Supporting Information

Sustainable electrosynthesis of porous CuN_3 films for functional energetic chips

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Computational details

DFT calculations have been employed to describe the reaction mechanism in our systems. All computations were executed on Gaussian 09 package. In our work, B3LYP with the def2TZVP basic set, has been employed to get Gibbs free energy in these structures. The Gibbs free energy of our structures, including the reactants and products, can be express by: $G = E_0 + G_{corr}$, where E_0 is the electronic energy, G_{corr} is correction to the Gibbs free energy due to internal energy. It is known that the vibrational frequencies of reactants and products need to be obtained to get the G_{corr}. In this work, electrochemical azidation reactions may be occurred have been considered as:

$$\mathrm{Cu} - \mathrm{e} + \mathrm{N_3^-} \rightarrow \mathrm{CuN_3} \quad (1)$$

$$\mathrm{CuN_3} - e + \mathrm{N_3^-} \rightarrow \mathrm{Cu(N_3)_2} \quad (2)$$

$$\mathrm{Cu} - 2\mathrm{e} + 2\mathrm{N_3^-} \rightarrow \mathrm{Cu(N_3)_2} \quad (3)$$

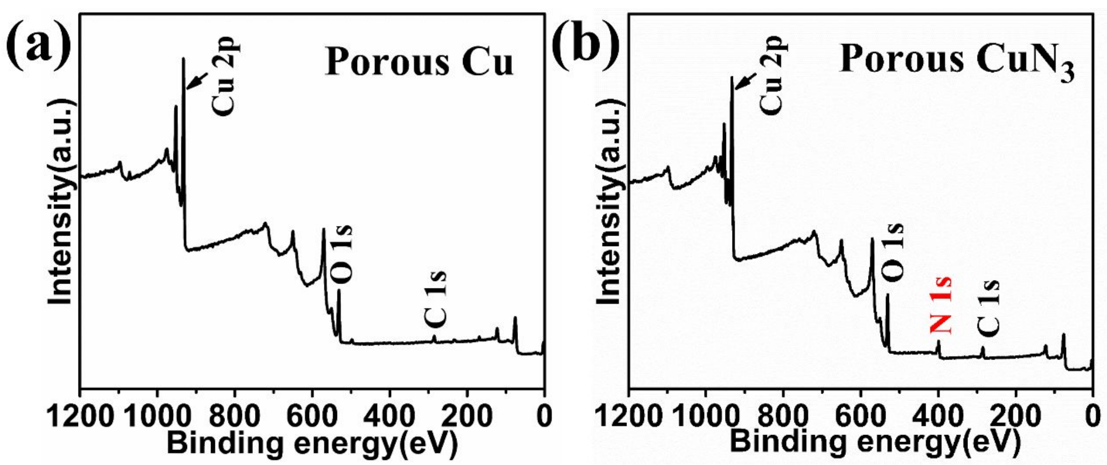

Figure S1. The XPS survey scan spectra of the (a) porous Cu and (b) CuN_3 film.

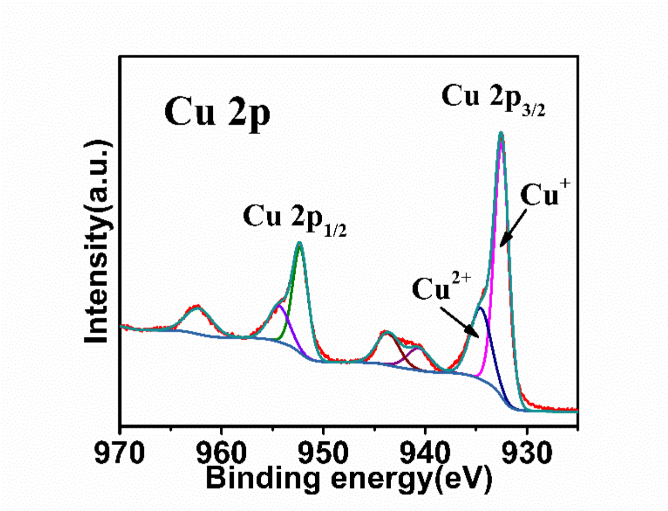

Figure S2. The high-resolution Cu 2p XPS spectrum of the porous CuN_3 film.

