Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Highly efficient photoelectrocatalytic reduction of CO_2 on the Ti_3C_2/g-C_3N_4 heterojunction with rich Ti^{3+} and pyri-N species

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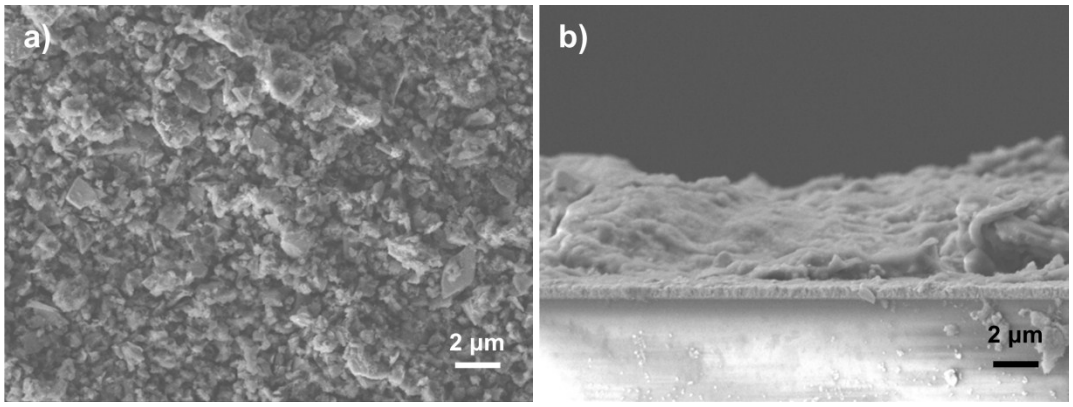

Figure S1. (a) FESEM image and (b) cross-sectional SEM image of Pd-TCCN photocathode

