Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Hierarchical three-dimensional copper selenide nanocubes microelectrodes for improved carbon dioxide reduction reaction

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Table S1. EIS elemental values of the developed CuSe NCs-**A**|CuMEs, CuSe NCs-**B**|CuMEs,

Catalyst	*Potential (V)*	*R1 (ohm)*	*R2 (ohm)*	*C (mF)*
*CuSe NCs-**A***	1.2	12.12	165.7	1.20
	1.4	13.2	20.4	1.23
	1.6	13.1	7.17	1.24
*CuSe NCs-**B***	1.2	7.81	50.04	1.42
	1.4	8.26	14.7	1.35
	1.6	8.24	4.62	1.37
*CuSe NCs-**C***	1.2	8.20	187.2	0.33
	1.4	43.2	10.9	0.26
	1.6	8.37	7.97	0.35

and CuSe NCs-**C**|CuMEs electrodes recorded in 1.0 M aqueous $KHCO_3$.

Table S2. EIS elemental values of the developed CuSe NCs-**A**|CuMEs, CuSe NCs-**B**|CuMEs, and CuSe NCs-**C**|CuMEs electrodes recorded in 0.1 M [Bmim]PF_6/CH_3CN.

Catalyst	*Potential (V)*	*R1 (ohm)*	*R2 (ohm)*	*C (mF)*
*CuSe NCs-**A***	1.2	3022	56.3	0.36
	1.4	3726	56.9	0.13
	1.6	1909	56.6	0.14
*CuSe NCs-**B***	1.2	294.1	19.4	2.02
	1.4	119.0	19.15	2.2
	1.6	90.7	19.25	4.1
*CuSe NCs-**C***	1.2	3367	38.2	0.2
	1.4	1981	36.8	0.4
	1.6	516.0	40.4	0.5

Table S3. List of the recently developed electrocatalysts and their CO_2RR activity.

Catalyst	Electrolyte	Onset	Catalytic current (mA cm^{-2})	FE (%)	References
$Cu_{1.63}Se$(1/3)	[Bmim]PF_6/CH_3CN/H_2O	~-1.81 vs Ag/AgCl	~41.5 @ -2.1 V vs. Ag/AgCl	77.6	1
$Pd_{83}Cu_{17}$	[Bmim]BF4	~-1.4 vs Ag/AgCl	-	80.0	2
Mo-Bi BMC/CP	0.5 M [Bmim]BF4 MeCN	-	~12.1 @ -0.7 V vs. RHE	71.2	3
Cu@Cu2O	0.1M $KHCO_3$	-	-	53.6	4
Pd-SnO_2	0.1M $NaHCO_3$	~-0.5 vs RHE	~1.3 @ -0.7 V vs. RHE	54.8	5
CuSe NCs-**B**	0.1 M [Bmim]PF_6/CH_3CN	~-1.1 vs Ag/AgCl	~120.3 @ -2.0 V vs. Ag/AgCl	62.7	This Work

BMC- bimetallic chalcogenide; CP- carbon paper.

