NIR-II Photothermal-Thermoelectric Effect Enhanced Electrochemical Sensing for Dopamine Detection in Sweat

Wenbin Qiu[1], Lipeng Zhao[1], Haichao Xiong[1], Huimin Qi[3], Jialin Pan[3], Hailong Wu[b], husheng Xu[1]*, Yujie Ma[2]*, Xuerong Shi[1]**

[1]School of Materials Engineering, Shanghai University of Engineering Science, Shanghai 201620, China; [2]Shanghai Key Laboratory of Molecular Imaging, Collaborative Innovation Center for Biomedicine, Shanghai, University of Medicine and Health Sciences, Shanghai 201318, China; [3]Shanghai University of Traditional Chinese Medicine, Shanghai, 201203, China.

Email of corresponding author: shixuer05@mails.ucas.ac.cn

1.1. Synthesis of Au NBPs

Au NBPs were synthesized using a seed-mediated growth method adapted from Sánchez-Iglesias et al [1]. Au seed nanoparticles were first prepared via rapid chemical reduction. Briefly, an aqueous CTAC solution (50 mM) containing sodium citrate (5 mM) and $HAuCl_4$ (10 mL, 0.25 mM) was vigorously stirred at room temperature, followed by the rapid injection of freshly prepared $NaBH_4$ solution (0.25 mL, 25 mM). The solution color immediately changed from pale yellow to brown, indicating the formation of gold seeds. After stirring for 2 min, the reaction vessel was sealed and transferred to an oil bath maintained at 80 °C, where it was gently stirred for 90 min. During this heat-treatment process, the solution color gradually evolved from brown to red. The resulting seed solution was then cooled to room temperature and stored for subsequent use. The final Au concentration in the seed solution was 0.25 mM.

For the growth of Au NBPs a predetermined volume of the seed solution was added dropwise under gentle stirring to a growth solution containing CTAB (100 mL, 0.1 M), $HAuCl_4$ (5 mL, 0.01 M), $AgNO_3$ (1 mL, 0.01 M), and HCl (2 mL, 1 M) in a round-bottom flask. The reaction mixture was maintained at 30 °C for 2 h to complete the anisotropic growth of Au NBPs.

1.2 Synthesis of MXene

$Ti_3C_2T_x$ MXene was prepared by etching Ti_3AlC_2 (MAX-phase) ternary carbide using MILD method in a solution of lithium fluoride (LiF) in hydrochloric (HCl) acid [2]. Etching mixture was prepared from 40 mL of 12 M HCl (37%), 10 mL of DI-water and then 3.2 g of LiF are dissolved in this solution. The mixture was placed in a plastic container with a volume of 50 mL. Then 2 g of Ti_3AlC_2 powder with particle sizes of less than 40 μm is gradually added into etching solution under continuous stirring for 24 h at 25 ℃. Then MXene slurry was rinsed with DI-water via repetitive centrifugation. As-prepared MXene slurry is further processed to obtain a colloidal solution of separated MXene flakes using mild delamination procedure assisted by intercalation of Li^+ ion between Ti_3C_2 sheets with following the separation of MXene into colloidal solution in water. We used the following protocol for the delamination: 2 g of lithium chloride (LiCl) were added to 40 mL of DI-water in a 50 mL plastic container. Etched MXene slurry is added to the prepared solution. The process is performed at 35℃ for 24 h under stirring. After that, MXene slurry is rinsed via repetitive cycles of centrifuging. After synthesis MXene sediment is stored at -18℃.