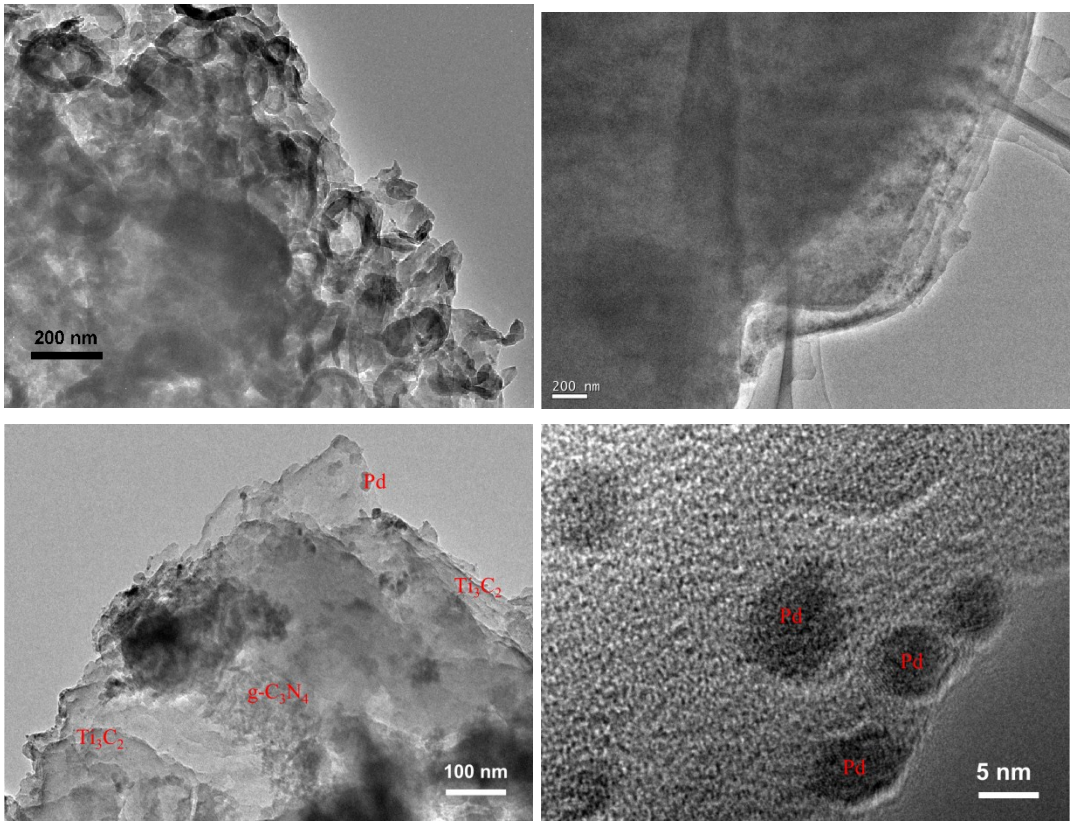

Figure S2. TEM images of (a) g-C_3N_4, (b) Ti_3C_2 and (c,d) Pd-TCCN3

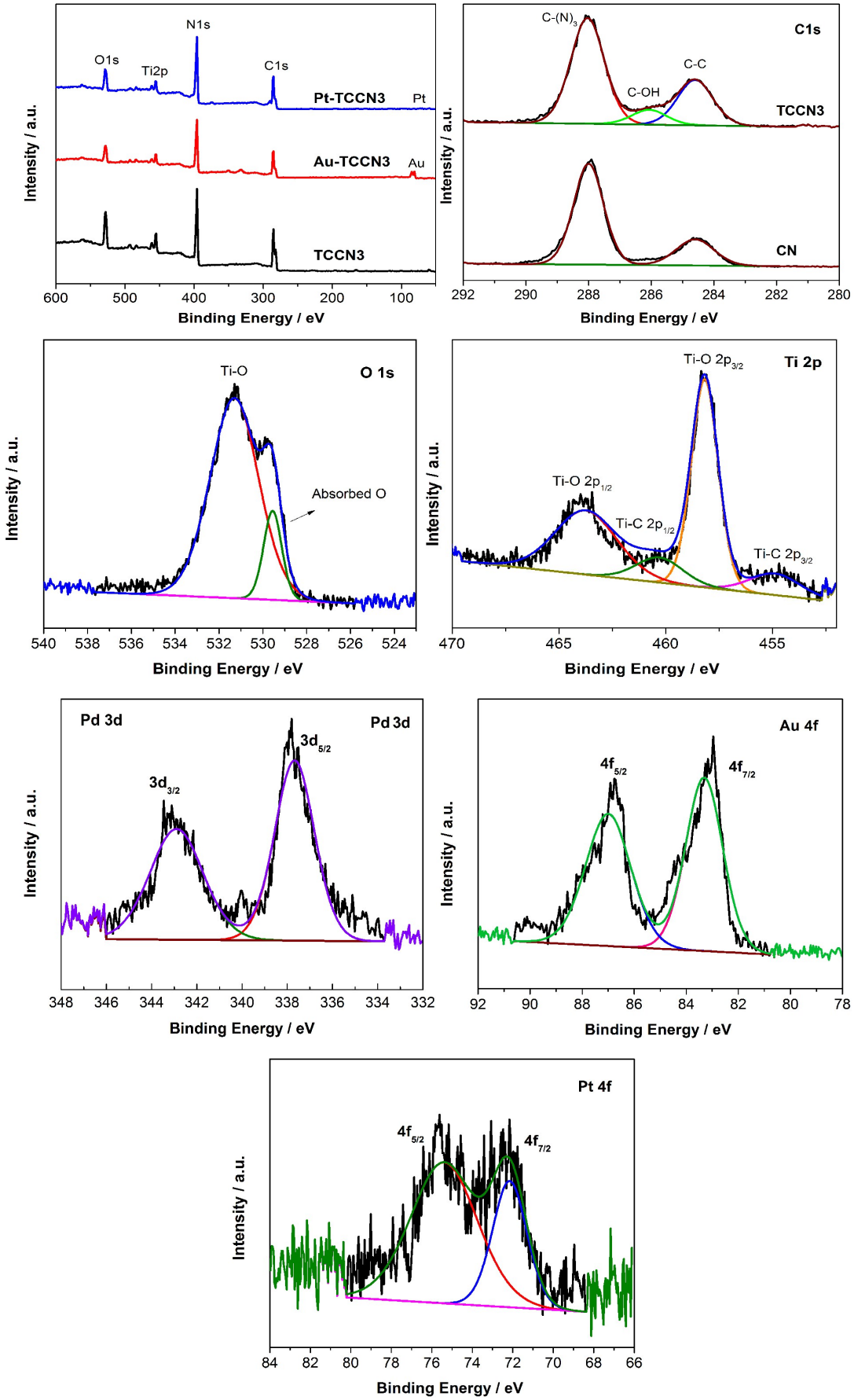

Figure S3. (a) XPS survey spectra of TCCN3, Au-TCCN3 and Pt-TCCN3 electrodes,

high-resolution XPS spectra of (b) C 1s (c) O 1s, (d) Ti 2p (e) Pd 1s, (f) Au 4f, and (g) Pt 4f