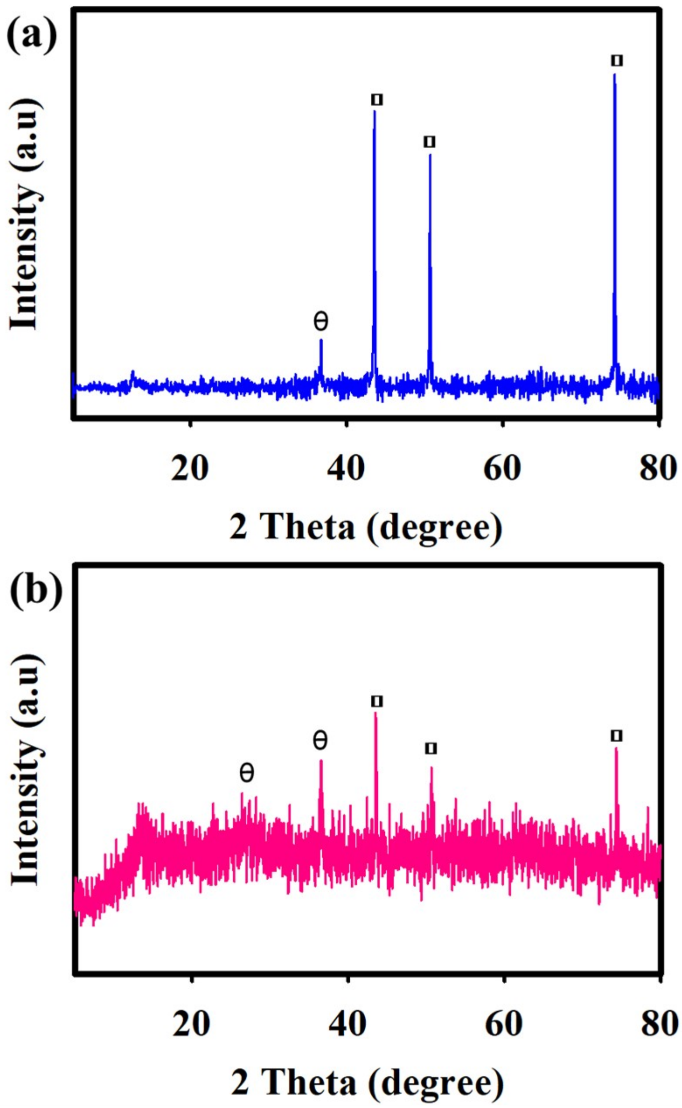

Fig. S1. XRD patterns of the Cu|CuMEs (**a**), Se|CuMEs (**b**) electrodes.

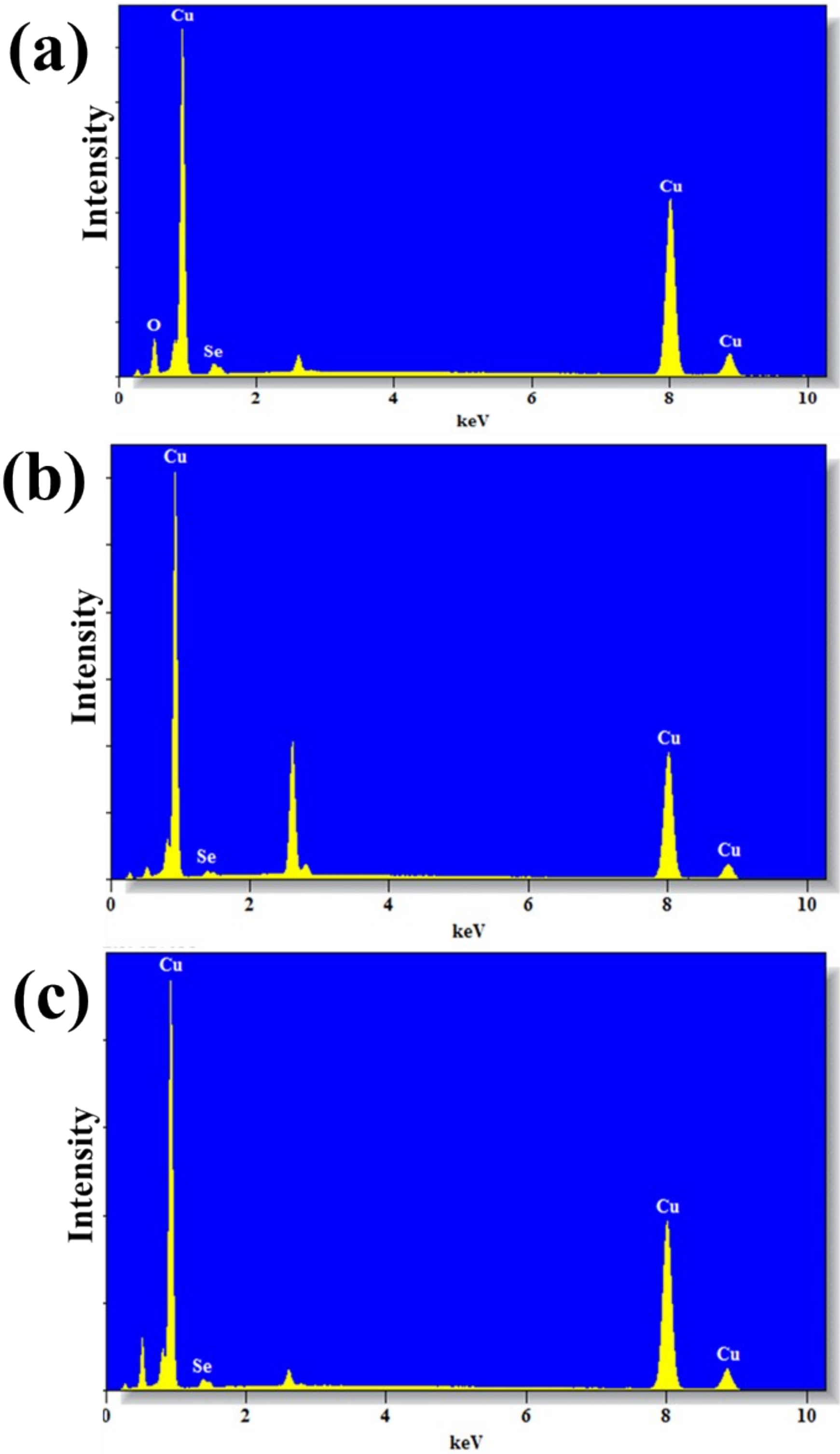

Fig. S2. HRSEM-EDX images of CuSe NCs-**A**|CuMEs (**a**), CuSe NCs-**B**|CuMEs (**b**), and CuSe NCs-**C**|CuMEs (**c**).

