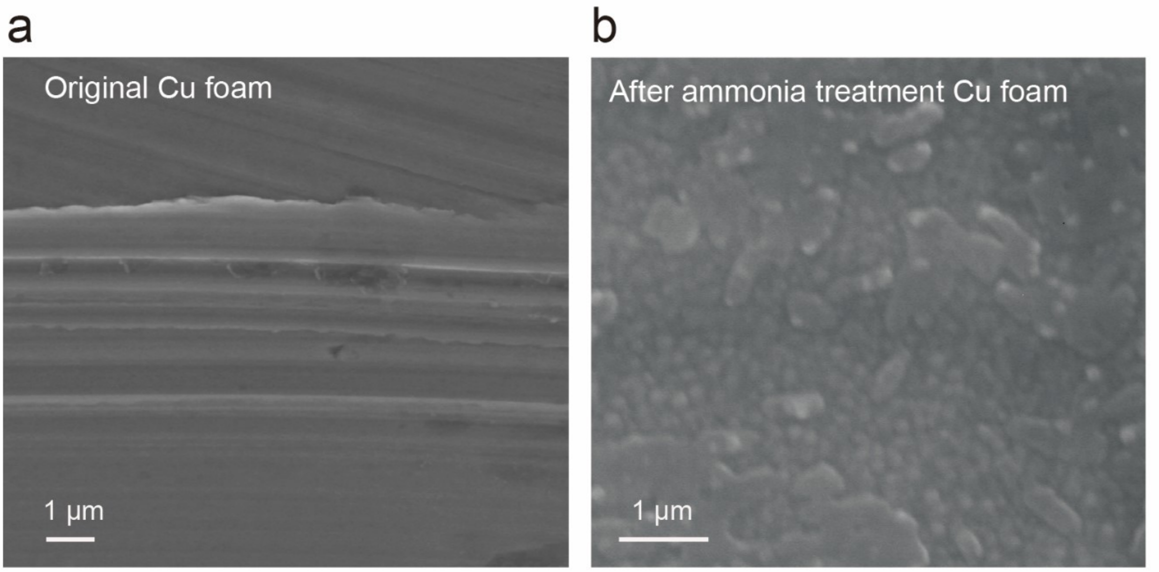

Figure S10. (a) SEM image of the original Cu foam displaying smooth surfaces. (b) SEM image of the Cu foam after ammonia treatment, revealing surface roughness.