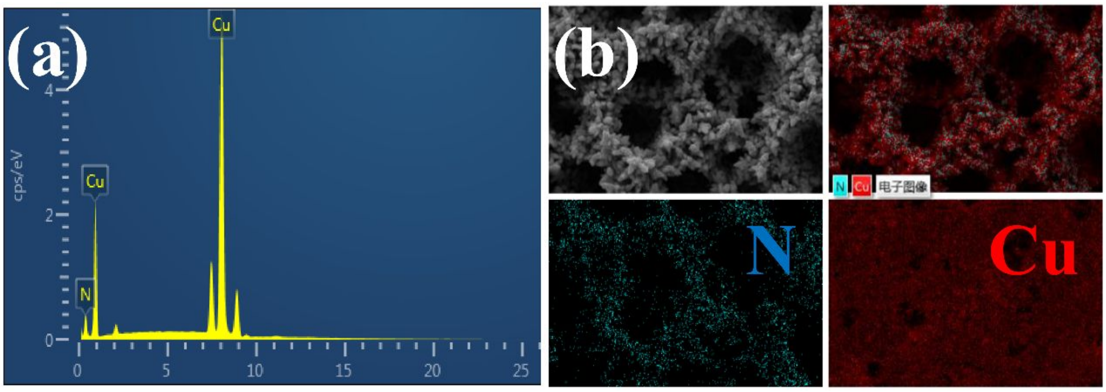

Figure S3. (a) The EDS and (b) elemental mapping images of Cu, N for the CuN_3 film. The current density and azidation time are set to 3.0 mA·cm^{-2} and 450 s, respectively.

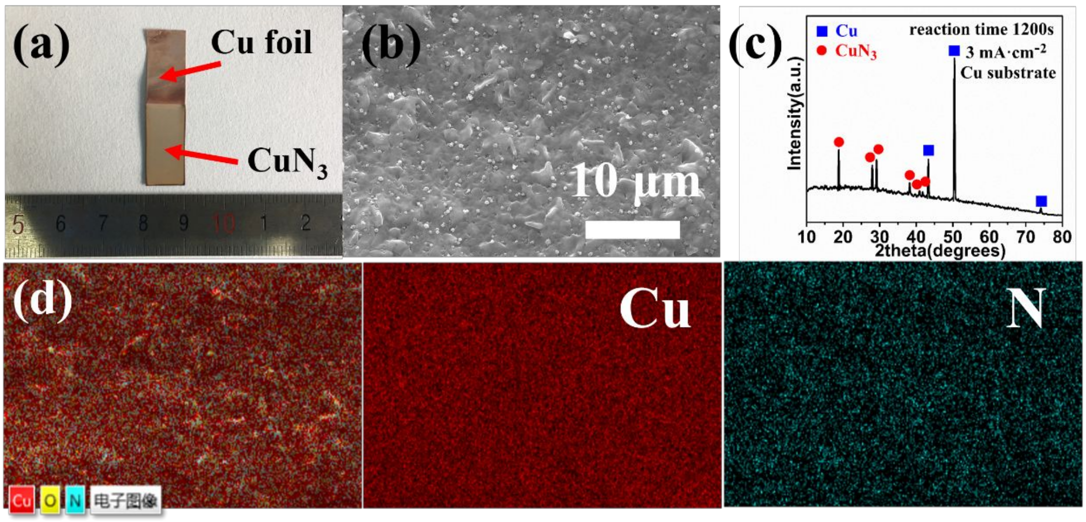

Figure S4. (a) An optical photo of the CuN_3 film on the Cu foil. (b) The SEM image of the CuN_3 film. (c) The XRD pattern of the CuN_3 film and (d) EDS elemental mapping images of Cu, N for the CuN_3 film. A Cu substrate is used as a working electrode at the current density of 3 $mA \cdot cm^{-2}$ with a reaction time of 450 s.

Table S1. Comparisons of energetic properties of CuN_3 materials prepared by different methods.

Sample	Energy release ($J \cdot g^{-1}$)	Peak temperature (°C)	Preparation method	Reference
porous CuN_3 film	1200	178	electrosynthesis	this work
porous CuN_3	-	187.7	gas-solid azidation	1
α-CuN_3 crystal	1488	172.5	crystallization	2
β-CuN_3 crystal	1156	178	modified crystallization	2

