

Supporting information:

Surface engineering in PbS *via* partial oxidation: Towards an advanced electrocatalyst for reduction of levulinic acid to γ -valerolactone

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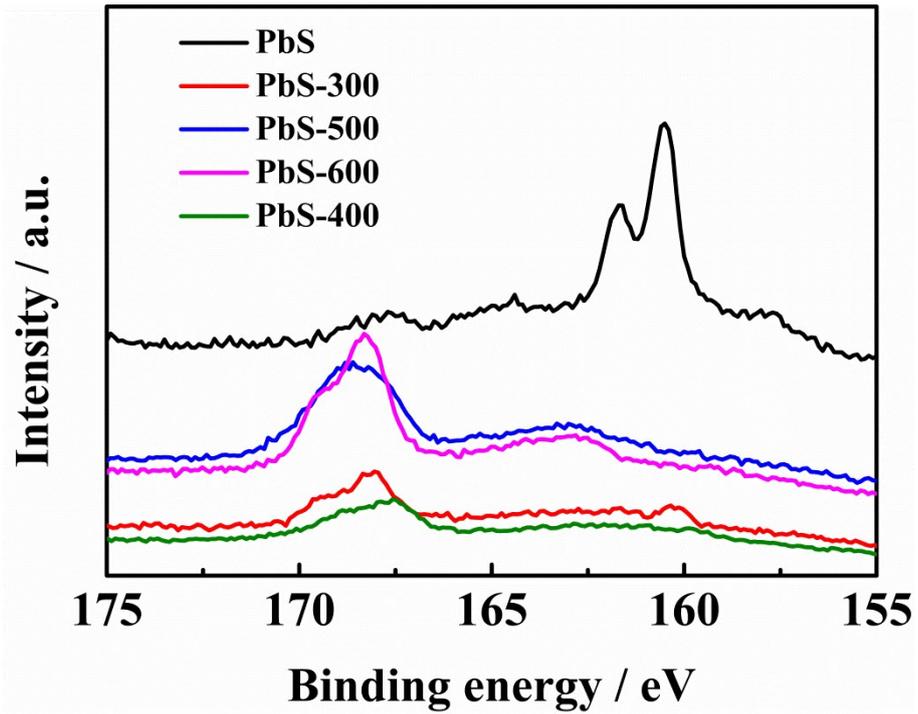


Fig. S1. XPS spectrum of S 2p in different PbS-X materials.

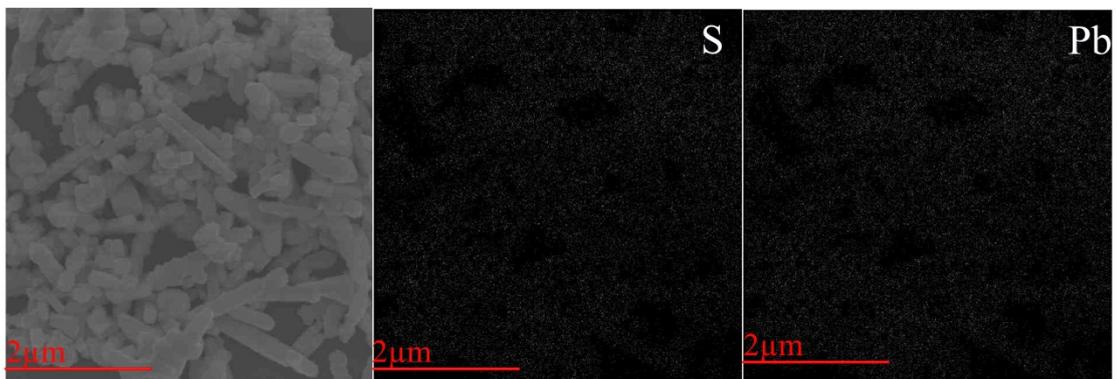


Fig. S2. Elements mapping of PbS.

