Newly-modeled graphene-based ternary nanocomposite for the magnetophotocatalytic reduction of CO_2 with electrochemical performance

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Experimental details

1. Characterization of the photocatalyst

The morphological states of the nanocomposite were analyzed by transmission electron microscopy (TEM, Hitachi H9500, Tokyo, Japan) and scanning electron microscopy (SEM-EDX; JSM-5600 JEOL, Akishima, Tokyo, Japan) with EDX incorporation. The interplane structure of the nanocomposite was analyzed by the high-resolution transmission electron microscopy (HRTEM, 300 kV Philips CM30). The surface chemical state was examined by X-ray photoelectron microscopy (XPS, PHI 5000 Versa Probe) with a monochromatized Al Ka X-ray source (10 kV, 1500 W, pass energy = 40 eV). The crystalline nature of the nanocomposite was examined by X-ray diffraction (XRD, SHIMADZU XRD-6000) equipped with a Cu Ka X-ray source (1.5406 Å). The functional groups in the sample were tested using a Fourier transform infrared (FTIR iS5, Thermoscience). The bandgap value was obtained using the Kubelka–Munk function obtained from the UV–vis DRS data (SHIMADZU UV-2600). The photocurrent value was tested using a computer-controlled Versa-STAT-3 electrochemical analyzer. The photoluminescence analysis (PL) was conducted at room temperature between 530-1000 nm regions, and the measurement used the 514 nm laser with ND 10% filter as a light source. The electrochemical phenomena of the samples were analyzed by electrochemical impedance spectra (EIS) using an electrochemical analyzer (Zahner, Germany) in a standard three-electrode system using the prepared samples as the working electrodes with an active area of ca. 0.25 cm^2, a Pt wire as the counter electrode, and Ag/AgCl (saturated KCl) as a reference electrode. The electrolytes were a mixed aqueous solution containing $K_3[Fe(CN)_6]$ (1 mmol/L), $K_4[Fe(CN)_6]$ (1 mmol/L), and KCl (0.1 mol/L).

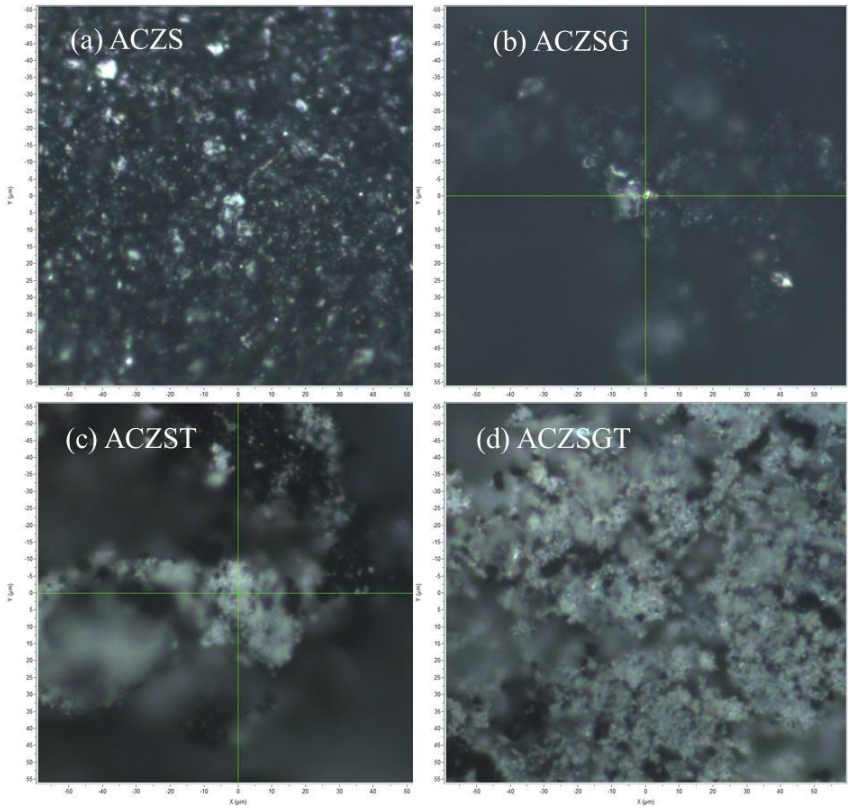


Figure S1. Sample state of the $AgCuZnS_2$, $AgCuZnS_2$-Graphene, $AgCuZnS_2$-TiO_2, $AgCuZnS_2$-Graphene-TiO_2 nanocomposite.

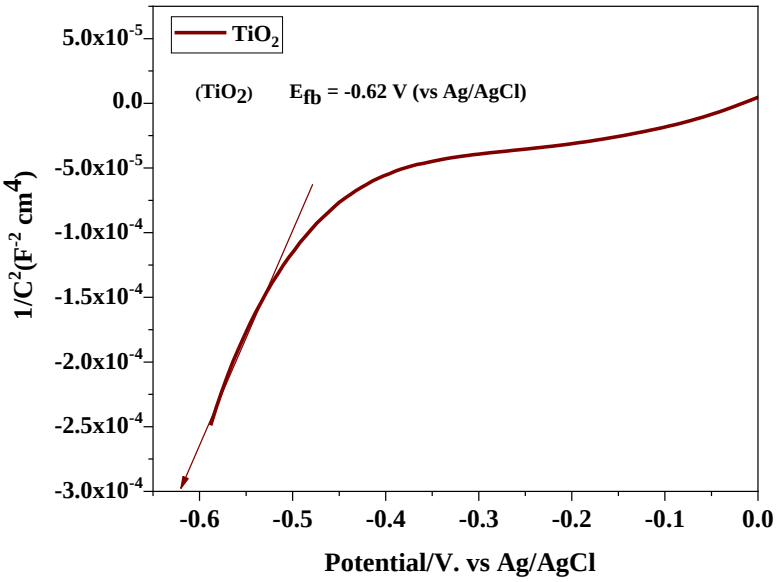


Figure S2. Mott-Schottky plot of the pure TiO_2.