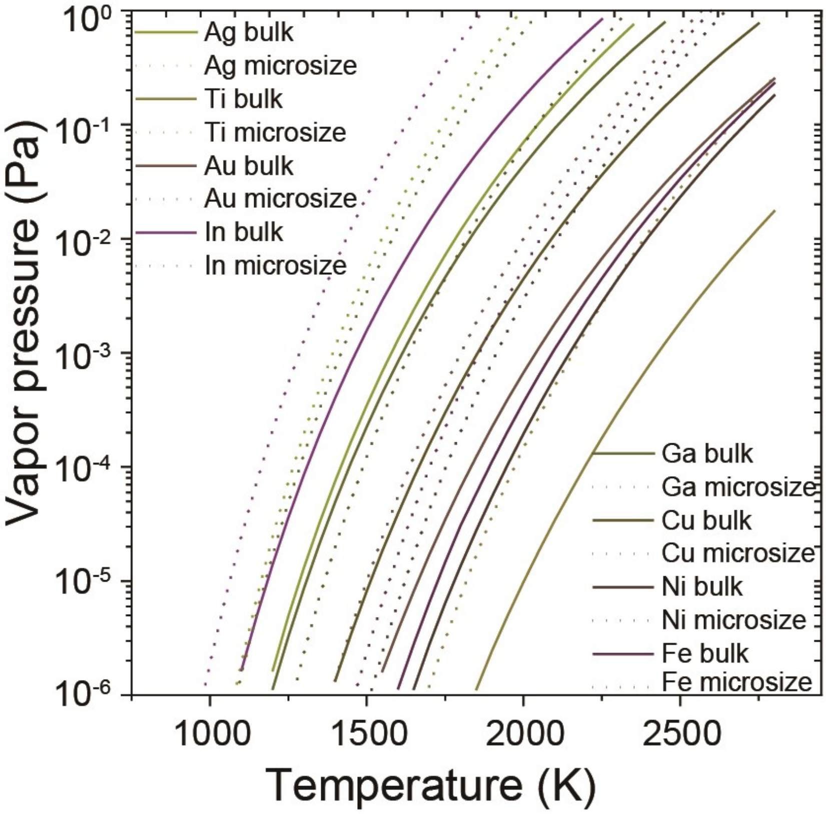

Figure S11. Vapor pressure comparison between untreated bulk Cu foam and Cu foam treated with ammonia.

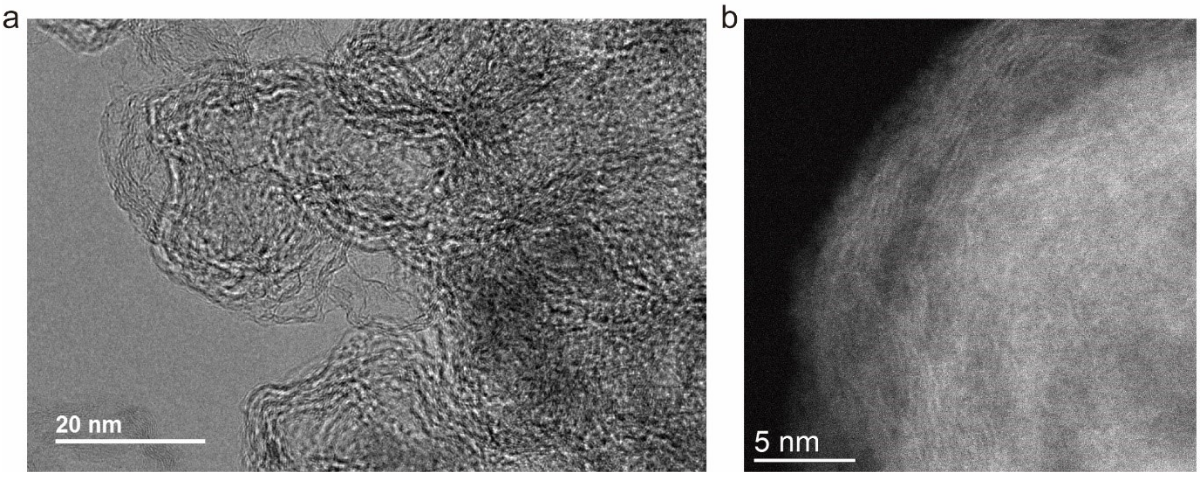

Figure S12. Characterization of the carbon black after ultrafast TRVD process with the original Cu foam as target. (a) TEM image. (b) HAADF-STEM images. Images indicate that there are no nanoparticles, cluster, or dispersed metal atom on the carbon black after ultrafast TRVD process using the original Cu foam as target.