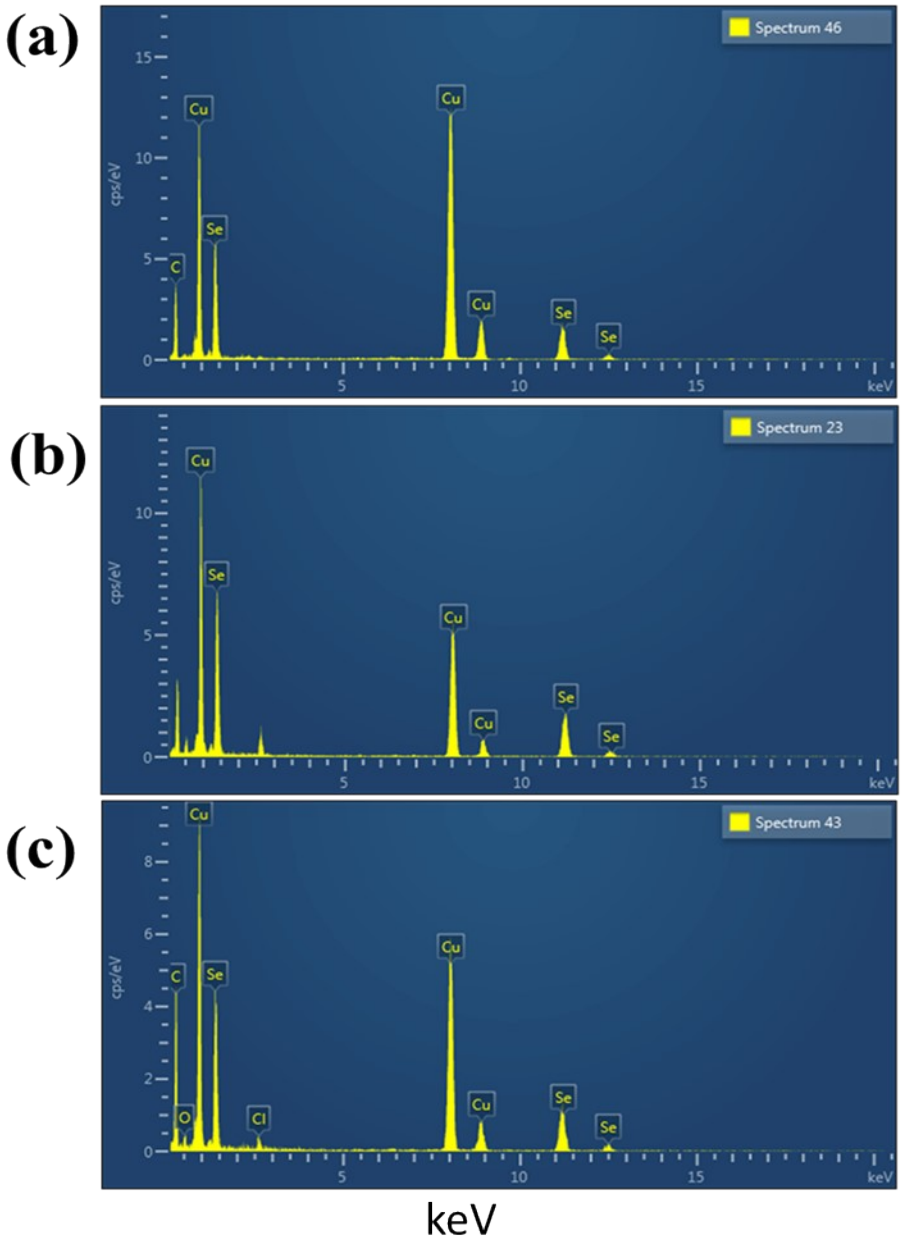

Fig. S3. HRTEM-EDX images of CuSe NCs-**A**|CuMEs (**a**), CuSe NCs-**B**|CuMEs (**b**), and CuSe NCs-**C**|CuMEs (**c**).