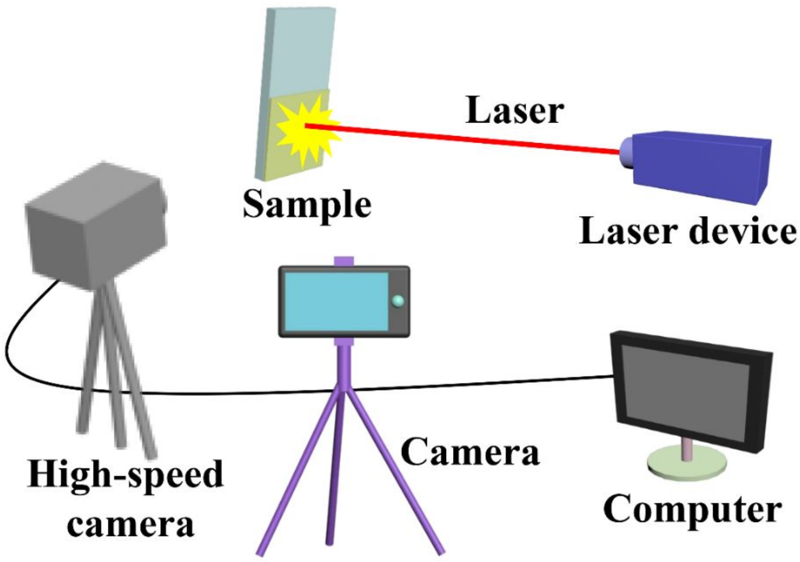

Figure S5. The schematic diagram of the laser-induced explosive test.

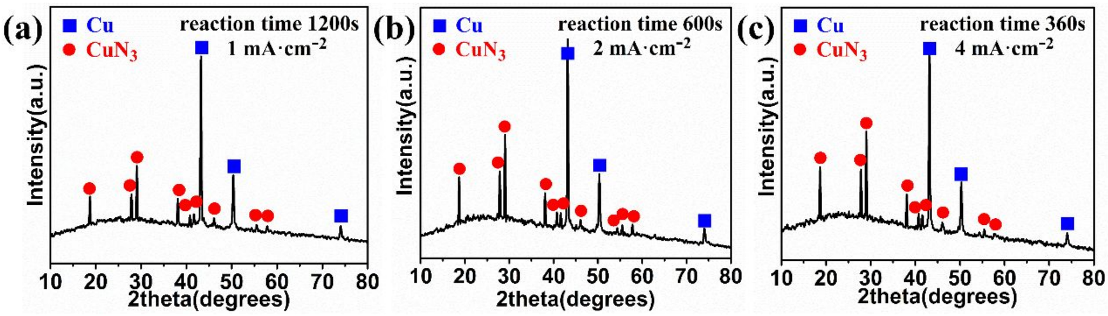

Figure S6. The XRD patterns of the CuN_3 films at the different current densities of (a) 1.0, (b) 2.0 and (c) 4.0 mA·cm^{-2}, respectively.

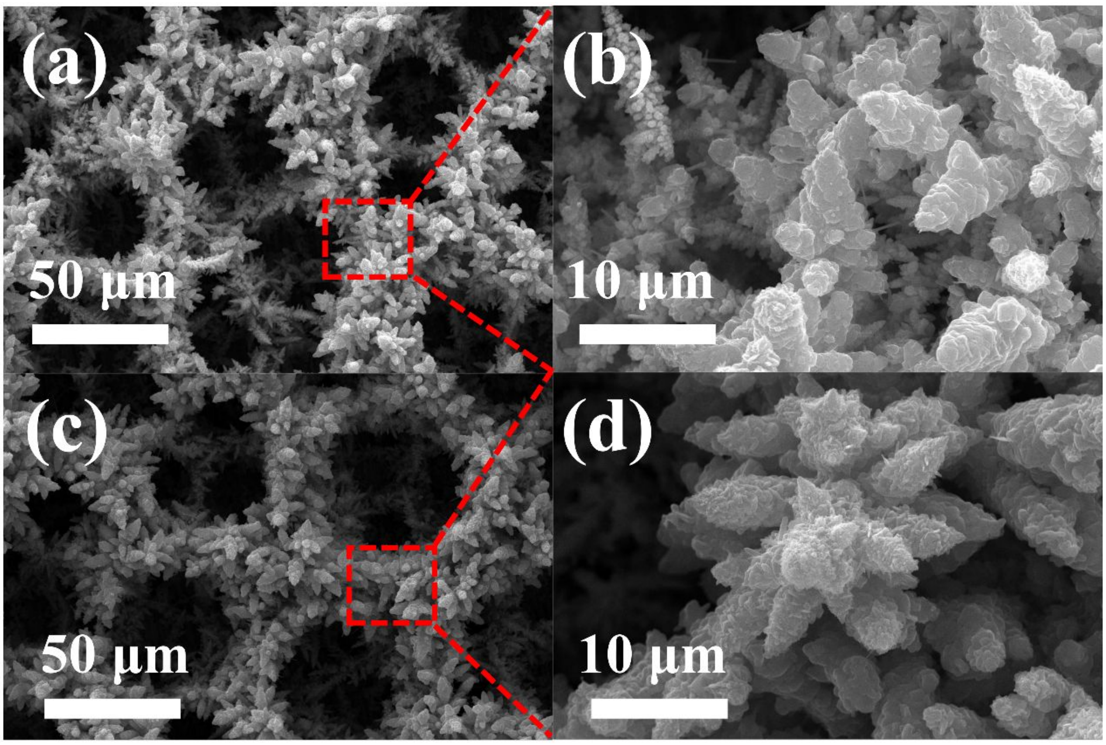

Figure S7. The SEM images of the CuN_3 films with different azidation times of (a,b) 150 s and (c,d) 300 s. The current density is set to 3.0 mA·cm^{-2}.