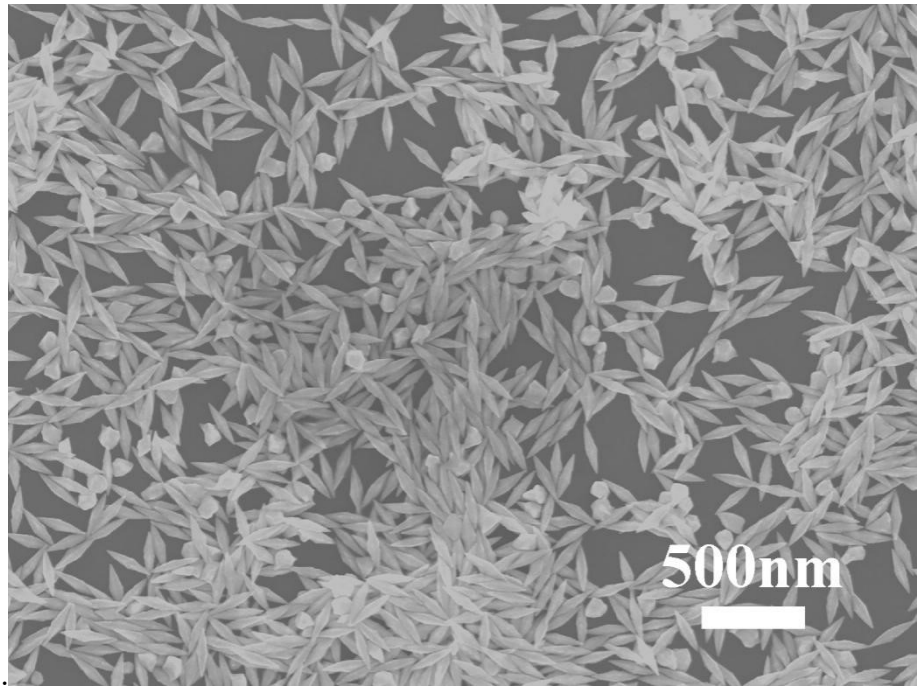


Figure S1 SEM images of Au NBPs.

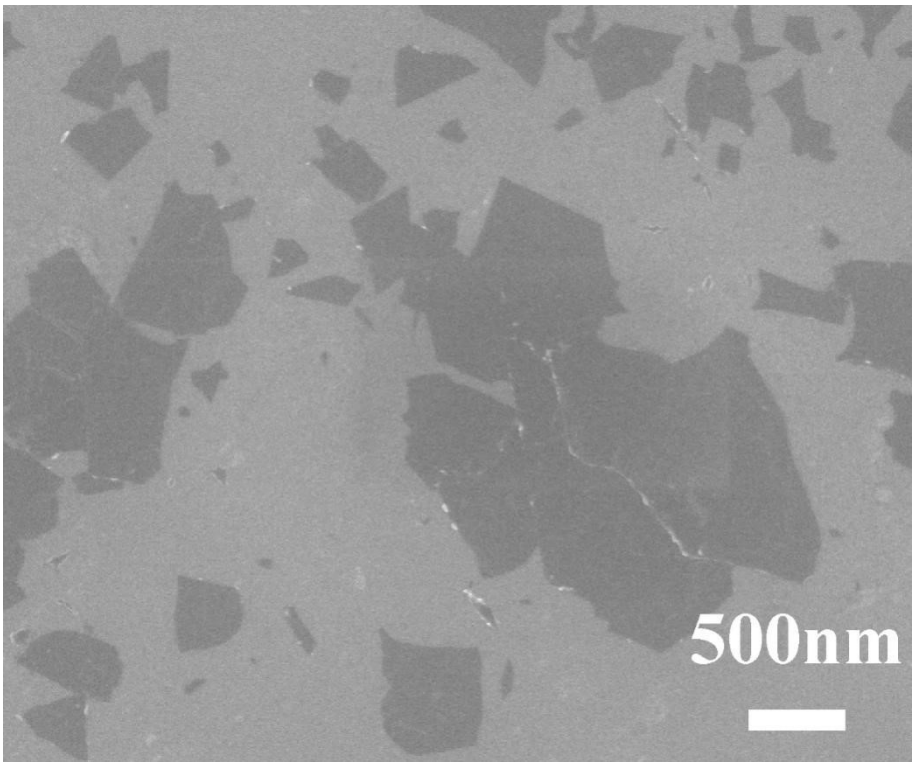


Figure S2 SEM images of MXene nanosheets.