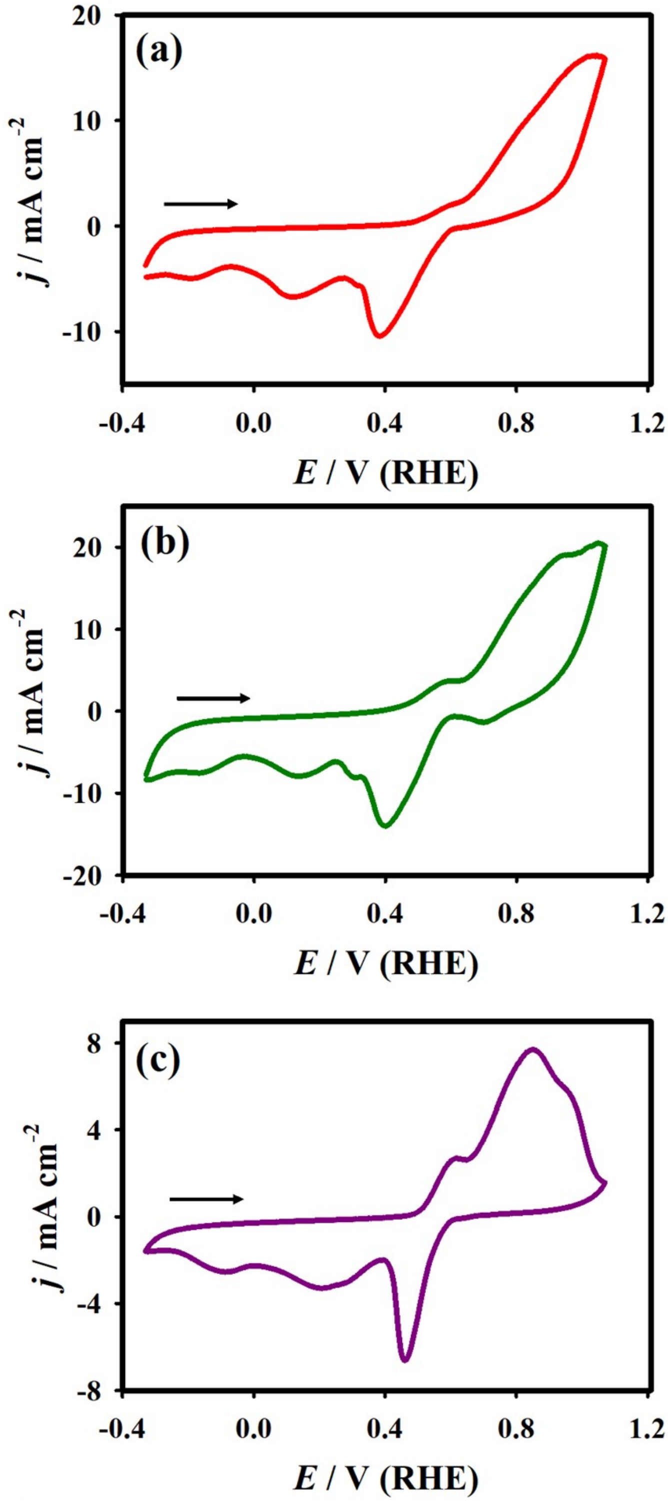

Fig. S4. CV curves of the CuSe NCs-**A**|CuMEs (**a**), CuSe NCs-**B**|CuMEs (**b**), and CuSe NCs-**C**|CuMEs (**c**) under CO_2 saturated 1.0 M aqueous $KHCO_3$ solution at a scan rate of 20 mV s^{-1}.