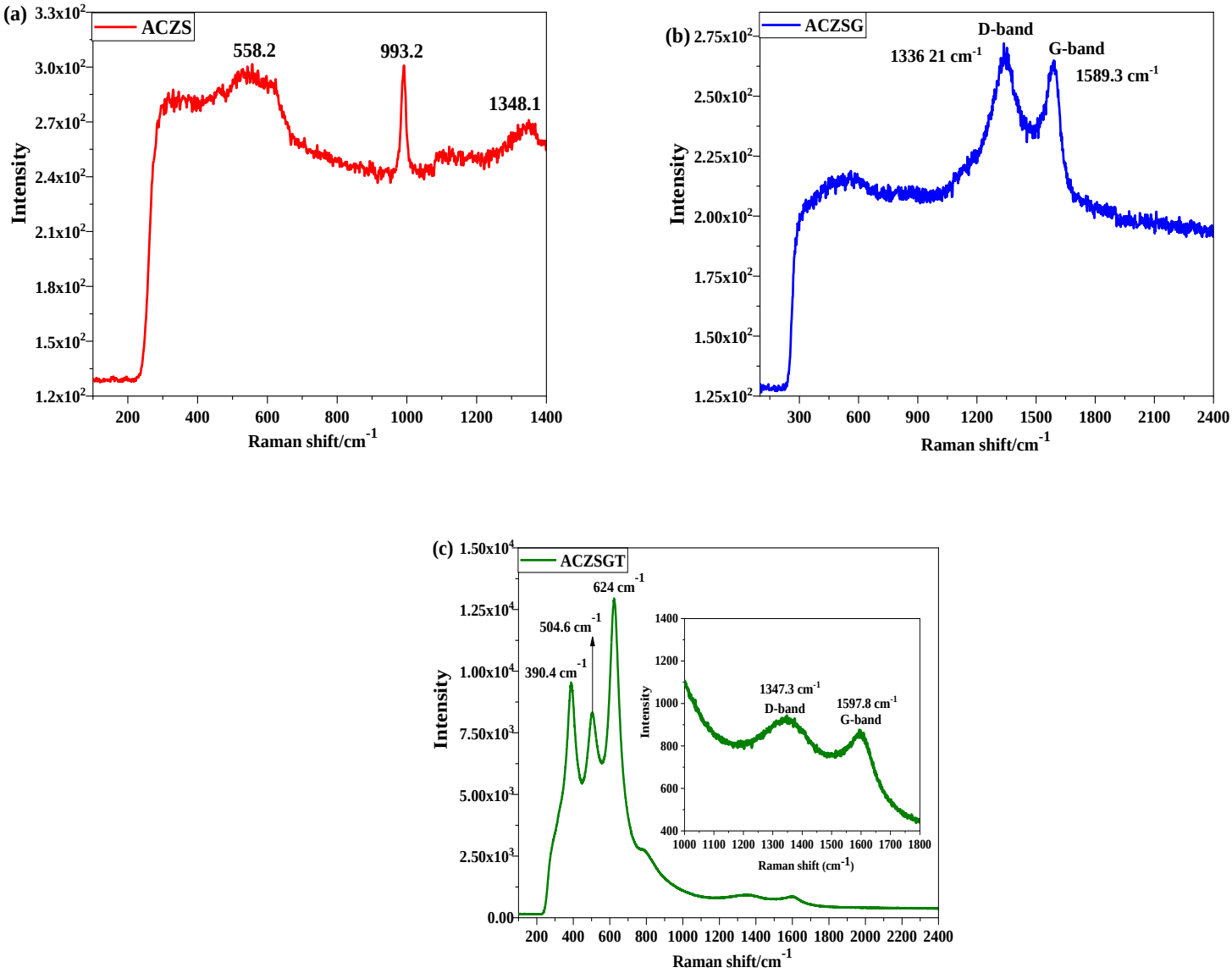


Figure S3. Raman spectra of the ACZS, ACZSG and ACZSGT nanocomposite.

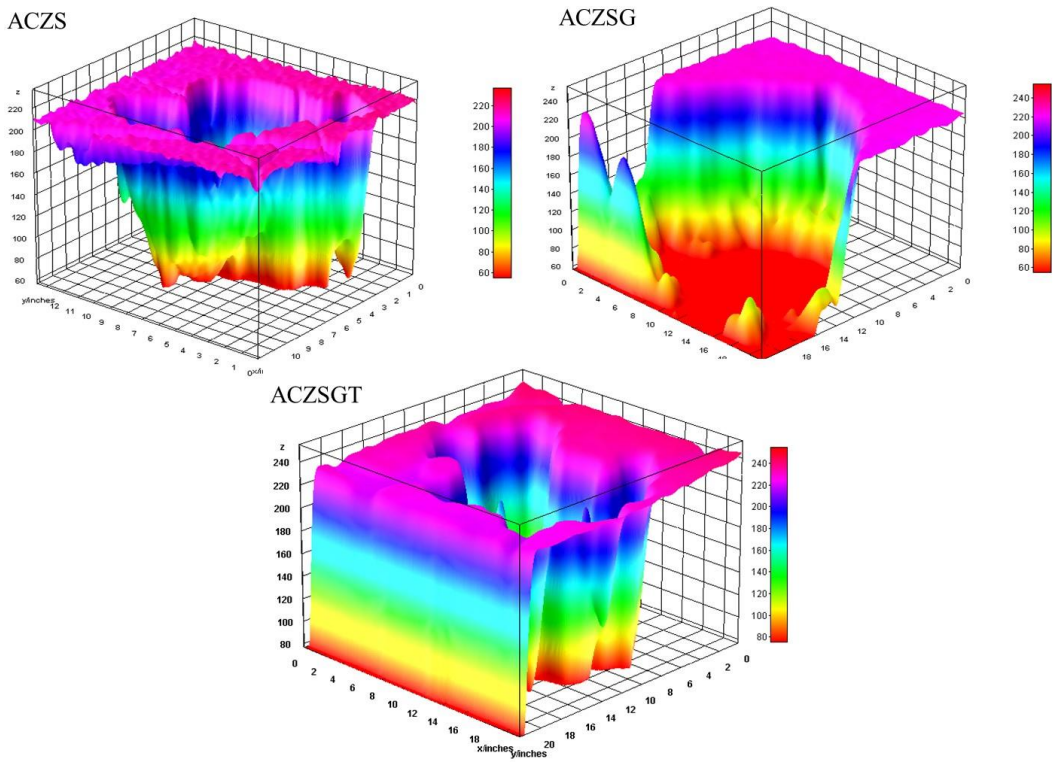
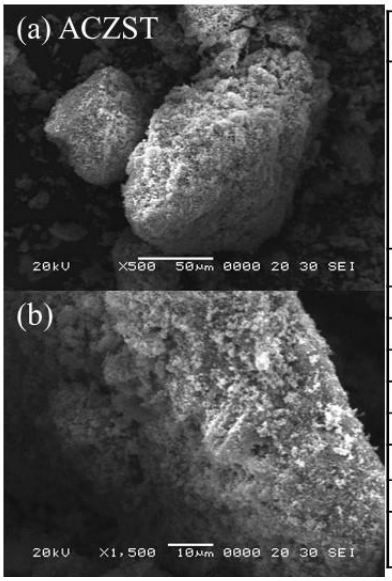


Figure S4. 3D-interactive surface plot of $AgCuZnS_2$, $AgCuZnS_2$-Graphene, $AgCuZnS_2$-Graphene-TiO_2 nanocomposite.