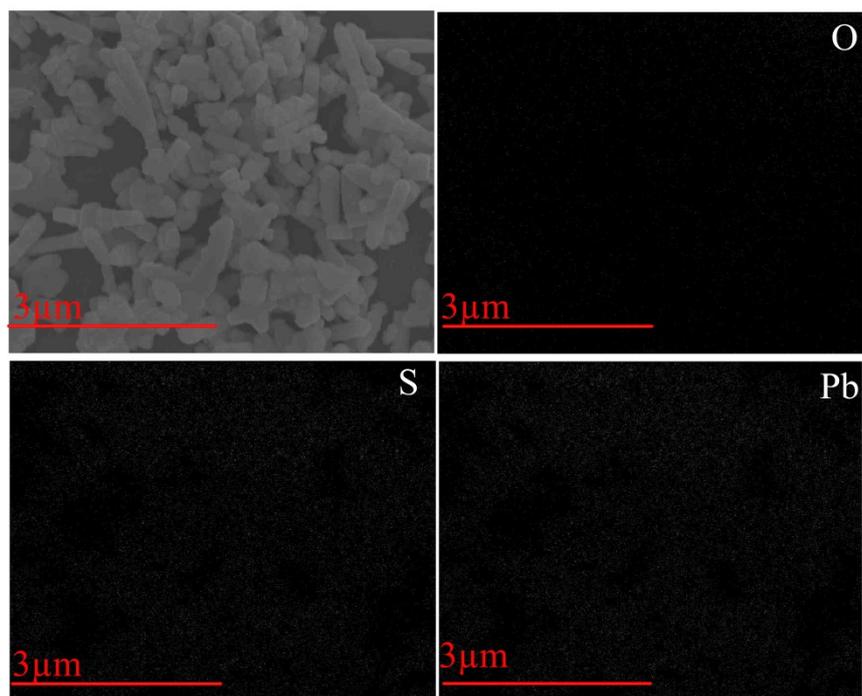


Fig. S3. Elements mapping of PbS-300.

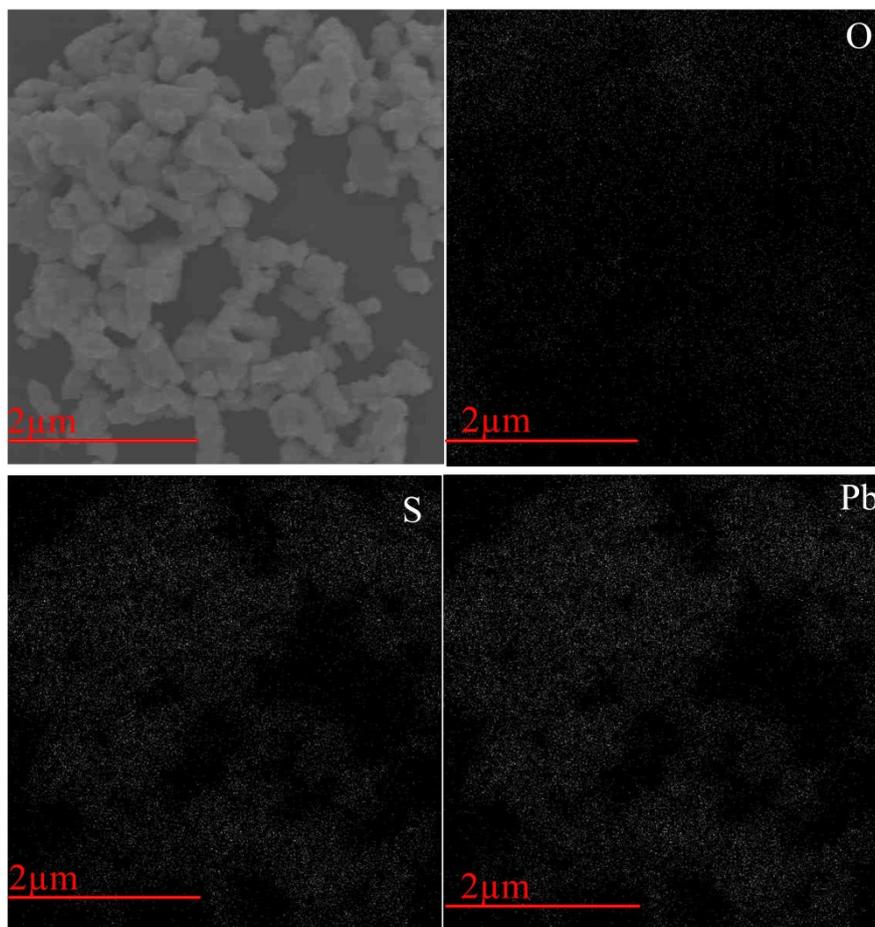


Fig. S4. Elements mapping of PbS-400.