Table S1. The N 1s species and concentration in CN and TCCN3 electrodes

Sample	C–N–C	N–$(C)_3$	N–H
CN	45.2	34	20.8
TCCN3	57.2	36.6	6.2

Table S2. The BET surface area, pore volume and pore size of all samples

Sample	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (nm)
CN	20.9	0.129	24.9
TCCN1	21.6	0.095	17.7
TCCN2	28.2	0.106	15.1
TCCN3	17.3	0.059	13.6

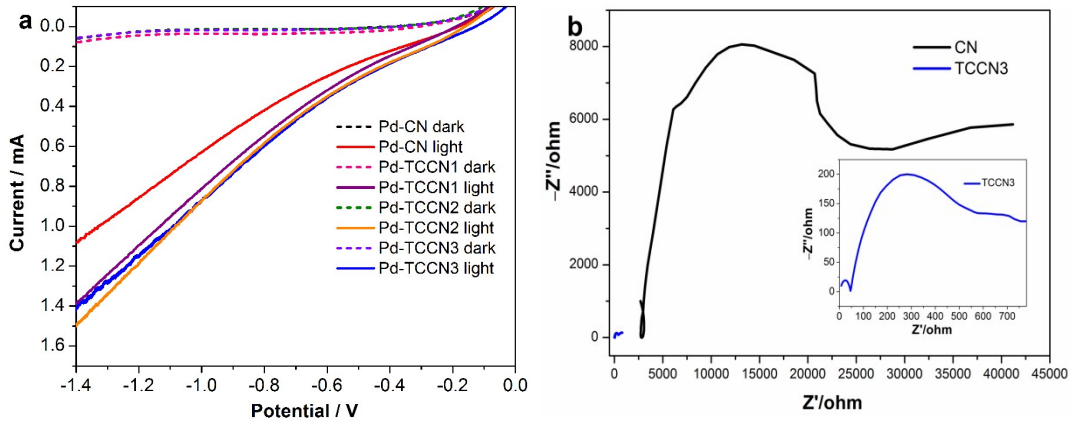

Figure S4. (a) LSV curves under dark and light irradiation conditions of different photocathodes and (b) EIS Nyquist plots of pristine CN and TCCN3 photocathodes