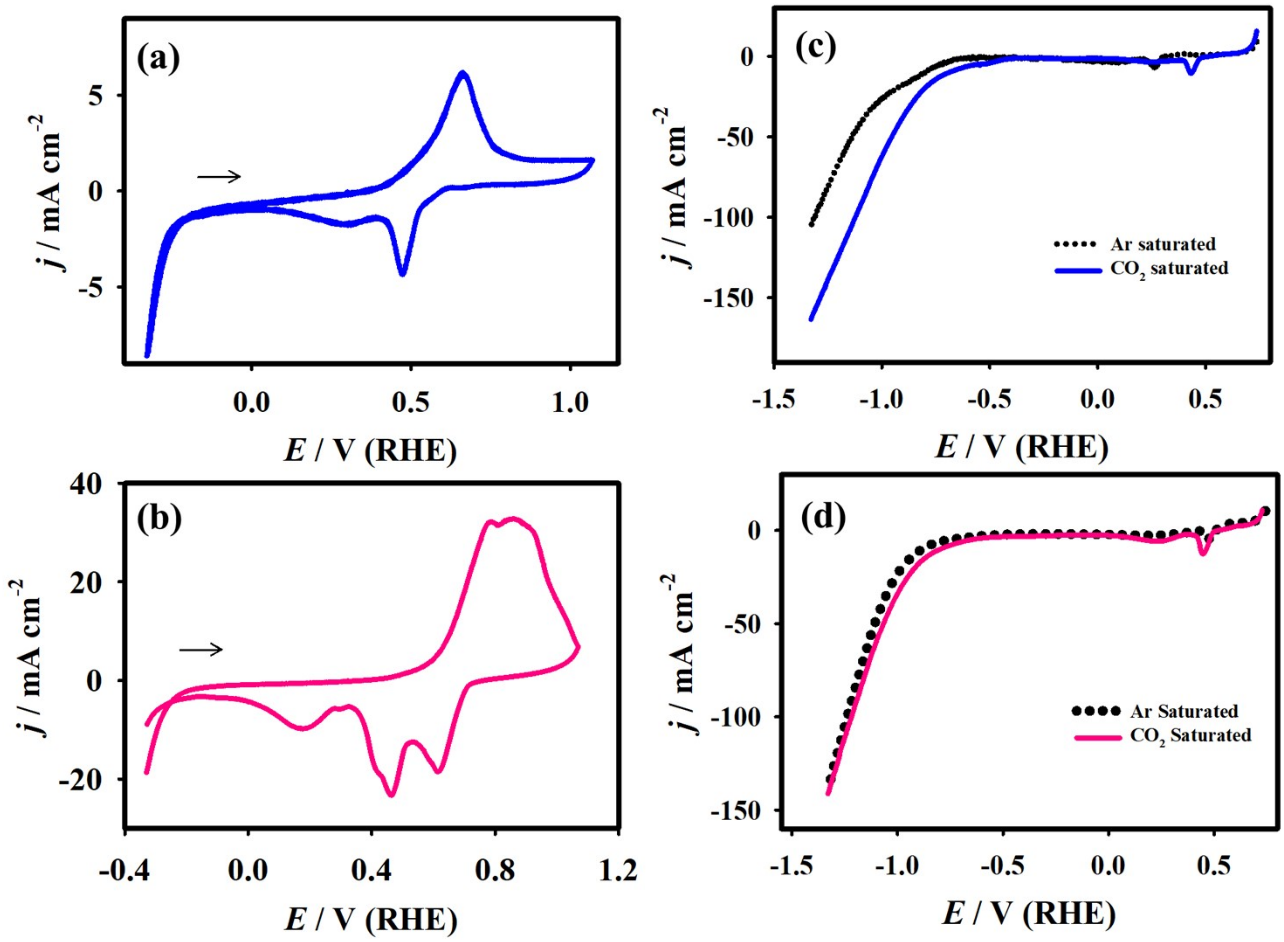

Fig. S5. The CV curves of Cu|CuMEs (**a**), Se|CuMEs (**b**) electrodes recorded in 1.0 M $KHCO_3$ at a scan rate of 20 mVs^{-1}. The LSV curves of the Cu|CuMEs (**c**), Se|CuMEs (**d**) electrodes at a scan rate of 20 mV s^{-1} in a 1.0 M $KHCO_3$ solution under Ar (dotted line) and CO_2 (solid line).