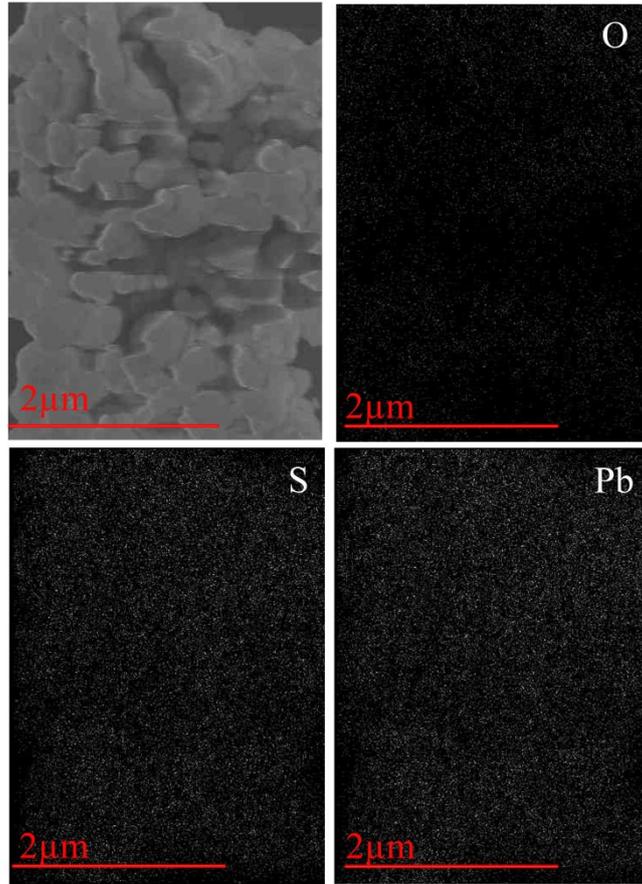


Fig. S5. Elements mapping of PbS-500.

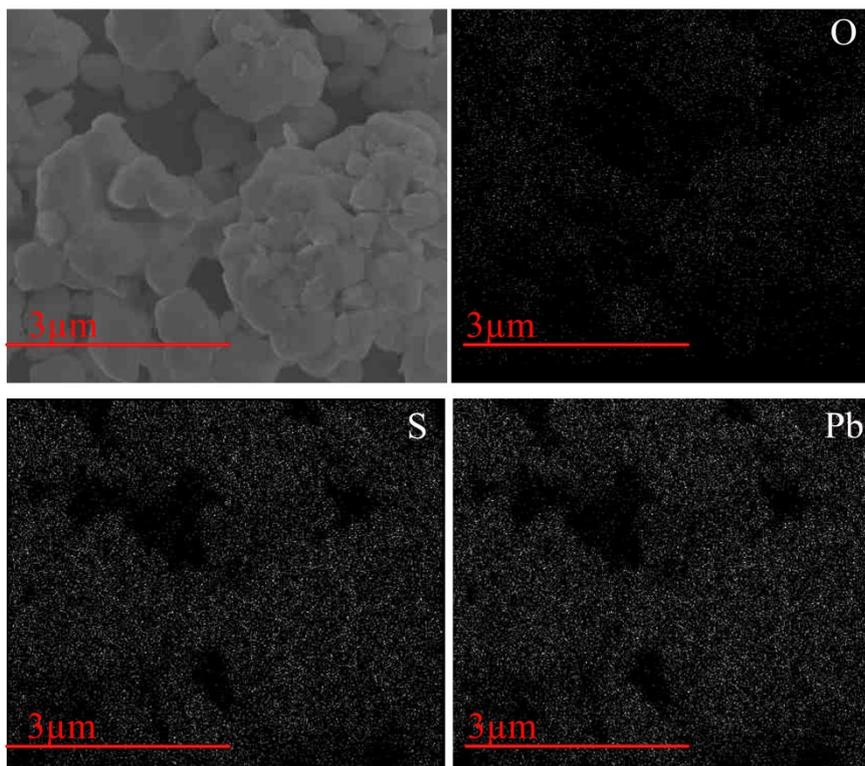


Fig. S6. Elements mapping of PbS-600.