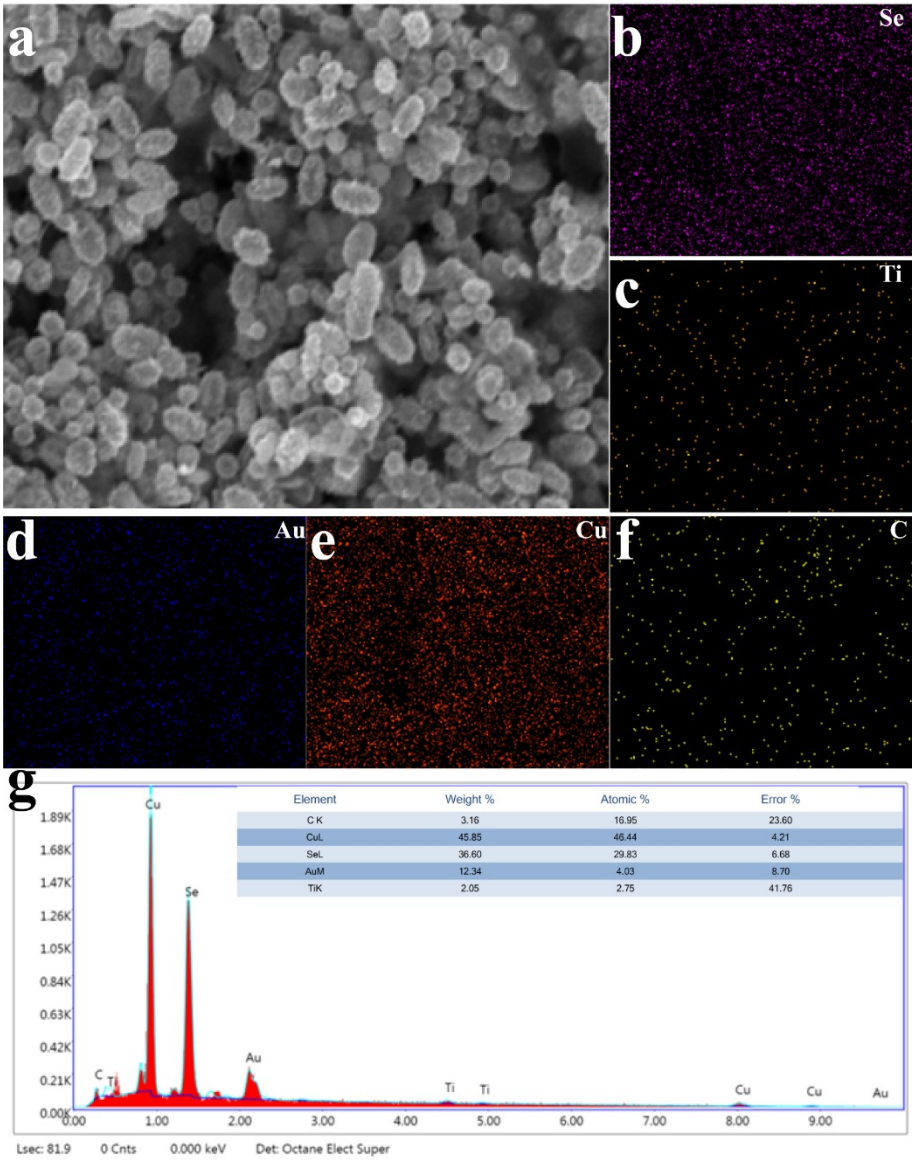
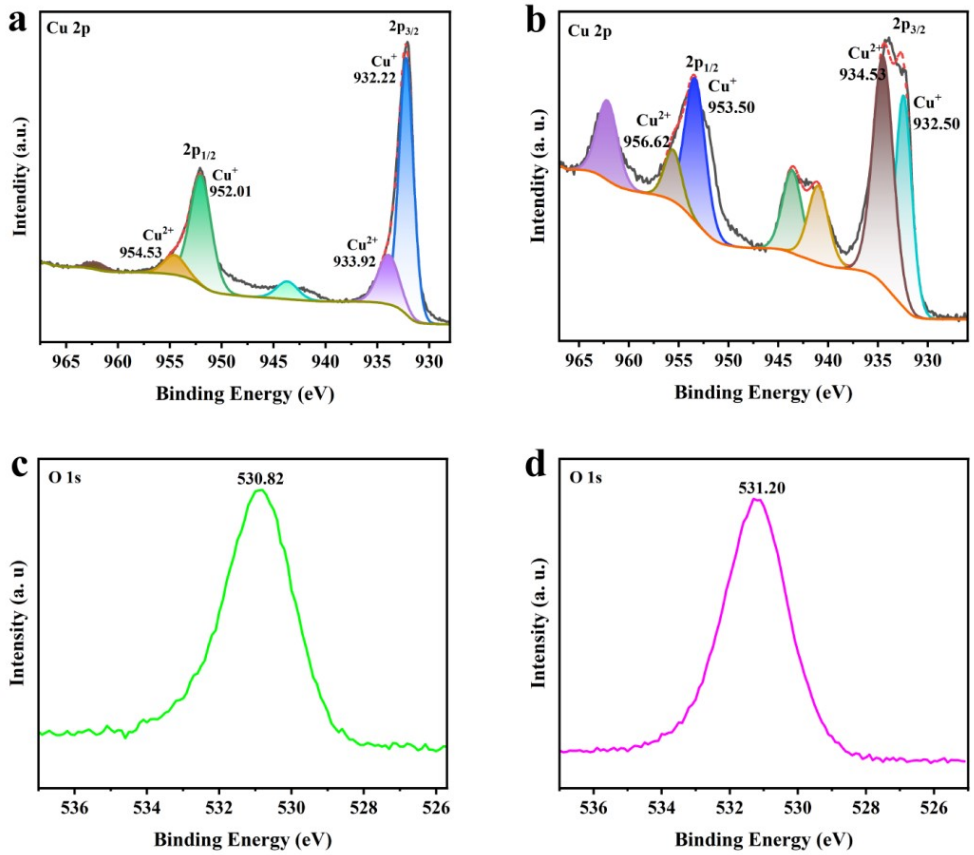