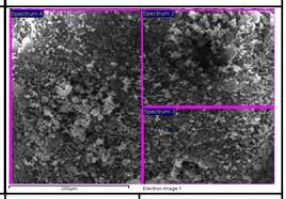
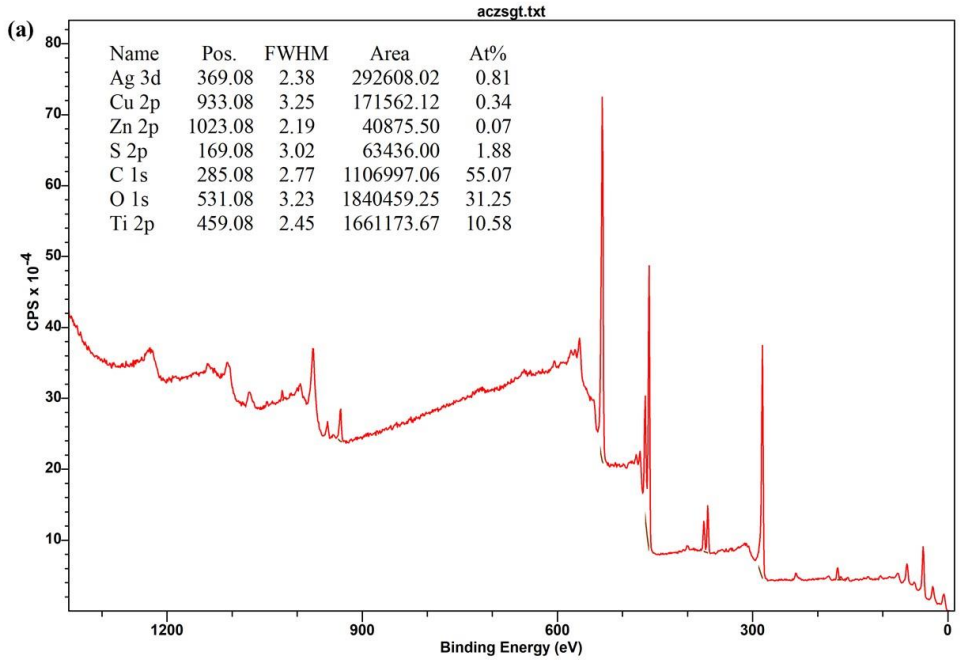
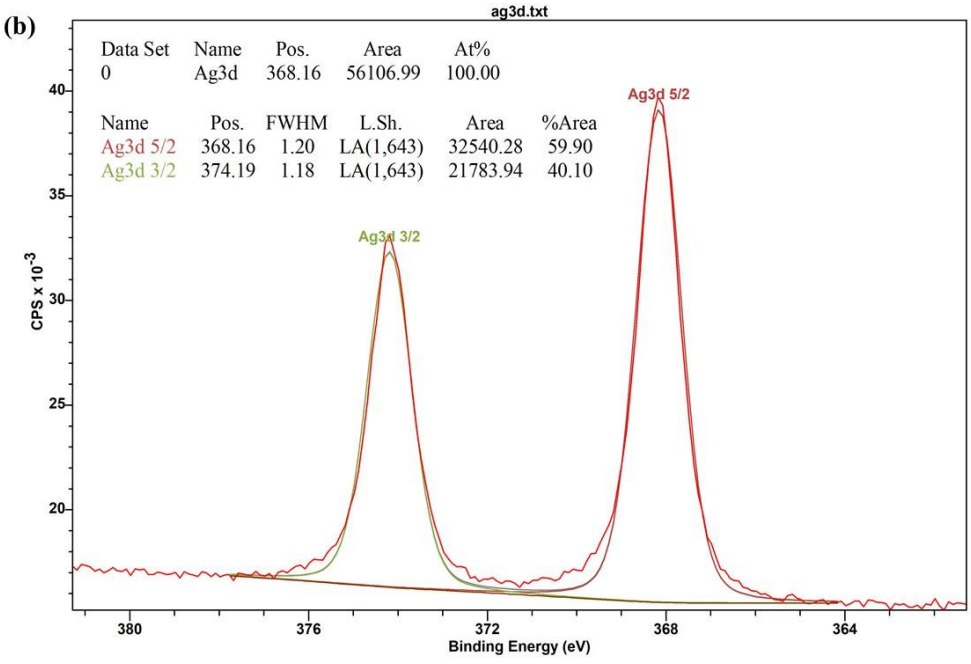
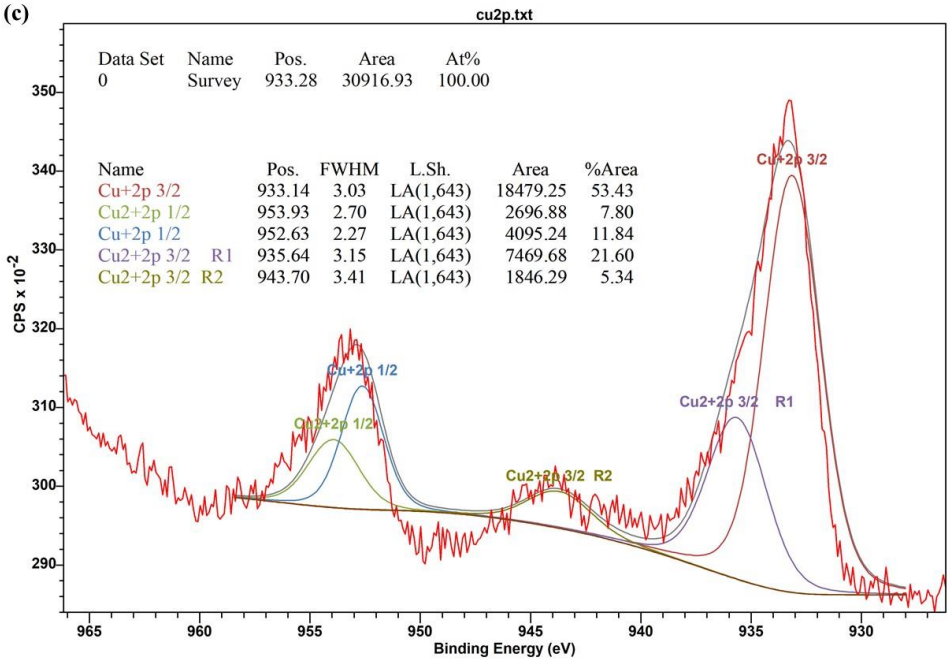
(c)	$AgCuZnS_2$-TiO_2	
1		
2	**Element**	**Weight%**
3	**Ag**	**12.87**
4	**Cu**	**11.39**
5	**Zn**	**13.77**
6	**S**	**8.85**
7	**C**	-
8	**Ti**	**32.71**
9	**O**	**20.91**
10	**Totals**	**100.00**

Figure S5. (a, b) SEM images, (c) EDX analysis of the $AgCuZnS_2$-TiO_2 nanocomposite.


(a)
aczsgt.txt
Name Pos. FWHM Area At%
Ag 3d 369.08 2.38 292608.02 0.81
Cu 2p 933.08 3.25 171562.12 0.34
Zn 2p 1023.08 2.19 40875.50 0.07
S 2p 169.08 3.02 63436.00 1.88
C 1s 285.08 2.77 1106997.06 55.07
O 1s 531.08 3.23 1840459.25 31.25
Ti 2p 459.08 2.45 1661173.67 10.58
CPS x 10^-4
Binding Energy (eV)
CasaXPS (This string can be edited in CasaXPS.DEF/PrintFootNote.txt)

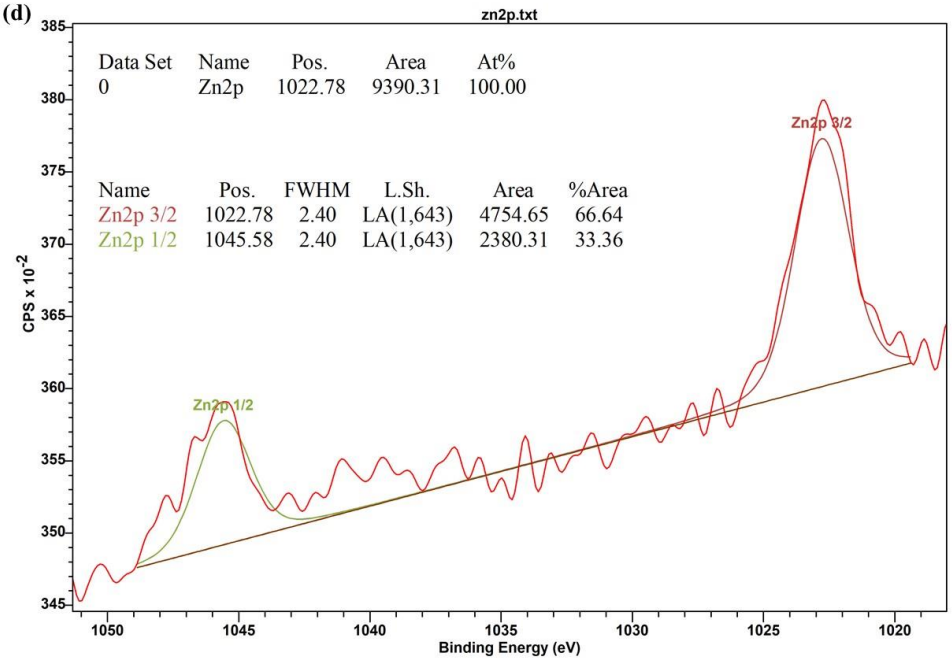

(b)
ag3d.txt
Data Set Name Pos. Area At%
0 Ag3d 368.16 56106.99 100.00
Name Pos. FWHM L.Sh. Area %Area
Ag3d 5/2 368.16 1.20 LA(1,643) 32540.28 59.90
Ag3d 3/2 374.19 1.18 LA(1,643) 21783.94 40.10
Ag3d 5/2
Ag3d 3/2
CPS x 10^-3
Binding Energy (eV)
CasaXPS (This string can be edited in CasaXPS.DEF/PrintFootNote.txt)

