

Electronic Supplementary Information

Photocatalytic activity enhancement of Cu₂O cubes functionalized with 2-ethynyl-6-methoxynaphthalene through band structure modulation

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Chemicals

Sodium dodecyl sulfate (NaC₁₂H₂₅SO₄, 100%, Mallinckrodt), anhydrous copper(II) chloride (CuCl₂, 97%, Sigma–Aldrich), sodium hydroxide (NaOH, 98.2%, Mallinckrodt), hydroxylamine hydrochloride (NH₂OH·HCl, 99%, Sigma–Aldrich), sodium oxalate (Na₂C₂O₄, 99.5%, Sigma–Aldrich), chromium trioxide (CrO₃, 99.5%, Acros Organics), methyl orange (C₁₄H₁₄N₃NaO₃S, Hayashi Pure Chemical), and 2-ethynyl-6-methoxynaphthalene (2E-6MN, 97%, Sigma–Aldrich) were used as received without further purification. Potassium sulfate (K₂SO₄, 99%, Sigma–Aldrich) was used as an electrolyte solution for the electrochemical measurements. Ultrapure distilled and deionized water (18.3 MΩ) was used to prepare aqueous solutions. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 97%, Matrix), a spin-trapping reagent, was purified with activated carbon.

Synthesis of Cu₂O crystals

For the synthesis of Cu₂O cubes and octahedra in 250-mL beakers, 1.392 g of SDS was dissolved in 152.8 and 144.8 mL of deionized water, respectively, and kept under vigorous stirring in a water bath at 31 °C. After dissolution of SDS, 1.6 mL of 0.1 M CuCl₂ solution was added. 8–10 min after the addition of 0.1 M CuCl₂ solution into the beakers, 3.2 mL of 1.0 M NaOH solution was added and stirred for 5 s. The solution color changed from colorless to light blue immediately due to the formation of Cu(OH)₂. Then 2.4 and 10.4 mL of 0.2 M NH₂OH·HCl solution were quickly injected with stirring for 10 s, and the aqueous solutions were aged for 50 and 120 min for the synthesis of Cu₂O cubes and octahedra, respectively.

To make Cu₂O rhombic dodecahedra, 27.68 mL of deionized water was added to

0.348 g of SDS in a 50-mL sample vial and kept under vigorous stirring in a water bath at 31 °C. After dissolution of SDS in water, 2 mL of 0.1 M CuCl₂ solution was injected and stirred for 8–10 min. Next, 0.72 mL of 1.0 M NaOH solution was added into the sample vial and stirred for 5 s. Then, 9.6 mL of 0.1 M NH₂OH·HCl solution was added into the sample vial and stirred for 5 s. Finally, the aqueous solutions were aged for 50 min.

After completion of the reaction, the Cu₂O particles were centrifuged at 5000 rpm for 3 min and washed several times with 1:1 volume ratio of water and ethanol and finally washed with 99.8% ethanol. The particles were dried by purging with nitrogen gas and stored in a vacuum chamber.

Calculations of the amounts of 2E-6MN needed for Cu₂O functionalization

From average particle sizes, single particle volumes and surface areas were determined as seen in Fig. S3. From density of Cu₂O (6.0 g/cm³), the number of particles, total particle surface area, and total surface copper atoms of each particle shape in 10 mg were obtained, using the surface copper atom densities reported before (10.98, 14.27, and 7.76 Cu atoms/nm² for the (100), (111), and (110) planes of Cu₂O, respectively).¹ For molar ratios of 1:5, 1:10, and 1:100 of surface Cu atoms to 2E-6MN, weights of 2E-6MN needed were calculated for addition into 5 mL of ethanol with dispersed Cu₂O crystals (Table S1). Next, for fair photocatalytic activity comparison, a fixed total particle surface area of 0.03 m² was chosen. From the number of particles having this total surface area, 7.89, 4.72, and 6.99 mg of 2E-6MN-functionalized Cu₂O rhombic dodecahedra, octahedra, and cubes were respectively used for the photocatalysis experiments (Table S2).