Figure S3 (a) SEM images, (b-f) EDX elements mapping images of Se, Ti,Au,Cu and C on the Au NBP@$Cu_{2-x}Se$@MXene, respectively. (g) Compendium of Element Distribution Maps of Au NBP@$Cu_{2-x}Se$@MXene.



Revised Fig. S4 XPS spectra of Cu 2p for Au NBP@$Cu_{2-x}Se$@MXene (a) and Au NBP@$Cu_{2-x}Se$ (b), respectively. XPS spectra of Cu O 1s for Au NBP@$Cu_{2-x}Se$@MXene (c) and Au NBP@$Cu_{2-x}Se$ (d), respectively.

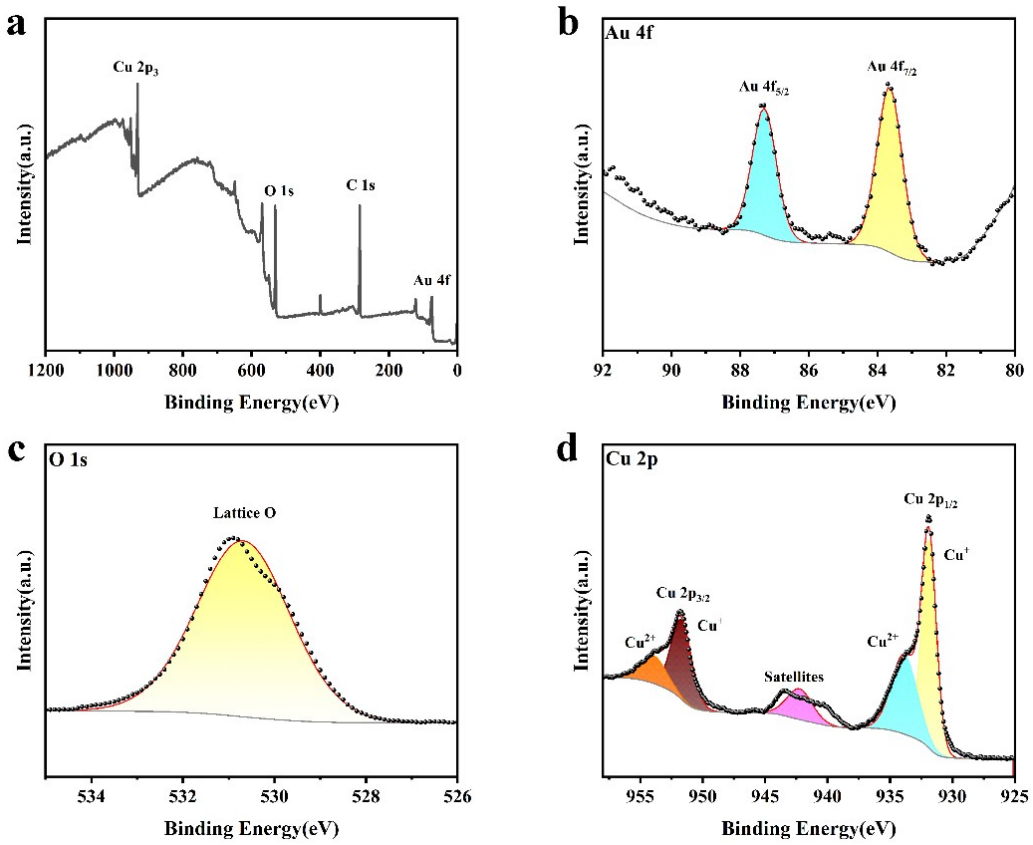


Figure S5 XPS spectra of the Au@Cu_2O (a)full spectrum,(b) Au 4f,(c) O 1s ,and (d)Cu 2p,respectively.