(c)



CasaXPS (This string can be edited in CasaXPS.DEF/PrintFootNote.txt)

(d)



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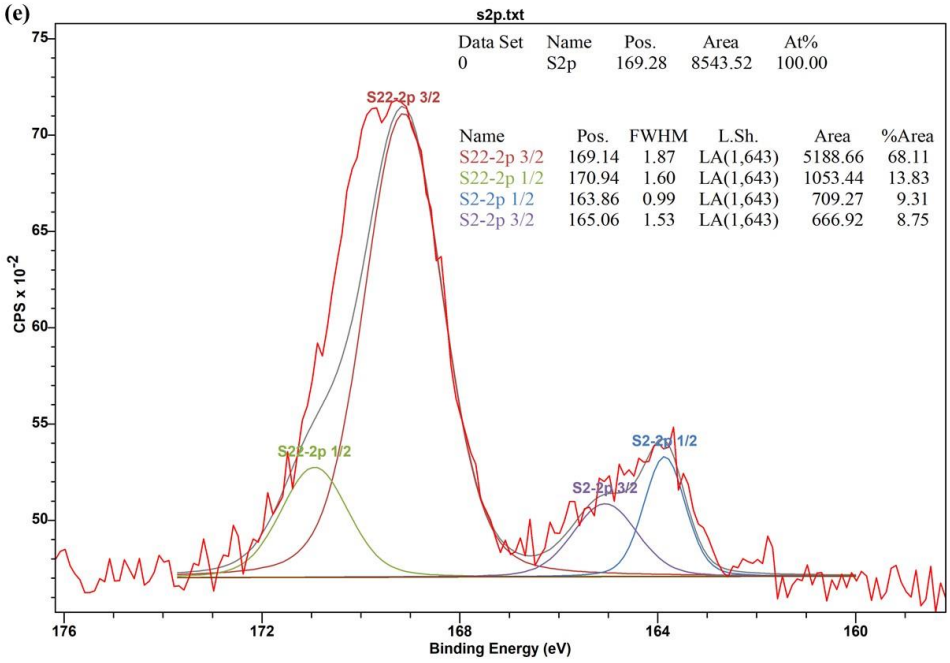
(e)



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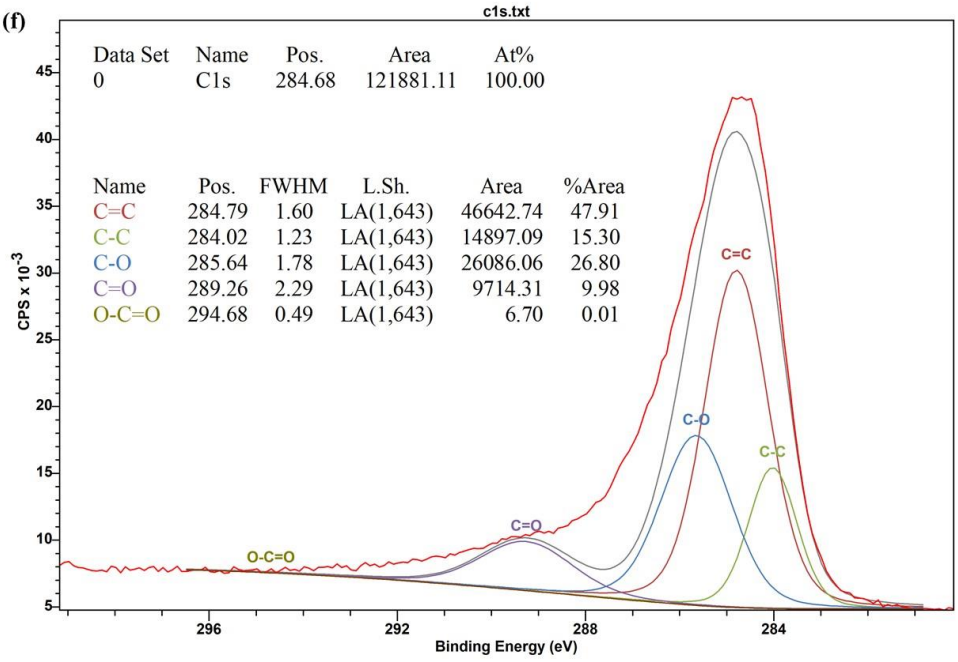
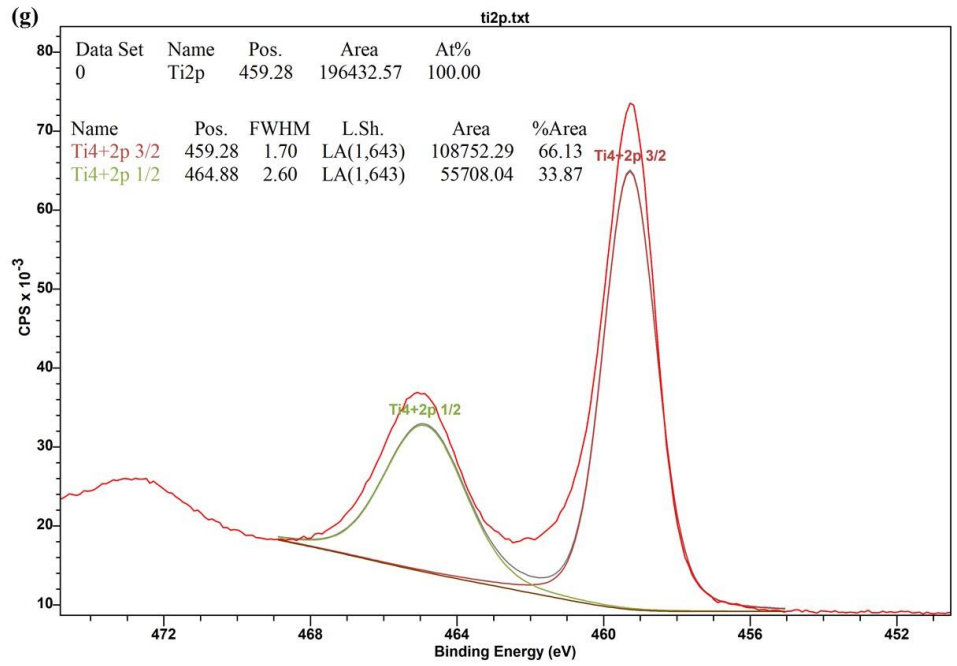
(f)



CasaXPS (This string can be edited in CasaXPS.DEF/PrintFootNote.txt)