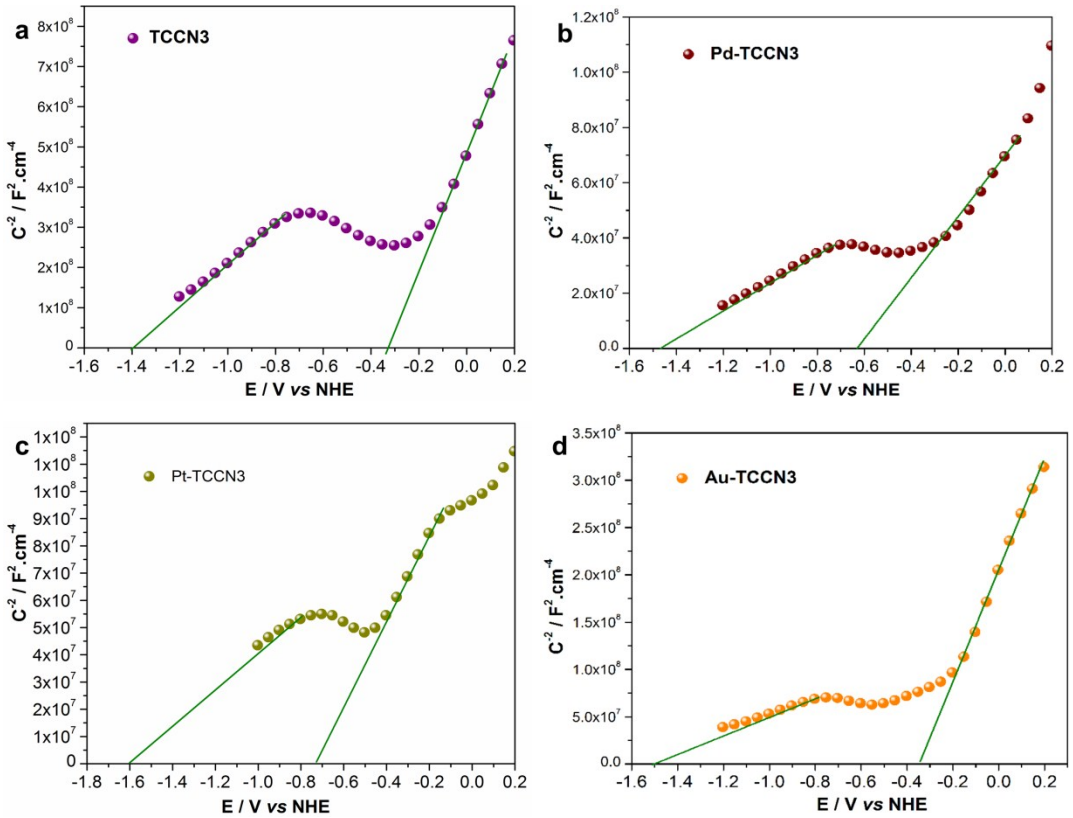

Figure S5. Mott-Schottky plots of TCCN3 and M-TCCN3 photocathodes

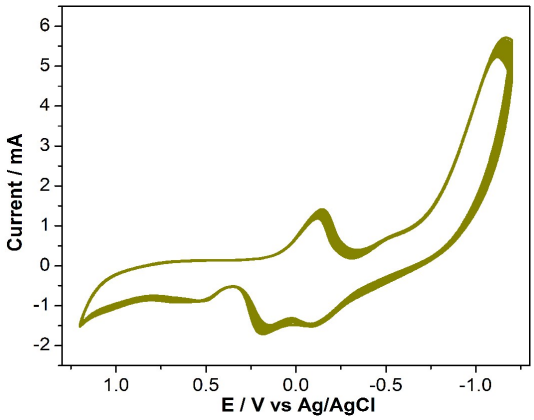

Figure S6. 100 continuous cyclic voltammograms of Pd-TCCN3 photocathode obtained at a scan rate of 50 mV s^{-1} in CO_2 saturated $KHCO_3$ (0.1 M) aqueous solution at dark condition

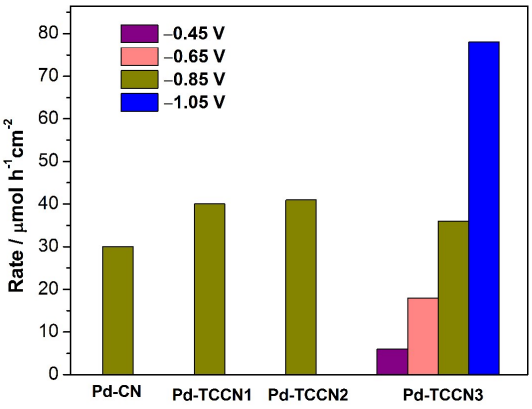

Figure S7. The H_2 evolution rate for different photocathodes of Pd-CN, Pd-TCCN1, and Pd-TCCN2 at −0.85 V; and for Pd-TCCN3 at −0.45V ~ −1.05 V in the two-electrode system

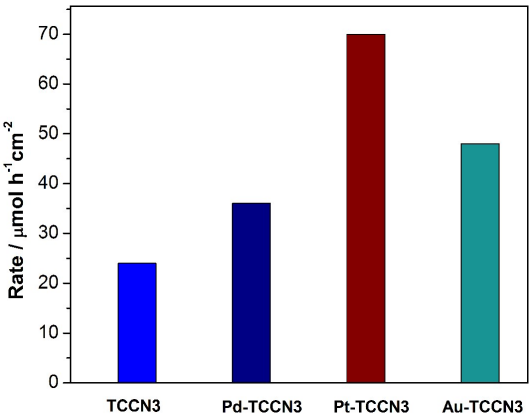

Figure S8. The H_2 evolution rate for different photocathodes of TCCN3, Pd-TCCN3, Pt-TCCN3 and Au-TCCN3 at −0.85 V in the two-electrode system