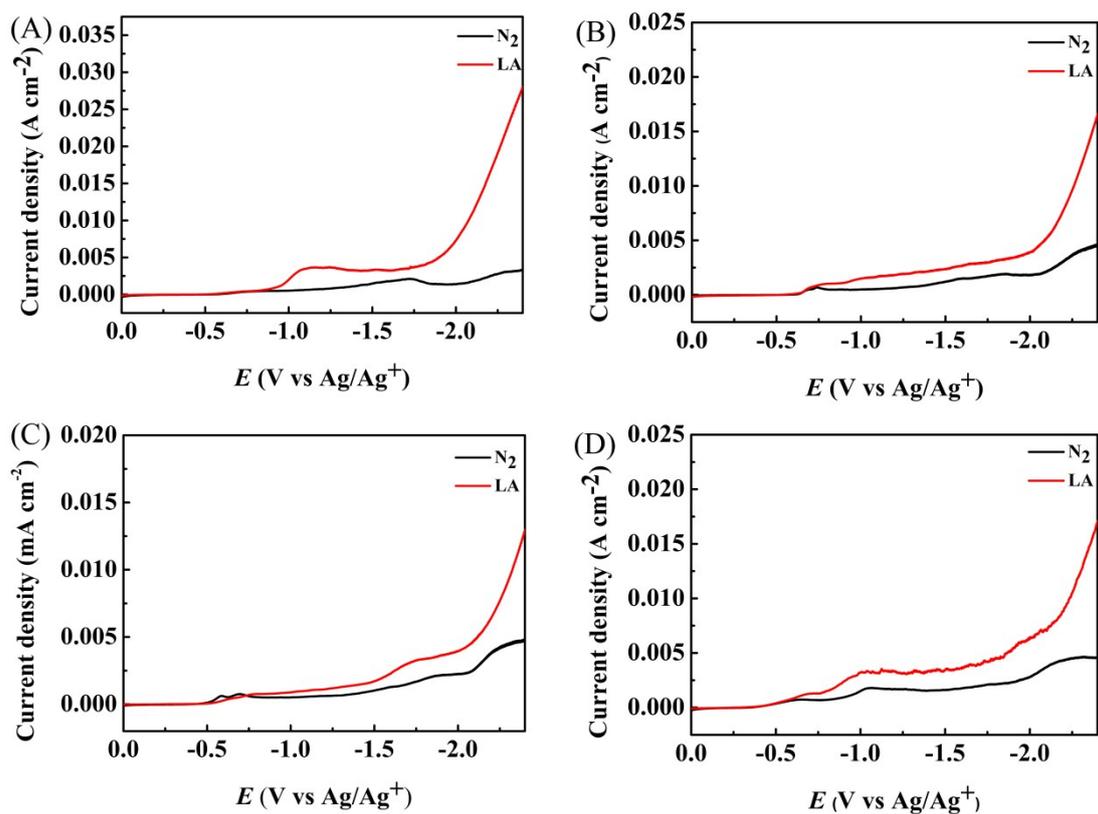


Fig. S7. LSV measurements using PbS-X/CP electrode for the electrochemical reduction of LA in the electrolyte of IL (1.8 wt%)-MeCN-H₂O (1.8 wt%) at room temperature. (A) PbS/CP, (B) PbS-300/CP, (C) PbS-500/CP, and (D) PbS-600/CP.