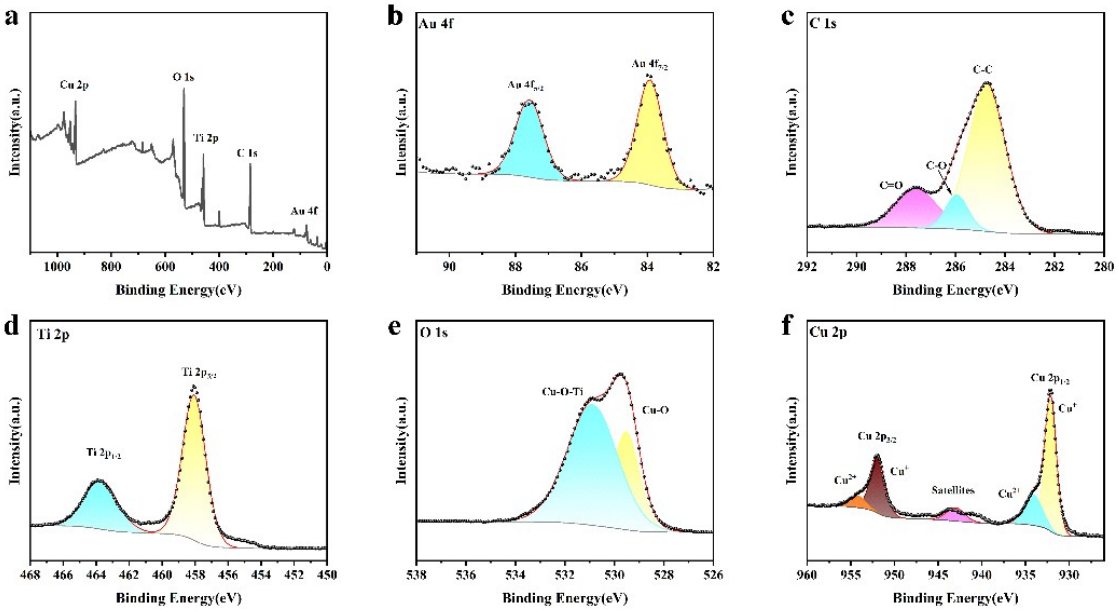


Figure S6 XPS spectra of the Au@Cu_2O@MXene (a)full spectrum,(b) Au 4f,(c) C 1s ,(d)Ti 2p,(e) O 1s , and (f)Cu 2p,respectively.