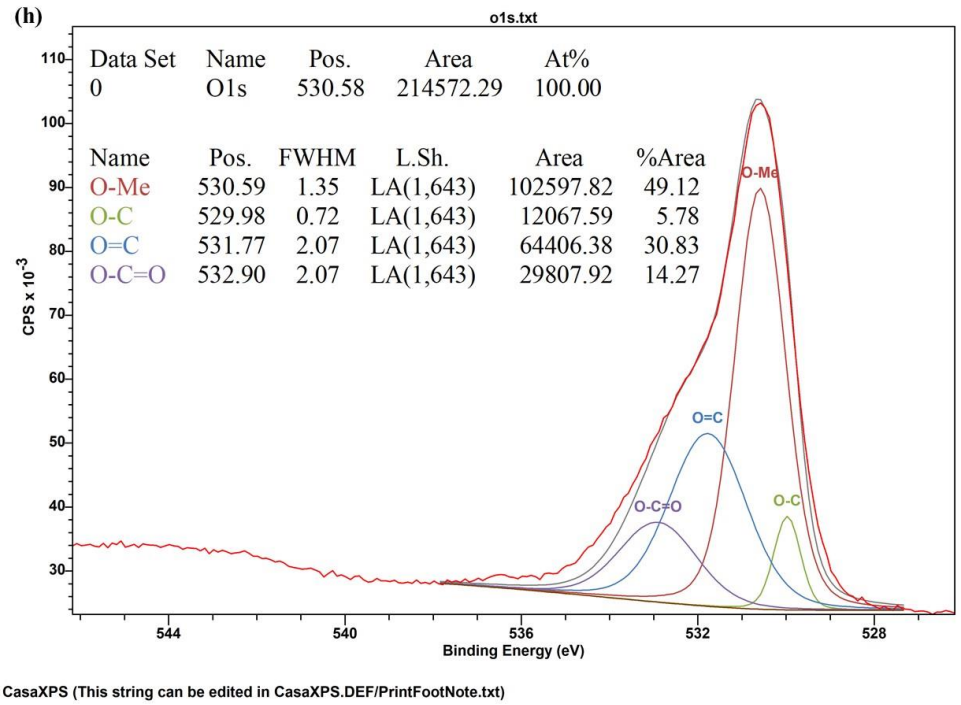


Figure S6. (a) XPS survey spectra and the high-resolution XPS spectra of $AgCuZnS_2$-Graphene-TiO_2, (b) Ag3d, (c) Cu2p, (d) Zn2p, (e) S2p, (f) C1s, (g) Ti2p and (h) O1s.

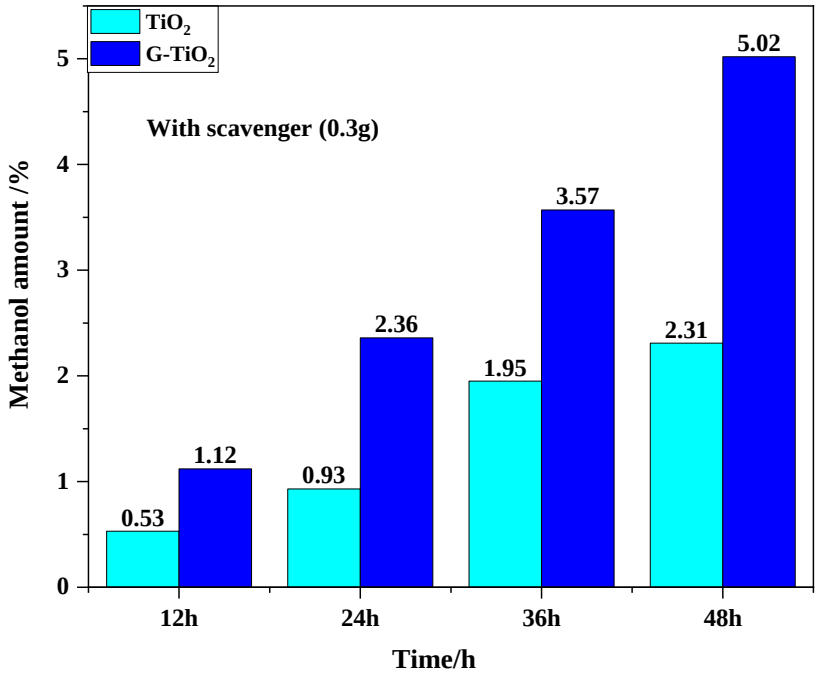
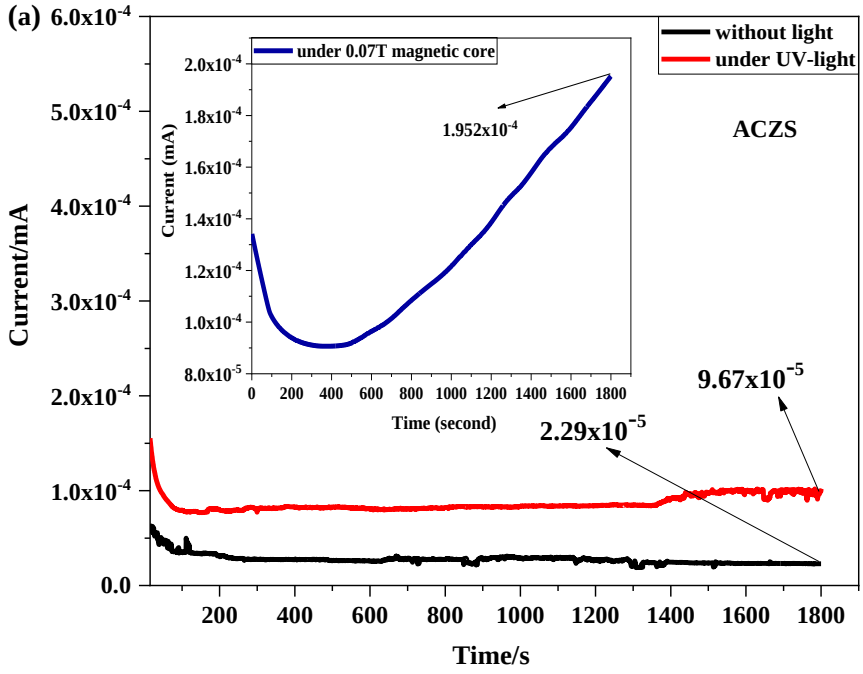
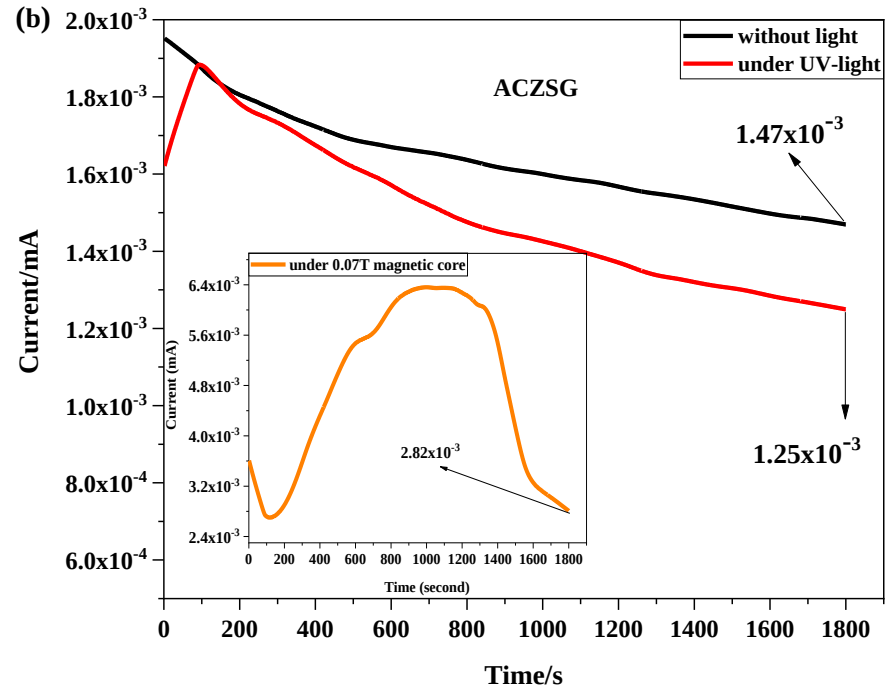
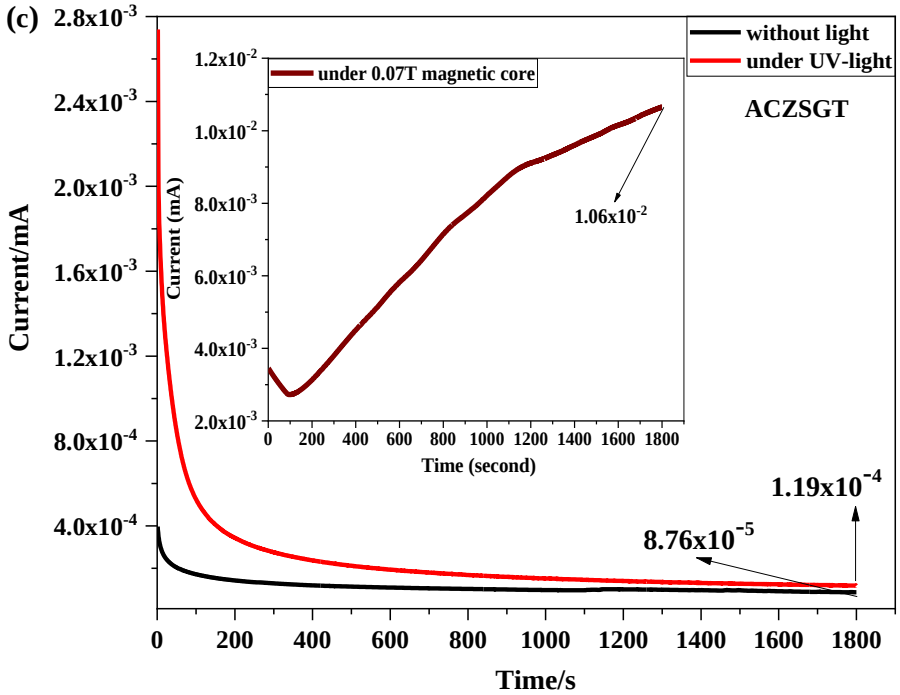