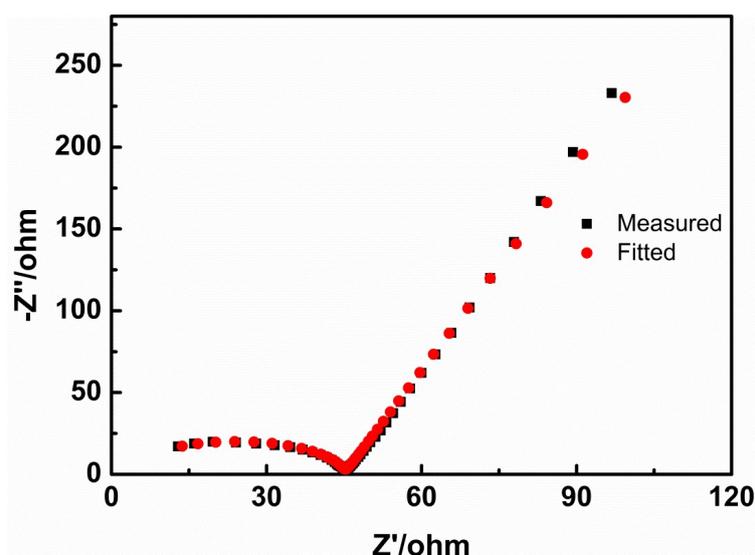


Fig. S8. The measured and fitted EIS spectra of PbS/CP in [Bmim]BF₄ (1.8 wt%)-MeCN-H₂O (1.8 wt%) electrolyte in the presence of LA.

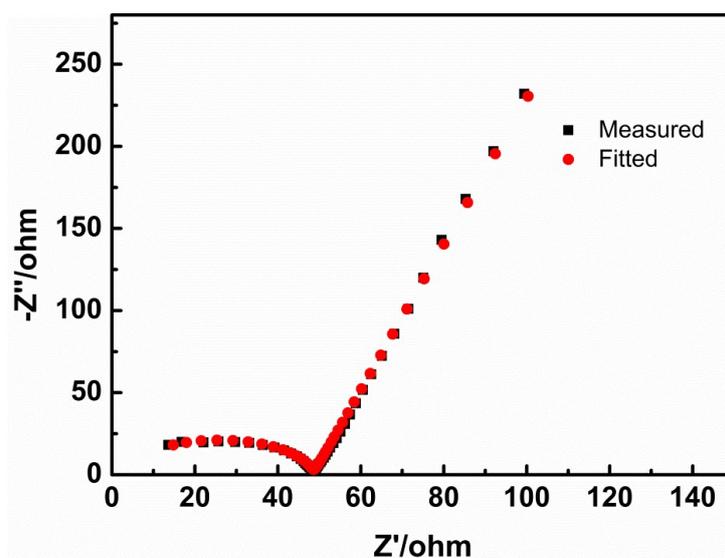


Fig. S9. The measured and fitted EIS spectra of PbS-300/CP in [Bmim]BF₄ (1.8 wt%)-MeCN-H₂O (1.8 wt%) electrolyte in the presence of LA.

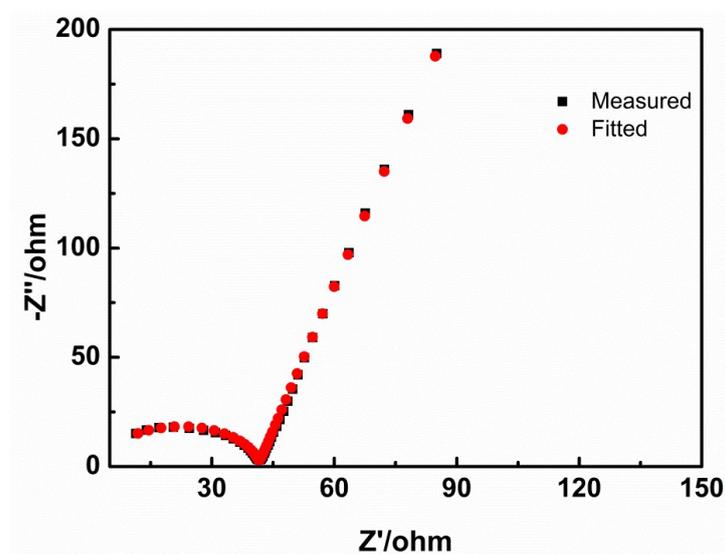


Fig. S10. The measured and fitted EIS spectra of PbS-400/CP in [Bmim]BF₄ (1.8 wt%)-MeCN-H₂O (1.8 wt%) electrolyte in the presence of LA.