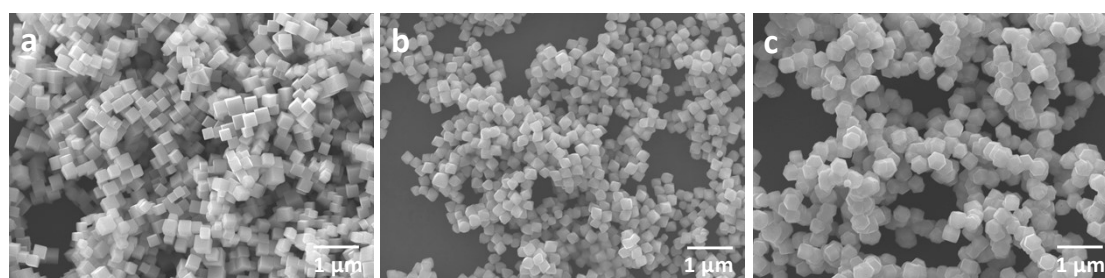


Fig. S1 SEM images of the synthesized Cu₂O (a) cubes, (b) octahedra, and (c) rhombic dodecahedra.

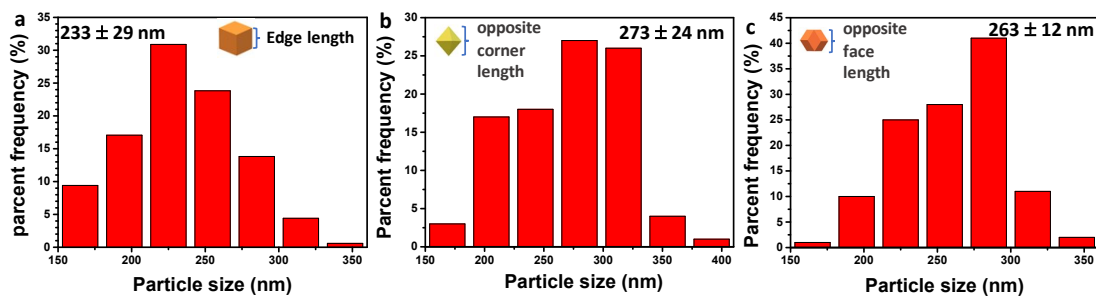


Fig. S2 Size distribution histograms of the synthesized Cu₂O (a) cubes, (b) octahedra, and (c) rhombic dodecahedra.

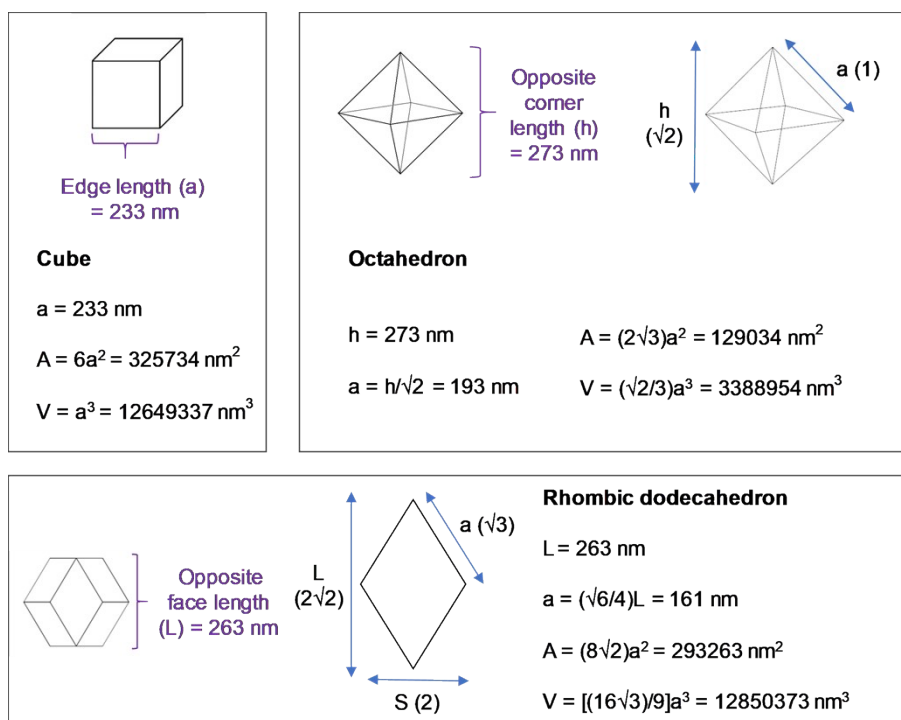


Fig. S3 Calculations of particle surface areas and volumes.