Figure S7. Methanol production rate on pure Graphene, Graphene-TiO_2 nanocomposite under UV-light irradiation.




(b)
without light
under UV-light
ACZSG
1.47x10-3
1.25x10-3
under 0.07T magnetic core
2.82x10-3
Current (mA)
Time (second)
Current/mA
Time/s


(c)
without light
under UV-light
ACZSGT
under 0.07T magnetic core
1.06x10-2
Current (mA)
Time (second)
1.19x10-4
8.76x10-5
Current/mA
Time/s

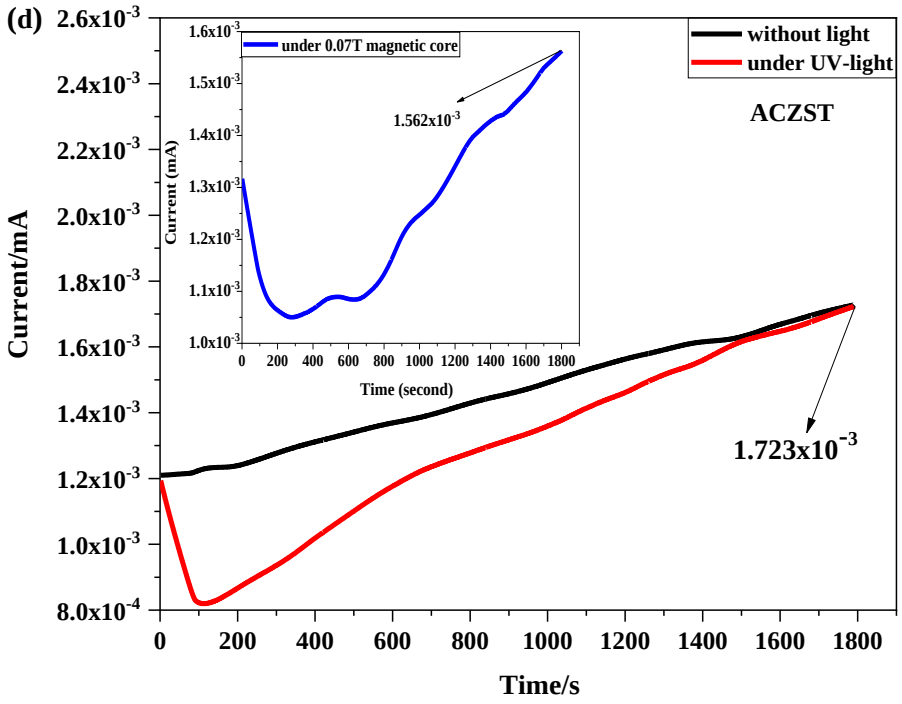
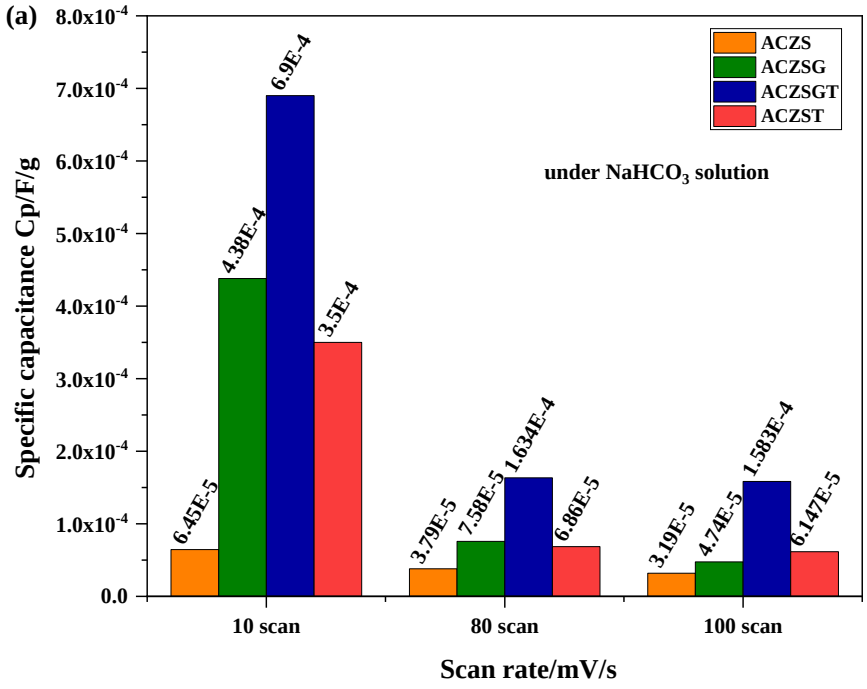
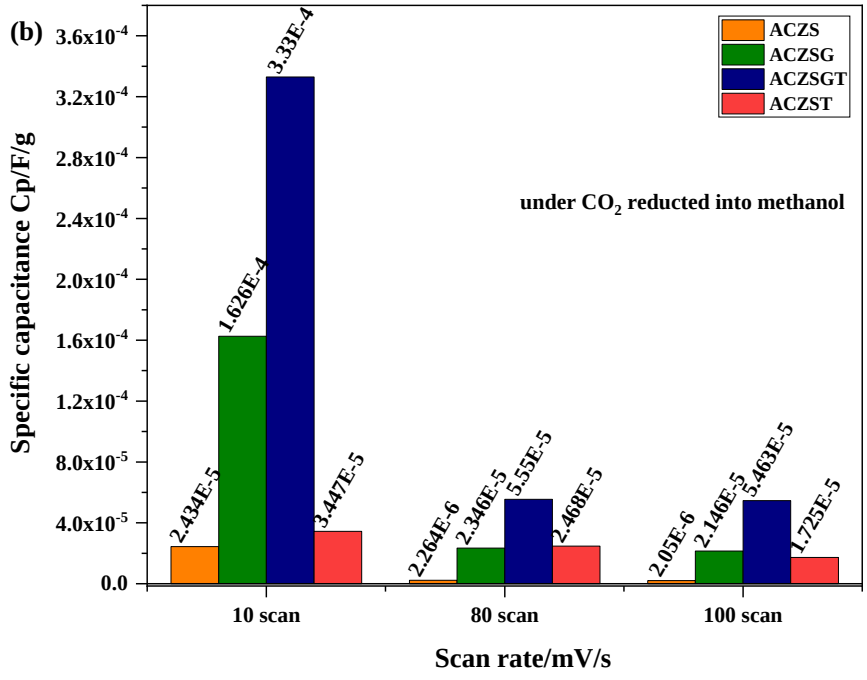


Figure S8. Chronoamperometry of $AgCuZnS_2$, $AgCuZnS_2$-Graphene, $AgCuZnS_2$-Graphene-TiO_2, $AgCuZnS_2$-TiO_2 nanocomposite (inner : under the 0.07T magnetic field condition).