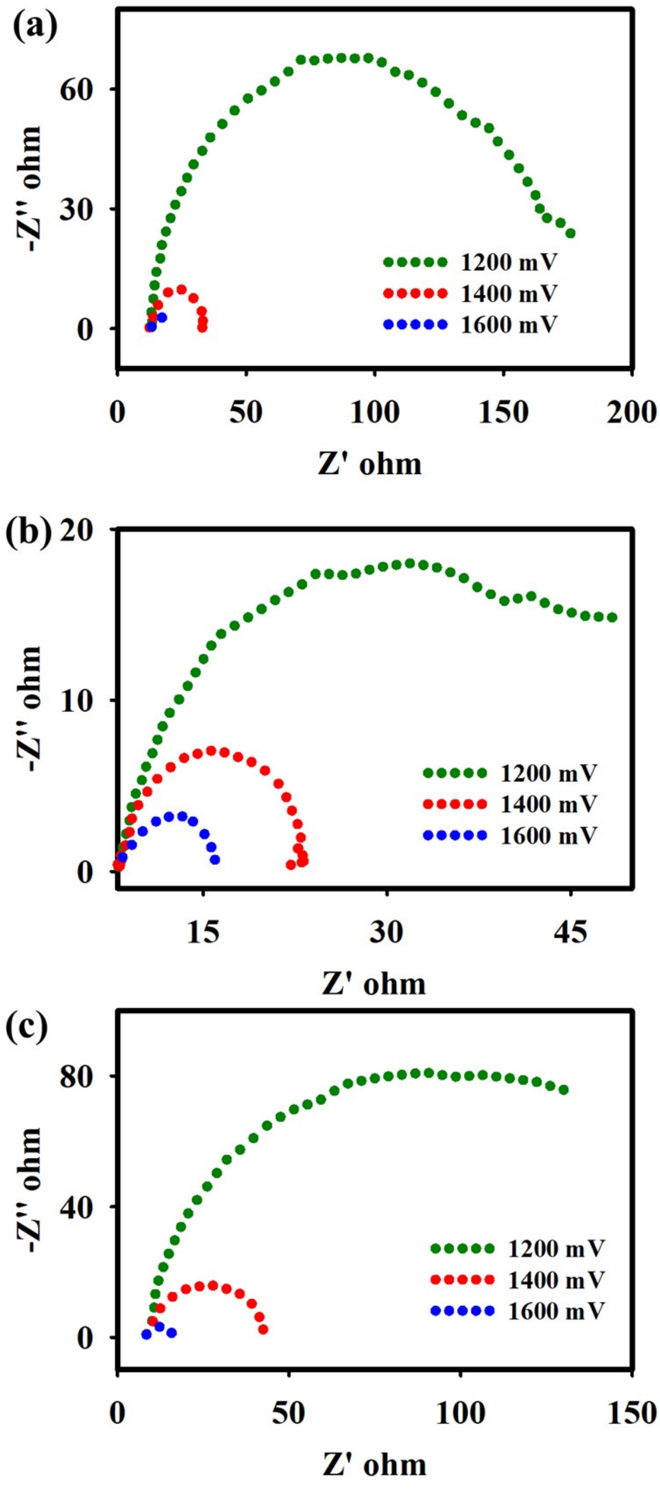

Fig. S6. EIS measurements of the CuSe NCs-**A**|CuMEs (**a**), CuSe NCs-**B**|CuMEs (**b**), and CuSe NCs-**C**|CuMEs (**c**) at the different applied potential under CO_2 saturated 1.0 M aqueous $KHCO_3$ solution.

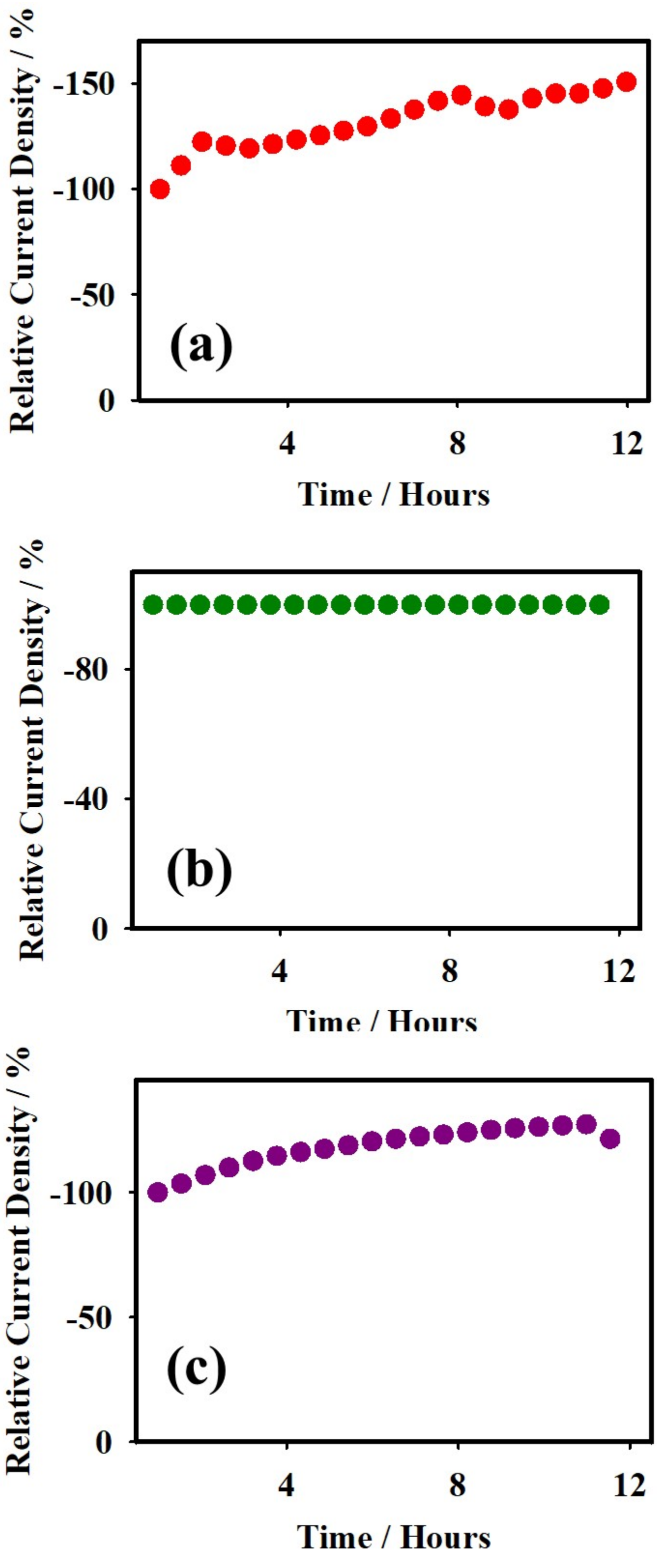

Fig. S7. Long term durability test for the CuSe NCs-**A**|CuMEs (**a**), CuSe NCs-**B**|CuMEs (**b**), and CuSe NCs-**C**|CuMEs (**c**) electrodes in 1.0 M aqueous $KHCO_3$ under CO_2 saturated at the constant potential of -0.93 V vs. RHE for 12 hours.