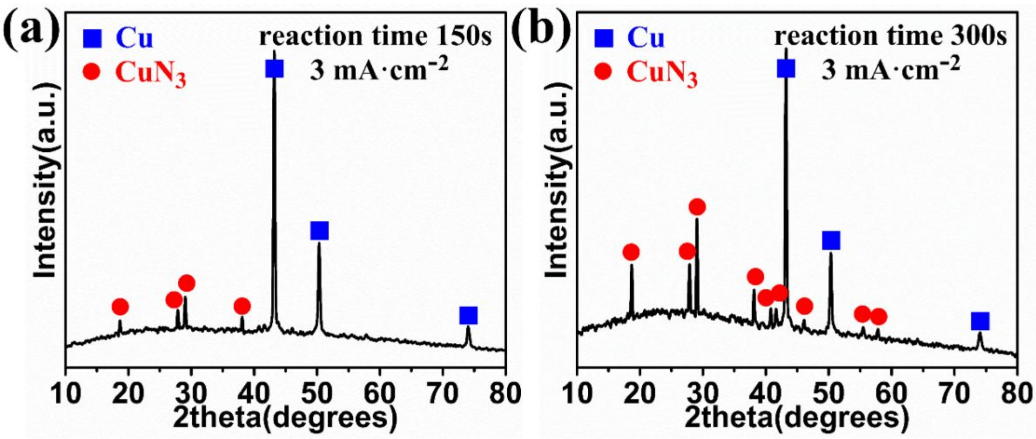

Figure S8. The XRD patterns of the CuN_3 films with different azidation times of (a) 150 s and (b) 300 s. The current density is set to 3.0 mA·cm^{-2}.

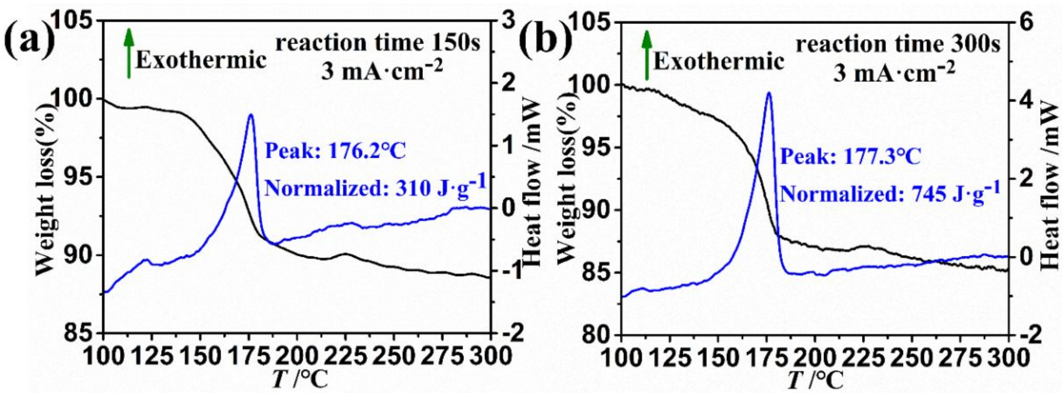

Figure S9. The DSC-TG curves of the CuN_3 films with different azidation times of (a) 150 s and (b) 300 s. The current density is set to 3.0 mA·cm^{-2}.

Video S1. A laser-induced explosive process of the CuN_3 film recorded by a mobile phone.

References

(1) Zhang, L.; Zhang, F.; Wang, Y.; Han, R.; Chen, J.; Zhang, R.; Chu, E. In-situ preparation of copper azide by direct ink writing. *Mater. Lett.* **2019**, *238*, 130-133, DOI 10.1016/j.matlet.2018.11.165.

(2) Liu, X.; George, J.; Maintz, S.; Dronskowski, R. Beta-CuN_3: the overlooked ground-state polymorph of copper azide with heterographene-like layers. *Angew. Chem., Int. Ed.* **2015**, *54* (6), 1954-1959, DOI 10.1002/anie.201410987.