(a)
ACZS
ACZSG
ACZSGT
ACZST
under NaHCO3 solution
Specific capacitance Cp/F/g
8.0x10-4
7.0x10-4
6.0x10-4
5.0x10-4
4.0x10-4
3.0x10-4
2.0x10-4
1.0x10-4
0.0
6.45E-5
4.38E-4
6.9E-4
3.5E-4
3.79E-5
7.58E-5
1.634E-4
6.86E-5
3.19E-5
4.74E-5
1.583E-4
6.147E-5
10 scan
80 scan
100 scan
Scan rate/mV/s


(b)
ACZS
ACZSG
ACZSGT
ACZST
under CO2 reducted into methanol
Specific capacitance Cp/F/g
3.6x10-4
3.2x10-4
2.8x10-4
2.4x10-4
2.0x10-4
1.6x10-4
1.2x10-4
8.0x10-5
4.0x10-5
0.0
2.434E-5
1.626E-4
3.33E-4
3.447E-5
2.264E-6
2.346E-5
5.55E-5
2.468E-5
2.05E-6
2.146E-5
5.463E-5
1.725E-5
10 scan
80 scan
100 scan
Scan rate/mV/s

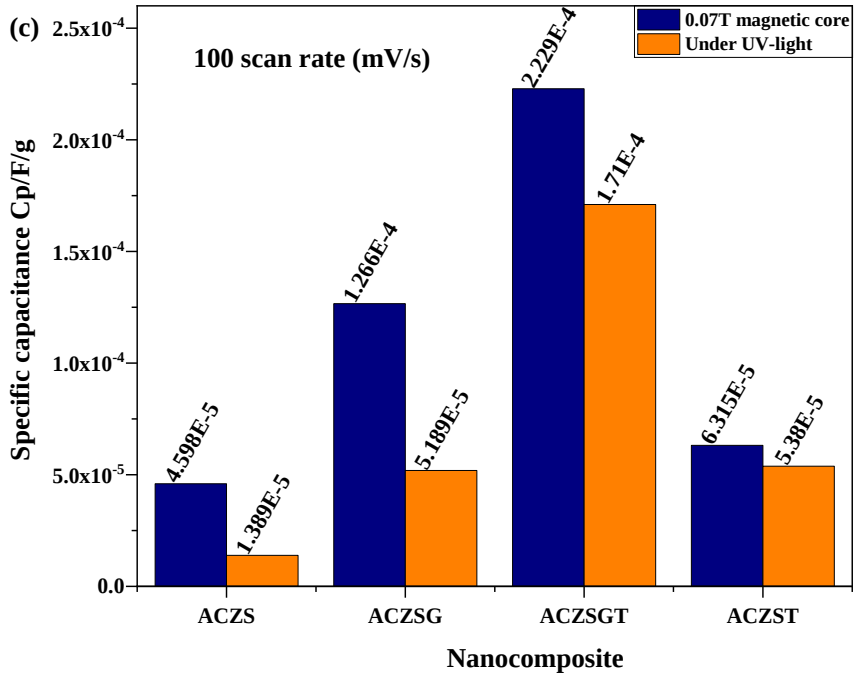


Figure S9. Specific capacitance of the $AgCuZnS_2$, $AgCuZnS_2$-Graphene, $AgCuZnS_2$-Graphene-TiO_2, $AgCuZnS_2$-TiO_2 working electrode (a) under $NaHCO_3$ solution, (b) CO_2 reduced to methanol, (c) under the UV-light irradiation and 0.07T magnetic core.