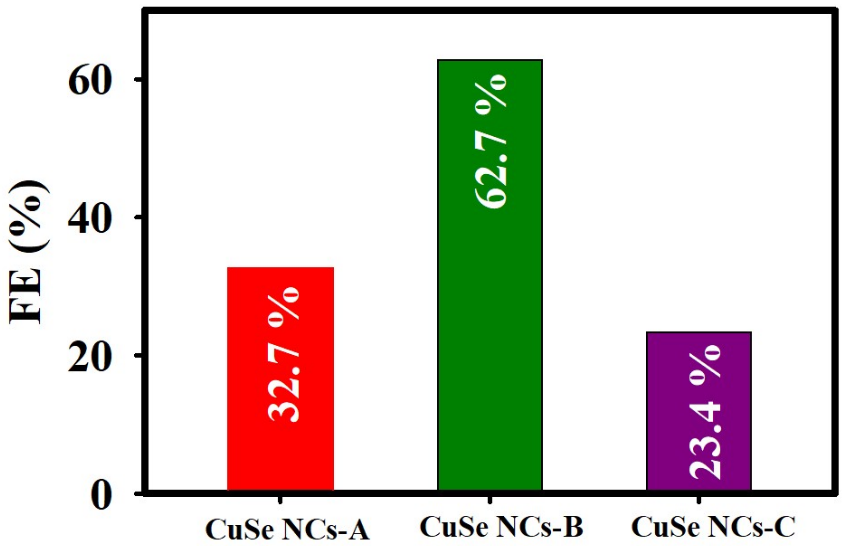

Fig. S8 Faradaic efficiency at −1.6 V (versus Ag/AgCl) under 0.1 M $[Bmim]PF_6$/MeCN at the CuSe NCs-**A|**CuMEs (red), CuSe NCs-**B|**CuMEs (green) and CuSe NCs-**C|**CuMEs (violet) microelectrodes.