Table S1 Calculations for the amounts of 2E-6MN molecules needed to functionalize different Cu₂O crystals.

	RD			Octahedra			Cubes		
Size (nm)	263			273			233		
Weight (mg)	10			10			10		
Surface area (nm ²)	3.8×10^{16}			6.3×10^{16}			4.3×10^{16}		
Surface Cu atoms	2.95×10^{17}			9.05×10^{18}			4.71×10^{17}		
Surface Cu atoms:2 E-6MN	1:5	1:10	1:100	1:5	1:10	1:100	1:5	1:10	1:100
Weight of 2E-6MN (mg)	0.44	0.89	8.9	1.37	2.74	27.4	0.7	1.4	14.2

Table S2 Calculations of the amounts of different Cu₂O crystals needed to have a total particle surface area of 0.3 m².

	RD	Octahedra	Cubes
Size (nm)	263	273	233
Fixed surface area (m ²)	0.3	0.3	0.3
Number of particles	1.0×10^{11}	2.3×10^{11}	9.2×10^{10}
Total volume (nm ³)	1.315×10^{18}	7.881×10^{17}	1.165×10^{18}
Weight (mg)	7.89	4.72	6.99

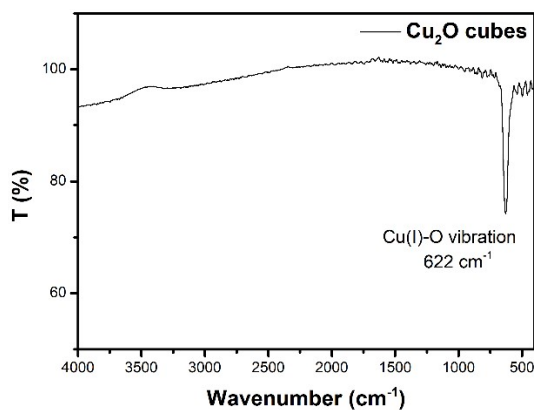


Fig. S4 FT-IR spectrum of pristine Cu₂O cubes.

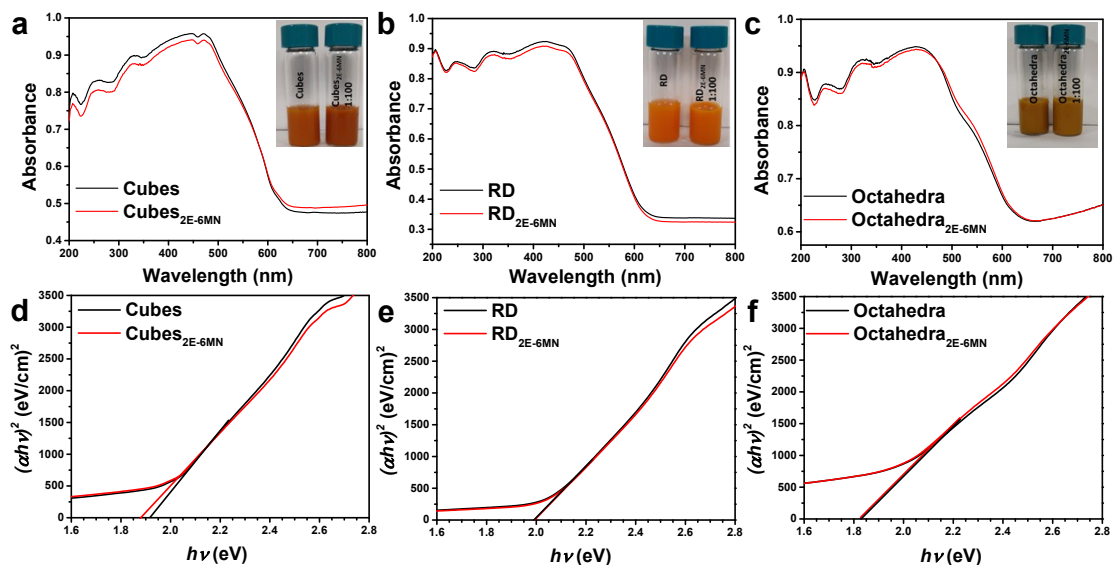


Fig. S5 (a–c) Diffuse reflectance spectra of the pristine and 2E-6MN-modified Cu_2O crystals and (d–f) the corresponding Tauc plots. Cu_2O particles with a surface Cu atom to 2E-6MN molar ratio of 1:100 were used. Photographs of the particle solutions are also shown.

