## **Electronic supporting information**

Selectively electrocatalytic CO<sub>2</sub> reduction to acetate on polymeric Cu-L (L=pyridinic N and carbonyl group) complex core-shell microspheres

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Fig. S1. The XRD pattern of p-CuL.



Fig. S2. Current variation in a 0.5M KHCO<sub>3</sub> CO<sub>2</sub>-saturated aqueous solution at potentials from -0.27V to -0.57V vs. RHE.



Fig. S3. FE-SEM graphs of p-CuL-6(A), p-CuL-8 (B).



**Fig. S4.** Repeat the CV cycle at a scan rate of 5-25mV·s<sup>-1</sup> within the potential range of 0-0.3V *vs.* Ag/AgCl to measure the electrochemical double-layer capacitance (DLC) of p-CuL-4 (A), p-CuL-6 (B), p-CuL-8 (C).



Fig. S5. jacetate normalized to ESCA at same potentials among three catalysts.

catalyst	Applied potential	Electrolyte	product	CH3COO <sup>-</sup> yield	Ref.
Cu <sub>2</sub> (CuTCPP) nanosheets	-1.55 V vs. RHE	CH <sub>3</sub> CN solution with 1 M H <sub>2</sub> O and 0.5 M ionic liquid 1-ethyl-3- methylimidazoliu m tetrafluoroborate (EMIMBF <sub>4</sub> )	СН <sub>3</sub> СОО <sup>-</sup> СО СН4 НСООН	FE=16.8%	Chem Sci, 2019,10: 2199–2205
Cu <sub>10</sub> -CNT	-1.4 V vs. RHE	0.5 M KHCO3	CH3COO <sup>-</sup> HCOOH CH3OH	TOF=208.7 ( $\mu$ molh <sup>-1</sup> g <sub>Cu</sub> <sup>-1</sup> )	Green Chem, 2017,19: 2406-2415
Fe-Cu Mixed Oxide	-0.4 V vs. Ag/AgCl (Photo- electrocatal ysis)	0.1 M NaHCO <sub>3</sub>	CH <sub>3</sub> COO <sup>-</sup>	FE=80%	ACS Catal. 2017,7(1): 177–180
(Cu) <sub>n</sub> ,(Ag) <sub>m</sub>	-1.33 V vs. RHE	0.5 M KHCO3	CH <sub>3</sub> COO <sup>-</sup> CO CH <sub>4</sub> HCOOH	FE=21.2%	PNAS 2018, 115(2): 278-283
Cu-CeO2	-1.8 V vs. RHE	0.1 M KHCO3	CH4 C2H4 CH3COOH HCOOH CO CH3OH	FE=5%	ACS Catal. 2018,8(8): 7113–7119

 Table S1. Progress in Carbon Dioxide Reduction on Copper-based Catalyst.

aatalwat	ICP-AES	Elemental analysis (wt%)				
cataryst	Cu	Ν	С	Н	0	
p-CuL-4	21.0wt%	28.6	20.3	2.9	21.0	
p-CuL-6	21.0wt%	28.6	20.1	2.9	22.1	
p-CuL-8	20.0wt%	28.9	20.3	2.9	22.0	

Table S2. The content of each element in the catalyst.