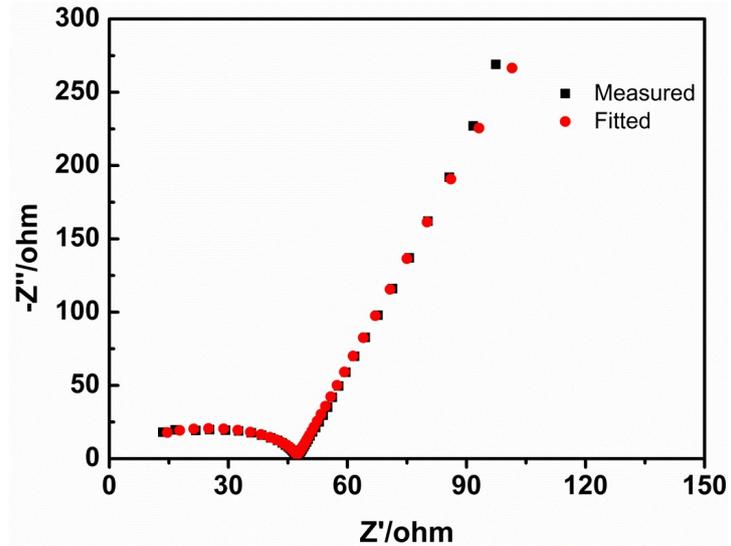


Fig. S11. The measured and fitted EIS spectra of PbS-500/CP in [Bmim]BF₄ (1.8 wt%)-MeCN-H₂O (1.8 wt%) electrolyte in the presence of LA.

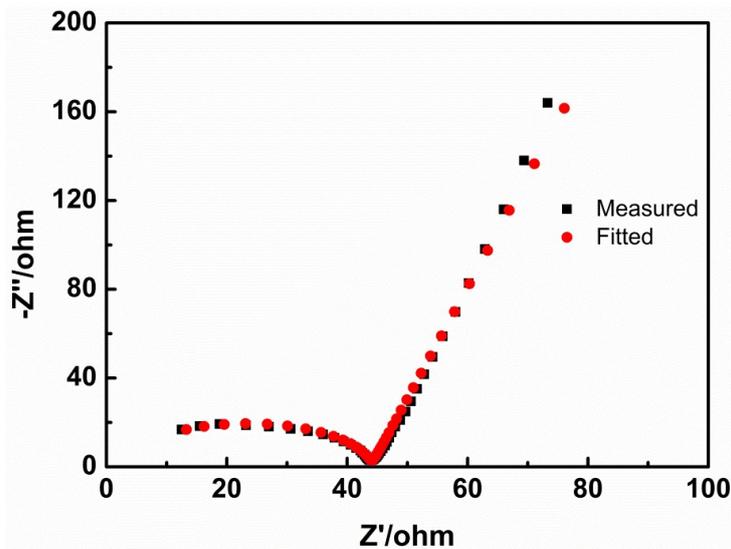


Fig. S12. The measured and fitted EIS spectra of PbS-600/CP in [Bmim]BF₄ (1.8 wt%)-MeCN-H₂O (1.8 wt%) electrolyte in the presence of LA.

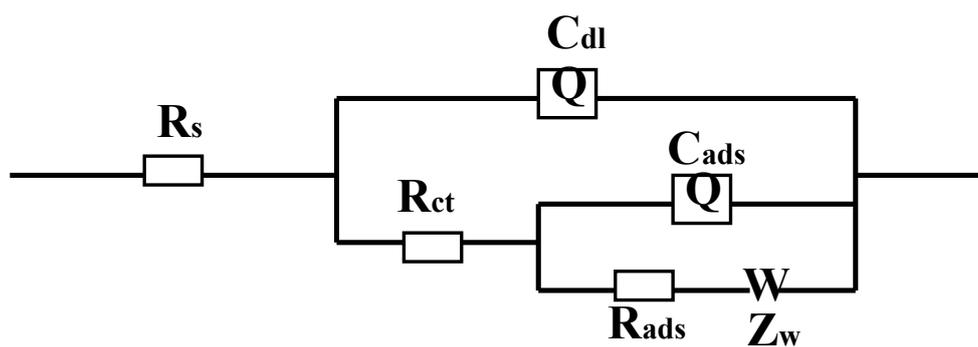


Fig. S13. Electrical equivalent circuit for fitting the measured impedance data. R_s , C_{dl} , R_{ct} , C_{ads} , R_{ads} , and Z_w represent solution resistance, double layer capacitance, electron transfer resistance, surface adsorption capacitance, surface adsorption resistance and Warburg impedance, respectively.