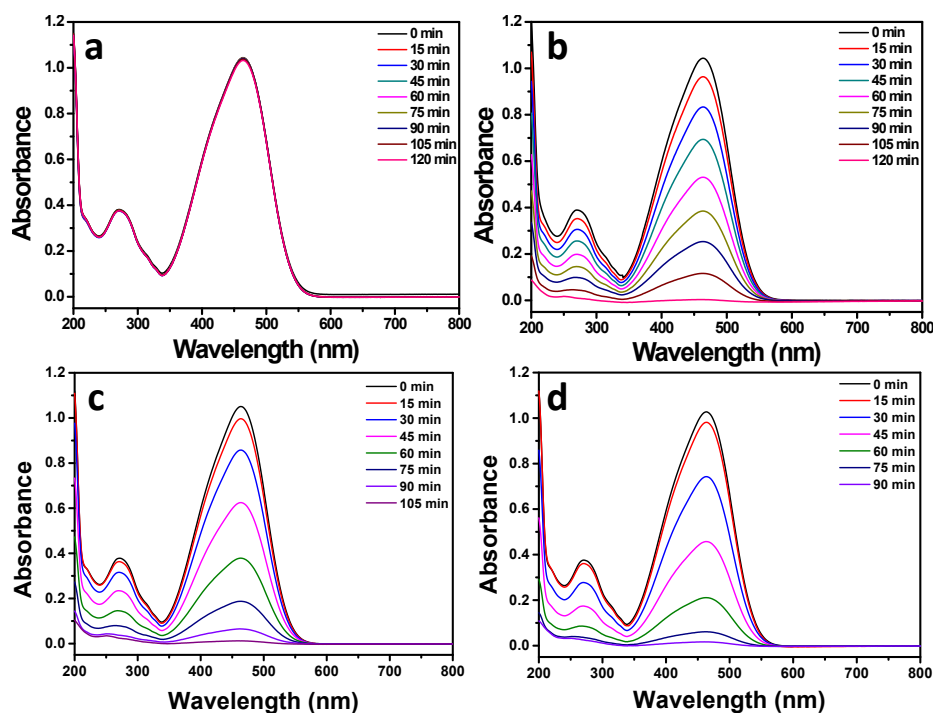


Fig. S6 UV-vis absorption spectra of methyl orange as a function of irradiation time using (a) pristine and (b–d) 2E-6MN-modified Cu_2O cubes as the photocatalysts with surface copper atoms to 2E-6MN molar ratios of (b) 1:5, (c) 1:10, and (d) 1:100.