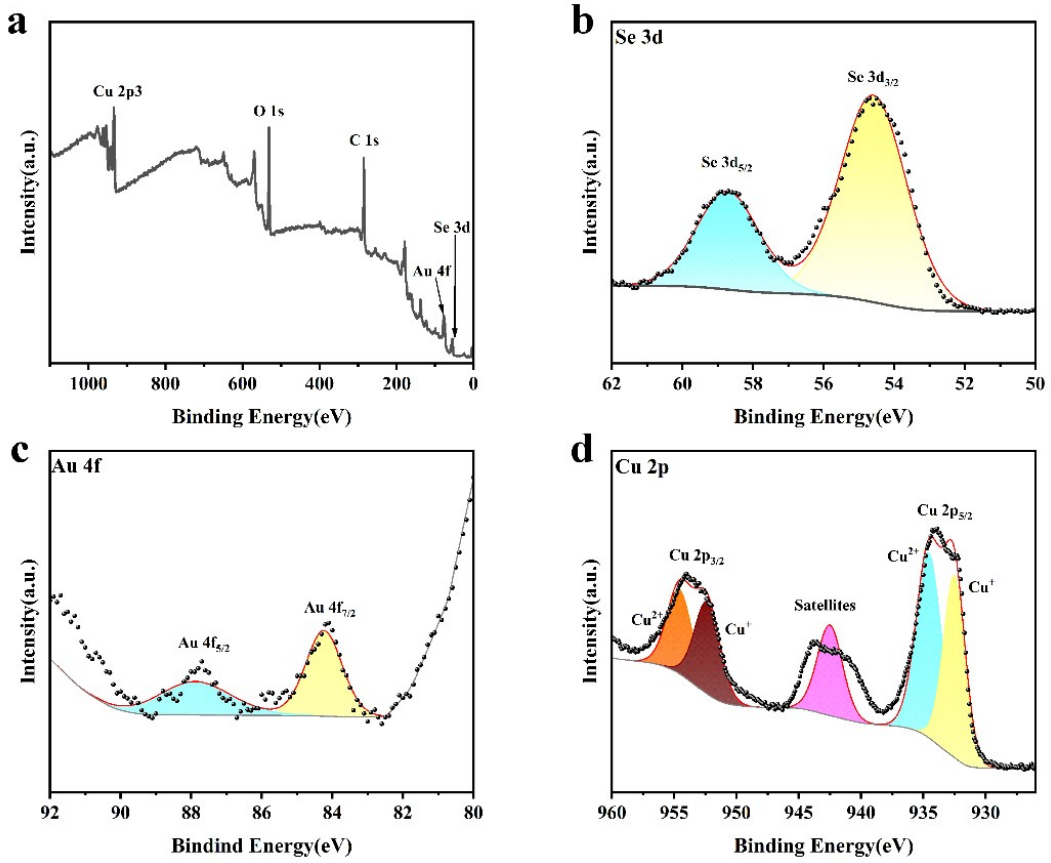
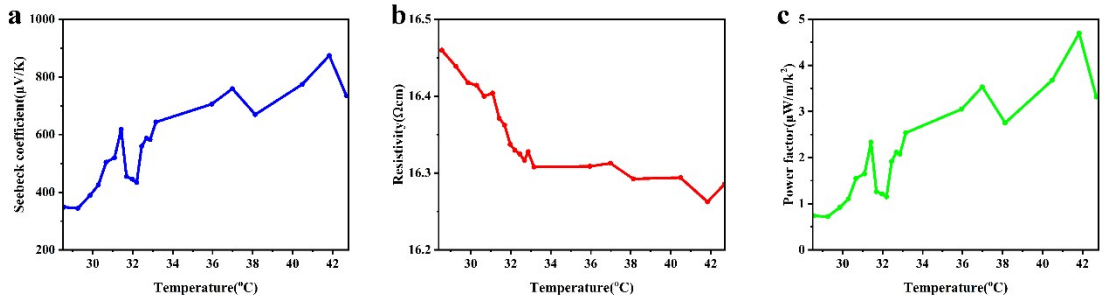
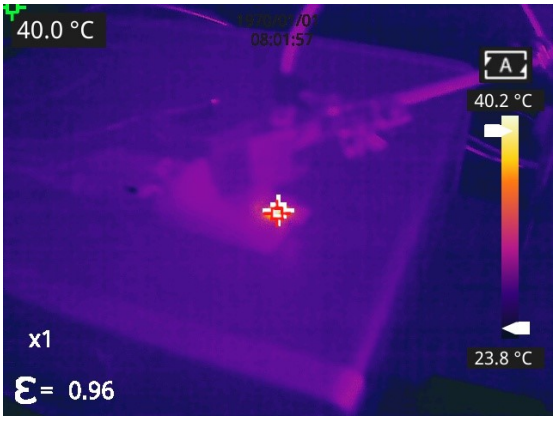


Figure S7 XPS spectra of the Au@$Cu_{2-x}Se$ (a)full spectrum,(b)Se 3d,(c) Au 4f, and (d)Cu 2p,respectively.



Revised Fig. S8 Thermoelectric properties of the Au NBP@$Cu_{2-x}Se$@MXene composite measured in the temperature range of 29-42 °C. (a) Temperature-dependent Seebeck coefficient (S); (b) electrical resistivity (ρ); (c) power factor (PF) as a function of temperature.



Revised Figure S9. Infrared thermographic image of the Au NBP@$Cu_{2-x}Se$@MXene electrode under continuous 1064 nm laser irradiation.

Reference

(1) Sánchez-Iglesias, A.; Winckelmans, N.; Altantzis, T.; Bals, S.; Grzelczak, M.; Liz-Marzán, L. M. High-Yield Seeded Growth of Monodisperse Pentatwinned Gold Nanoparticles through Thermally Induced Seed Twinning. J. Am. Chem. Soc. 2017, 139 (1), 107–110. https://doi.org/10.1021/jacs.6b12143.

(2) Alhabeb, M.; Maleski, K.; Anasori, B.; Lelyukh, P.; Clark, L.; Sin, S.; Gogotsi, Y. Guidelines for Synthesis and Processing of Two-Dimensional Titanium Carbide ($Ti_3C_2T_x$ MXene). Chem. Mater. 2017, 29 (18), 7633–7644. https://doi.org/10.1021/acs.chemmater.7b02847.