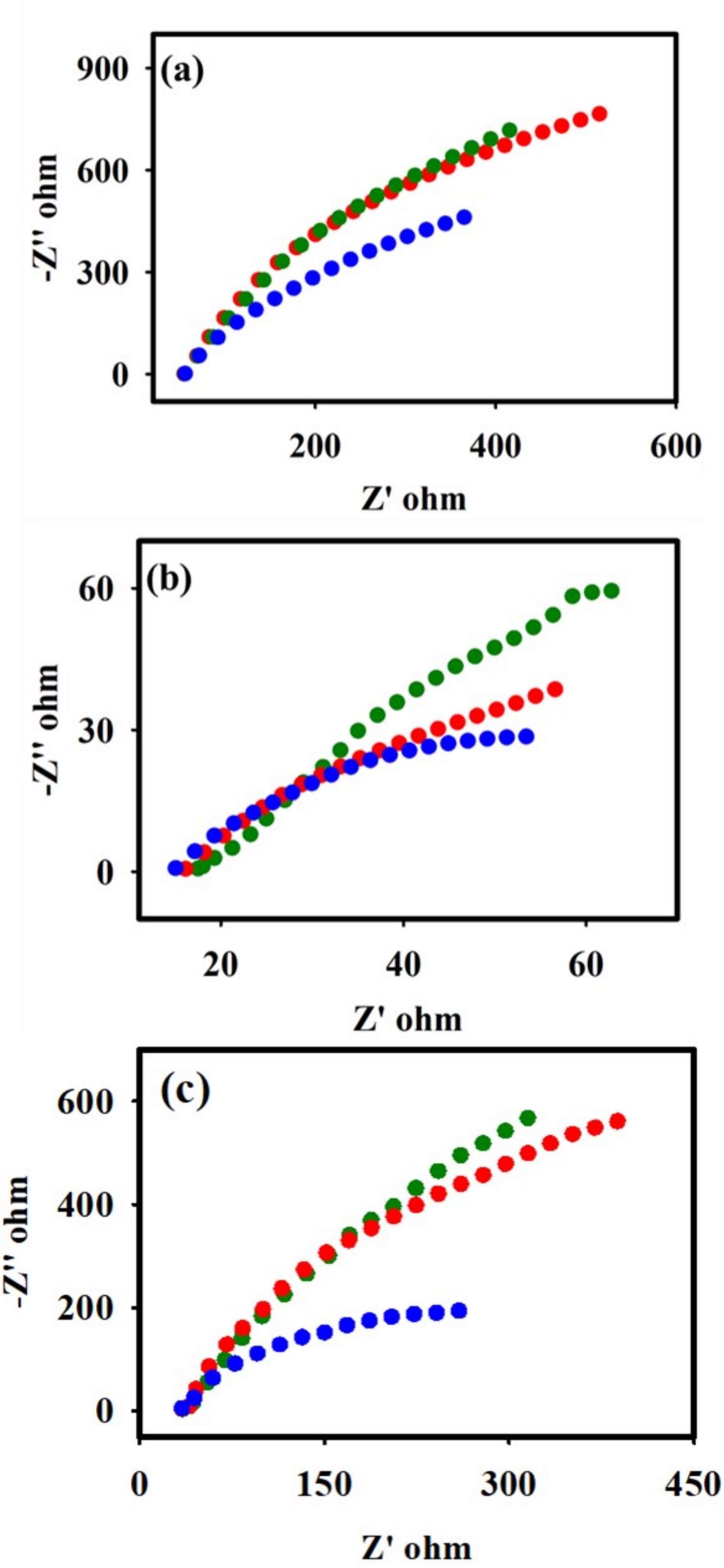

Fig. S9. EIS results of the CuSe NCs-**A**|CuMEs (**a**), CuSe NCs-**B**|CuMEs (**b**), and CuSe NCs-**C**|CuMEs (**c**) under CO_2 saturated [Bmim]PF_6/MeCN at different potentials of 1.2 V(green), 1.4 V(red) and 1.6 V (blue).

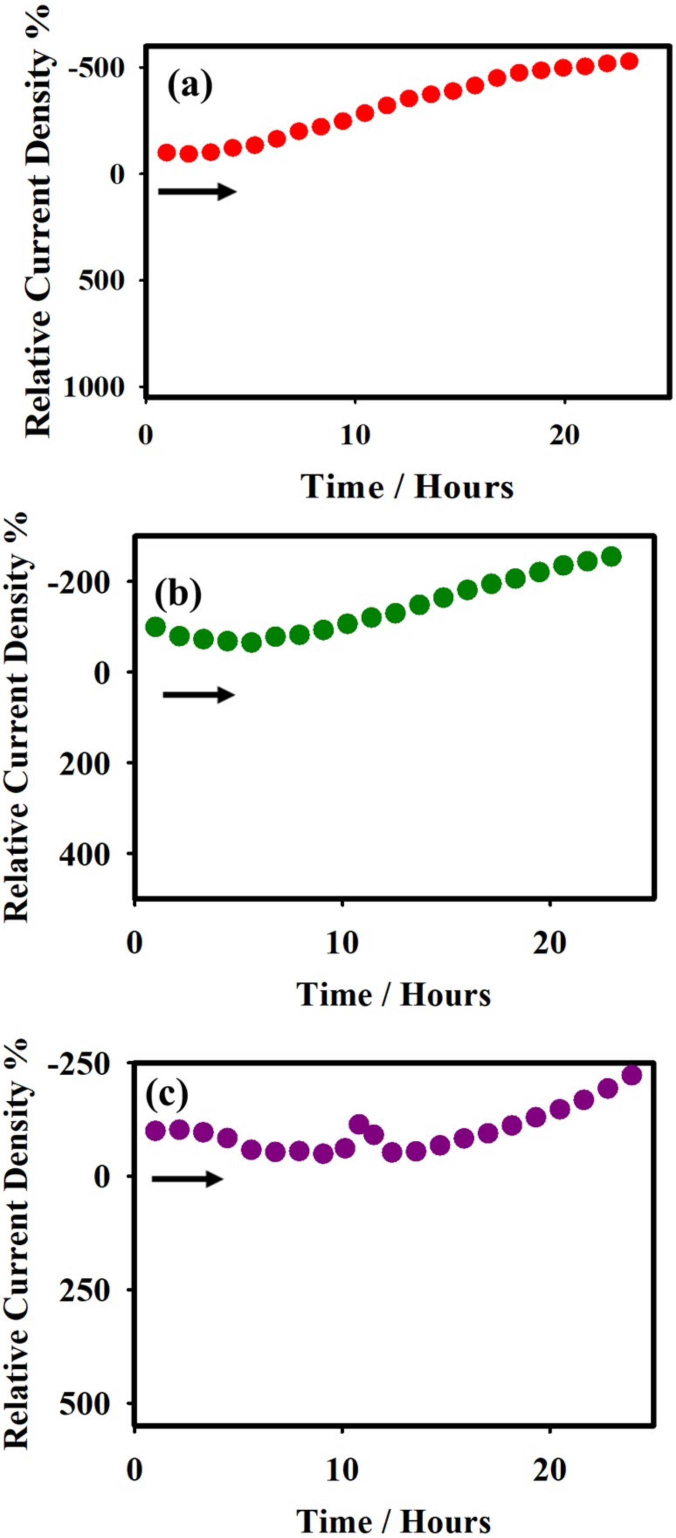

Fig. S10. Durability test for the CuSe NCs-**A**|CuMEs (**a**), CuSe NCs-**B**|CuMEs (**b**), and CuSe NCs-**C**|CuMEs (**c**) under CO_2 saturated [Bmim]PF_6/MeCN at the constant potential of -1.6 V (vs. Ag/AgCl) for 24 hours.

References

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