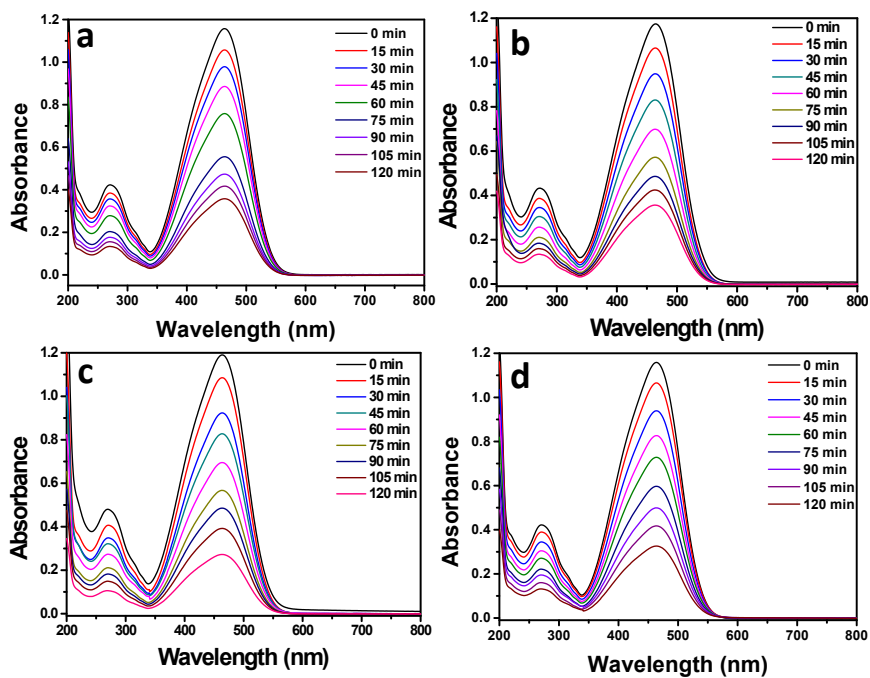


Fig. S7 UV-vis absorption spectra of methyl orange as a function of irradiation time using (a) pristine and (b-d) 2E-6MN-modified Cu₂O octahedra as the photocatalysts with surface Cu atoms to 2E-6MN molar ratios of (b) 1:5, (b) 1:10, and (c) 1:100.

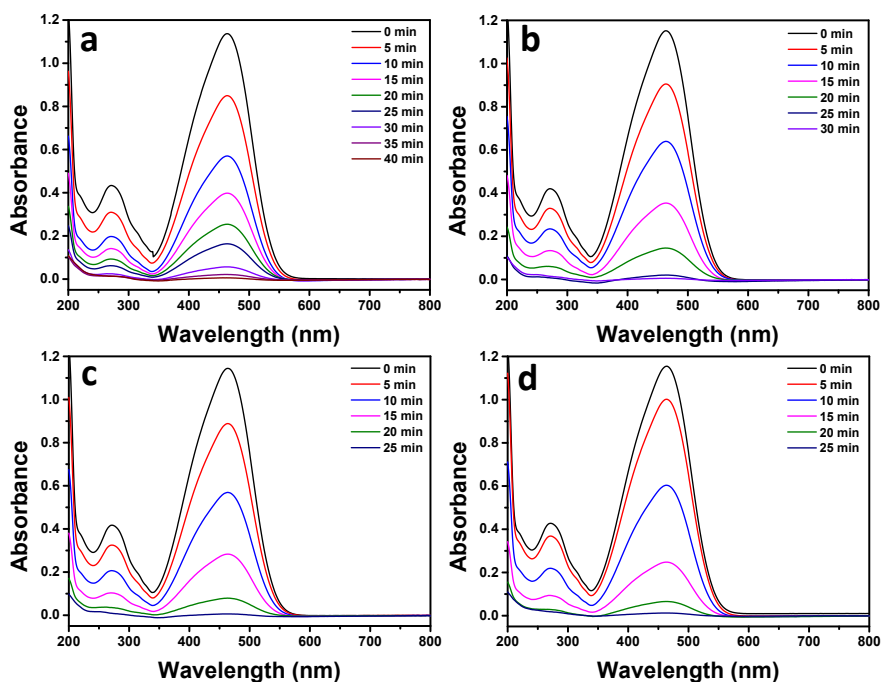


Fig. S8 UV-vis absorption spectra of methyl orange as a function of irradiation time using (a) pristine and (b-d) 2E-6MN-modified Cu₂O rhombic dodecahedra as the photocatalysts with surface Cu atoms to 2E-6MN molar ratios of (b) 1:5, (b) 1:10, and (c) 1:100.

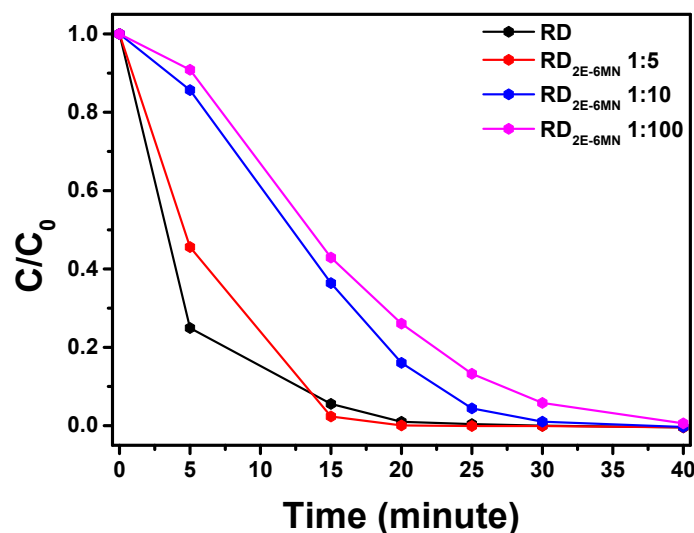


Fig. S9 Extents of MO photodegradation using pristine and modified Cu₂O rhombic dodecahedra that have been observed in one experiment.