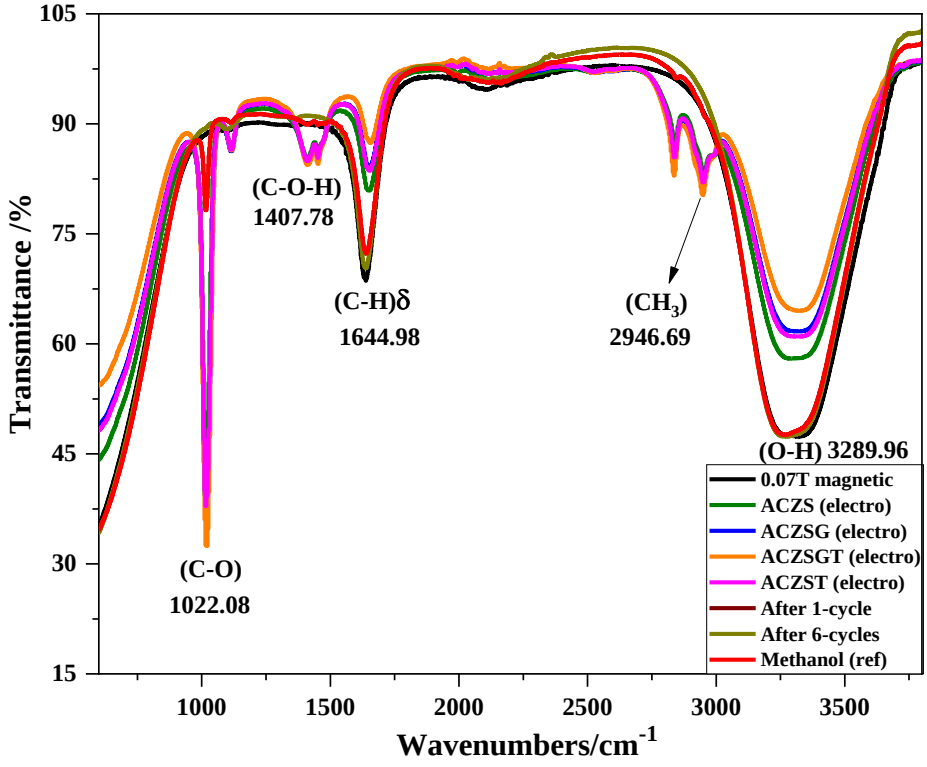


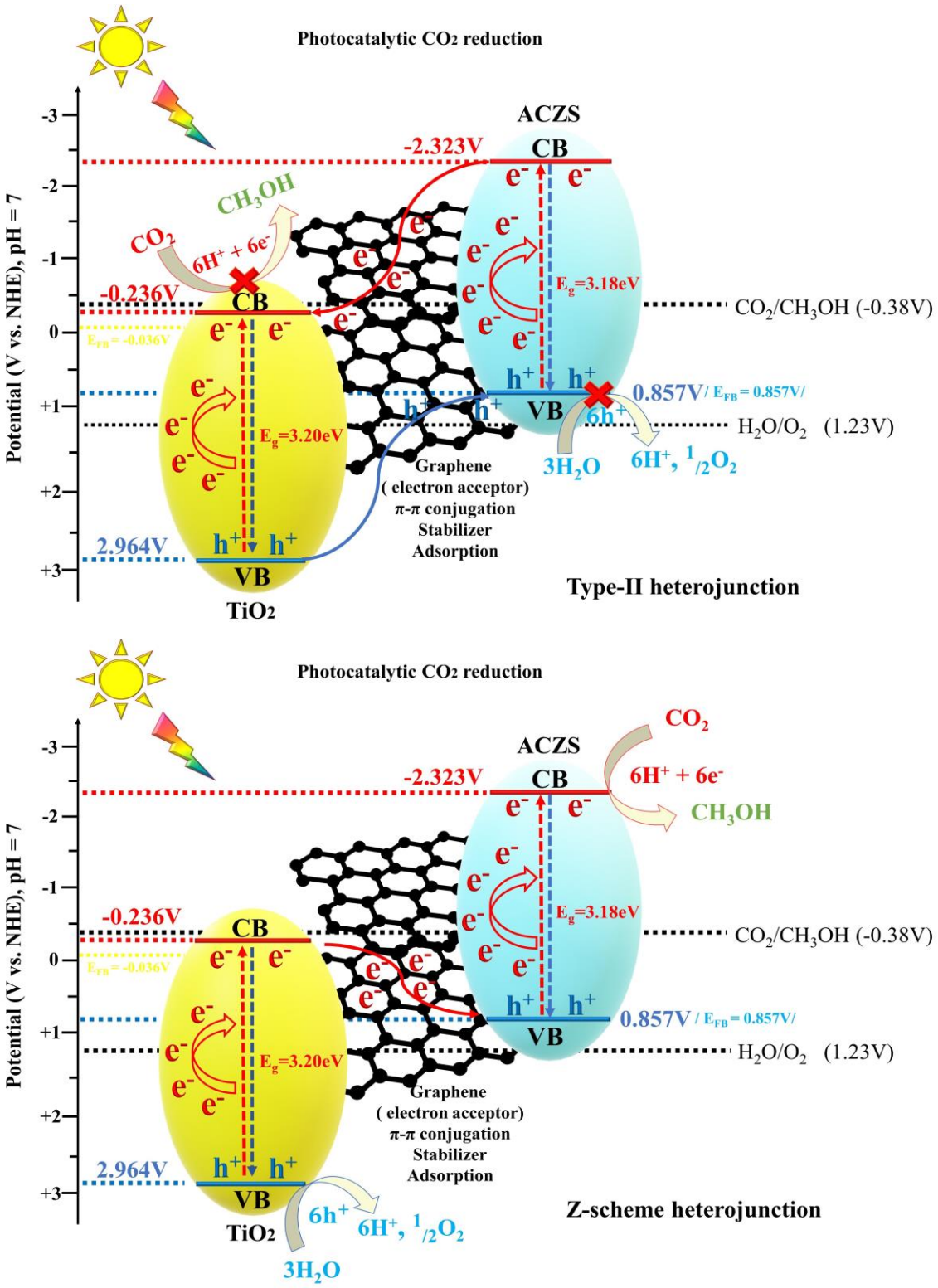
Figure S10. FTIR spectra of the final product (methanol CH_3OH) after the photocatalytic and electrochemical reduction.

Table S1. Electrochemical data (under $NaHCO_3$ electrolyte, CO_2 dissolved solution) with potentials listed vs. Ag/AgCl under different scan rate.

Compound name	Electrolyte	Scan rate /mV s^{-1}	Redox potential /V
ACZS	$NaHCO_3$	10, 80, 100	-0.80 V, 1.19 V
ACZSG			-0.80 V, 1.20 V
ACZSGT			-0.81 V, 1.21 V
ACZST			-0.81V, 120V/ -0.57V, 1.20V/ -0.50V, 1.00V
ACZS	CO_2 dissolved	10, 80, 100	-0.77 V, 0.69 V/ -0.79 V, 0.80 V
ACZSG			-0.77 V, 0.61 V/ -0.67 V, 0.63 V
ACZSGT			-0.80 V, 0.52 V/ -0.77 V, 0.51 V
ACZST			-0.80 V, 0.44 V/ - 0.80 V, 0.45 V

Table S2. The integrated area, specific capacitance, energy density calculation of each electrode from CV test.

№	Sample	Experiment condition	Scan rate /mV/s	Area of Integration	Specific capacitance /Cp F/g	Energy density /Wh/kg
1	ACZS	*$NaHCO_3$*	10	$6.17x10^{-4}$	$6.45x10^{-5}$	82.56
			80	$3.17x10^{-3}$	$3.79x10^{-5}$	37.14
			100	$2.14x10^{-3}$	$3.19x10^{-5}$	31.26
		CO_2 to Methanol	10	$2.62x10^{-4}$	$2.43x10^{-5}$	39.43
			80	$1.95x10^{-4}$	$2.26x10^{-6}$	3.67
			100	$4.32x10^{-4}$	$2.05x10^{-6}$	3.32
		Under the UV-light	100	$9.91x10^{-4}$	$1.39x10^{-5}$	27.55
		With 0.07T magnetic core	100	$5.48x10^{-3}$	$4.59x10^{-5}$	91.23
2	ACZSG	*$NaHCO_3$*	10	$3.31x10^{-3}$	$4.38x10^{-4}$	632.91
			80	$4.58x10^{-3}$	$7.58x10^{-5}$	109.53
			100	$3.58x10^{-3}$	$4.74x10^{-5}$	68.49
		Methanol	10	$1.30x10^{-3}$	$1.63x10^{-4}$	263.41
			80	$1.50x10^{-3}$	$2.35x10^{-5}$	38.00
			100	$1.70x10^{-3}$	$2.15x10^{-5}$	34.76
		Under the UV-light	100	$4.59x10^{-3}$	$5.19x10^{-5}$	102.95
		With 0.07T magnetic core	100	$1.12x10^{-2}$	$1.27x10^{-4}$	251.18
3	ACZSGT	*$NaHCO_3$*	10	$2.90x10^{-3}$	$6.90x10^{-4}$	676.20
			80	$5.10x10^{-3}$	$1.64x10^{-4}$	138.07
			100	$5.70x10^{-3}$	$1.58x10^{-4}$	113.98
		CO_2 to Methanol	10	$1.80x10^{-3}$	$3.33x10^{-4}$	539.46
			80	$3.00x10^{-3}$	$5.55x10^{-5}$	89.91
			100	$2.36x10^{-3}$	$5.46x10^{-5}$	88.50
		Under the UV-light	100	$1.02x10^{-2}$	$1.71x10^{-4}$	339.27
		With 0.07T magnetic core	100	$1.32x10^{-2}$	$2.23x10^{-4}$	436.93
4	ACZST	*$NaHCO_3$*	10	$1.6x10^{-3}$	$6.50x10^{-4}$	252.00
			80	$1.34x10^{-3}$	$6.86x10^{-5}$	49.39
			100	$2.1x10^{-3}$	$6.147x10^{-5}$	44.25
		CO_2 to Methanol	10	$3.71x10^{-4}$	$3,45x10^{-5}$	55.84
			80	$1.08x10^{-3}$	$2.47x10^{-5}$	39.98
			100	$6.06x10^{-4}$	$1.72x10^{-5}$	27.94
		Under the UV-light	100	$4.56x10^{-3}$	$5.38x10^{-5}$	106.74
		With 0.07T magnetic core	100	$3.07x10^{-3}$	$6.32x10^{-5}$	125.29



Scheme S1. Schematic illustration of the charge carrier migration process on the $AgCuZnS_2$-Graphene-TiO_2 by i. type-II heterojunction and ii. Z-scheme heterojunction.