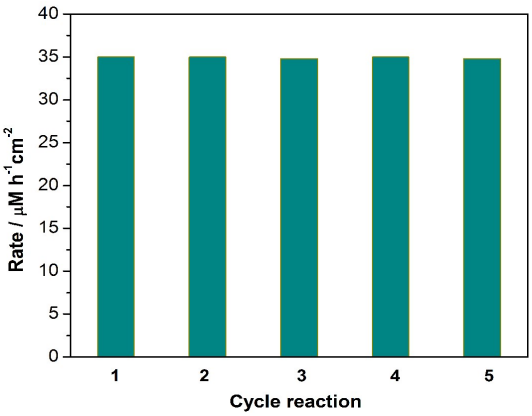

Figure S9. Five cycles of reaction with Pd-TCCN3 served as the photocathode at −

0.85 V ($HCOO^-$) in the two-electrode system

Table S3. The selectivity of liquid products for different photocathode at different voltage

Photocathode	Voltage (V)	S_{HCOO-} (%)	S_{MeOH} (%)
Pd-CN	−0.85	82.4	17.6
Pd-TCCN1	−0.85	62.1	37.9
Pd-TCCN2	−0.85	66.6	33.4
Pd-TCCN3	−0.85	72.1	27.9
TCCN3	−0.85	0	100
Pt-TCCN3	−0.85	0	100
Au-TCCN3	−0.85	0	100
Pd-TCCN3	−0.45	0	100
Pd-TCCN3	−0.65	49.8	30.2
Pd-TCCN3	−1.05	80.6	19.4

∗ Selectivity (S)

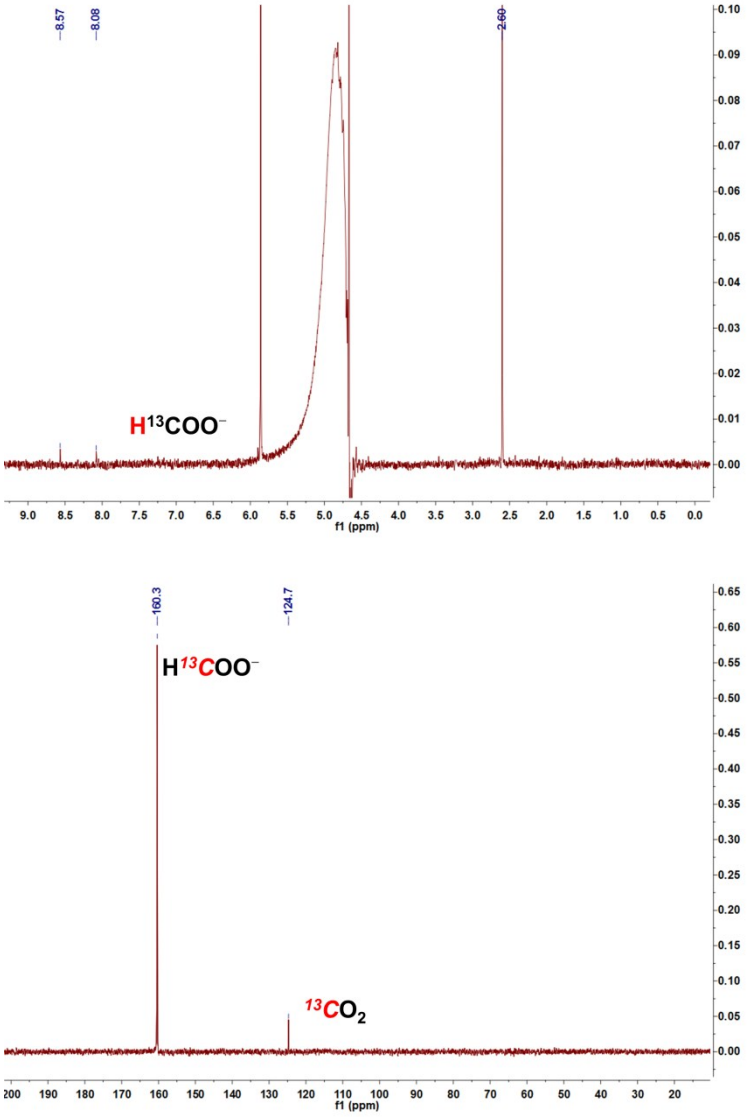

Figure S10. ^{1}H NMR and ^{13}C NMR spectra of the isotope labeling experiment results