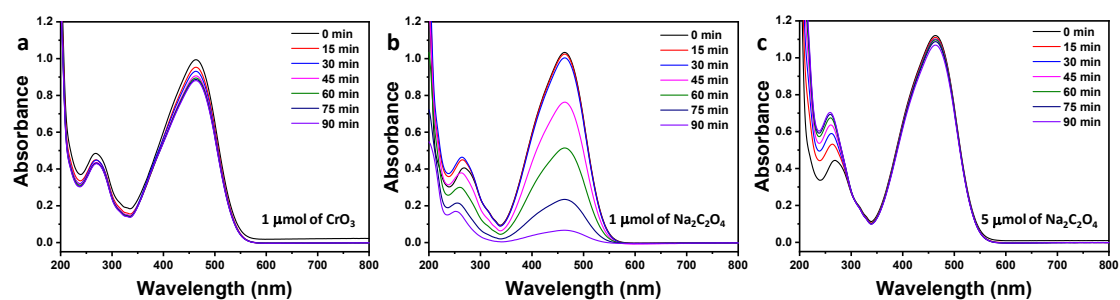
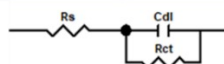


Fig. S10 UV-vis absorption spectra of methyl orange as a function of irradiation time using 1:100 2E-6MN-modified Cu₂O cubes as the photocatalyst and in the presence of (a) 1 μmole of CrO₃, (b) 1 μmole of Na₂C₂O₄, and (c) 5 μmole of Na₂C₂O₄.

Table S3 Charge transfer resistance (R_{ct}) values for different Cu₂O samples and the equivalent circuit used to fit the EIS data.

Sample	R_s (Ω)	C_{dl} (μF)	R_{CT} ($K\Omega$)
Cubes	65.74	3.8	9.3
Cubes _{2E-6MN} 1:100	22.8	6.4	5.6
RD	24.38	17.9	5.5
RD _{2E-6MN} 1:100	23.37	40.4	2.9
Octahedra	25.47	33.4	6.5
Octahedra _{2E-6MN} 1:5	25.08	33.7	6.1



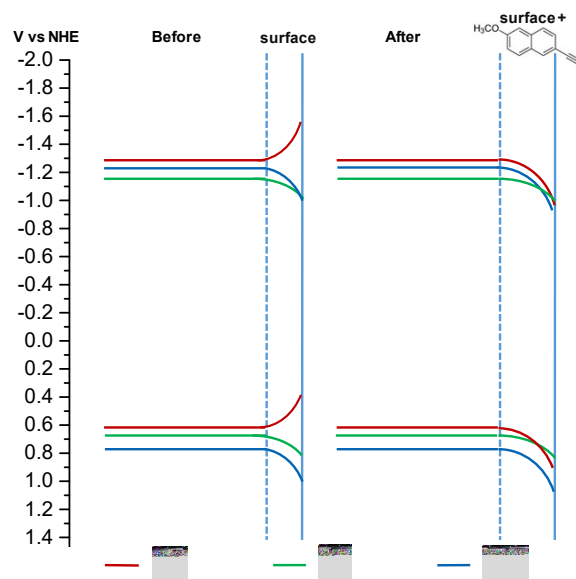


Fig. S11 Adjusted band diagram of different Cu_2O crystals before and after 2E-6MN modification. The valence band energies use values from our previous work, while the conduction band energies use the determined band gaps from this work.² The idea is that the new surface is now consisted of the original thin surface layer of Cu_2O causing the facet-dependent behaviors plus the 2E-6MN monolayer.

references

- 1 K. Chanda, S. Rej and M. H. Huang, M. H. *Chem.–Eur. J.*, 2013, **19**, 16036–16043.
- 2 T.-Y. Liang, S.-J. Chan, A. S. Patra, P.-L. Hsieh, Y.-A. Chen, H.-H. Ma and M. H. Huang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 11515–11523.