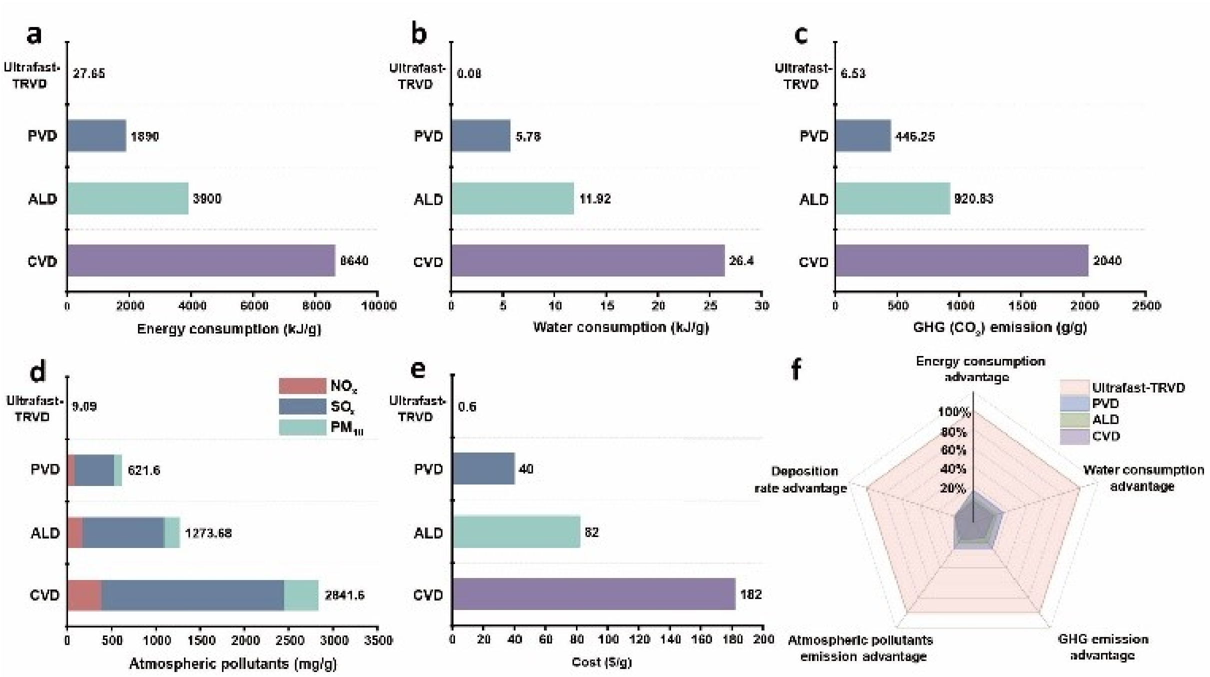

Figure S13. (a, b) Comparison of energy and water consumption for synthesizing 1 g of Cu-based materials using various deposition methods. (c, d) Evaluation of greenhouse gas (GHG) and air pollutant emissions for synthesizing 1 g of Cu-based materials across different schemes. (e) Analysis of energy costs associated with the synthesis of 1 g of Cu-based materials using different deposition techniques. (f) Radar chart comparing the performance of ultrafast TRVD with other deposition methods in terms of energy efficiency, GHG emissions, and cost. We conducted a comprehensive study on the techno-economic analysis (TEA) of the ultrafast TRVD, PVD, ALD, and CVD processes (detailed calculations are provided in Table S1). As depicted in Figure S10a and b, the ultrafast TRVD demonstrates a significant advantage in terms of energy and water consumption due to its ultra-high vapor deposition efficiency. Specifically, the synthetic energy consumption for producing the Cu-based catalyst is merely 27.65 kJ g^{-1}, while water consumption is only 0.08 g/g, markedly lower than those of PVD, ALD, and CVD. Moreover, the ultrafast TRVD method substantially mitigates greenhouse gas (GHG) emissions, achieving an impressive ~99.7% reduction compared to the CVD process (Figure S10c). This approach is also highly effective in controlling air pollutant emissions, generating only 9.09 g of air pollutants per gram of Cu-based catalyst, which is less than 1% of the emissions produced by the CVD method (Figure S10d). Figure S10e highlights the energy costs associated with each scheme, revealing that the energy costs for PVD, ALD, and CVD are significantly higher than those for ultrafast TRVD. Our ultrafast TRVD solution maximizes energy efficiency, resulting in a substantial reduction in energy costs. Specifically, the energy cost for producing 1 g of Cu-based catalyst is only US$0.6, which is dramatically lower than the cost for CVD (US$182). Figure S10f consolidates the data, illustrating the superior performance of the ultrafast TRVD scheme in terms of energy efficiency, GHG emissions, and cost. Although this assessment is based on laboratory-scale data, we anticipate that actual industrial costs will be even lower. This study unequivocally presents an effective solution for reducing environmental impact and offers an innovative approach for achieving low-cost vapor deposition, thereby addressing both environmental and economic challenges in industrial production.