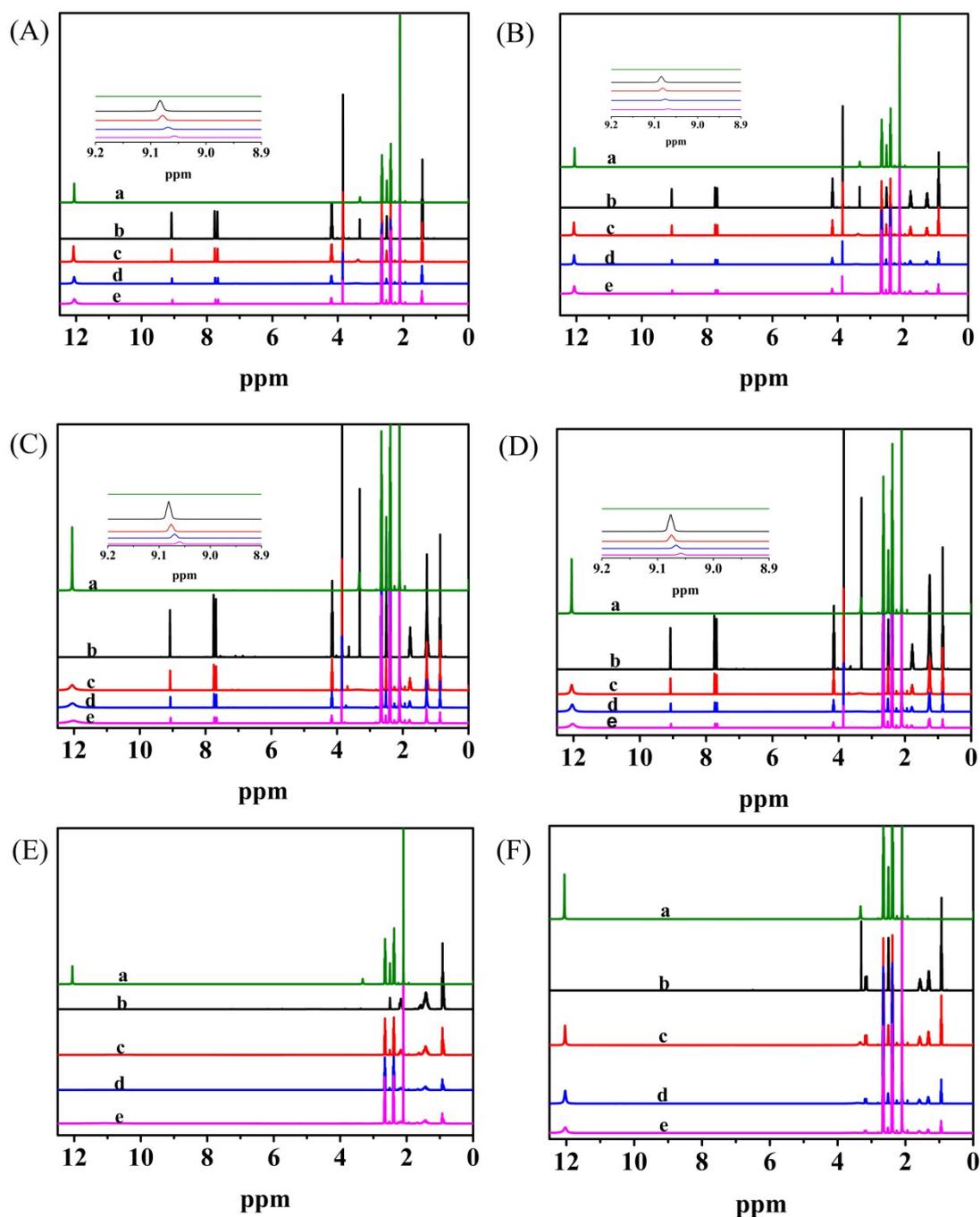


Fig. S14. ^1H NMR spectra of LA and different ILs. [Emim]BF₄ (A), [Bmim]BF₄ (B), [Hmim]BF₄ (C), [Omim]BF₄ (D), [TBP]BF₄ (E), and [TBA]BF₄ (F). (a and b represented LA and IL respectively. c, d, and e represented the mixture of IL and LA. The amount of IL was 12 mg and the amount of LA was 30 μL , 70 μL , and 110 μL in c, d and e, respectively. DMSO- d_6 was used as solvent.)

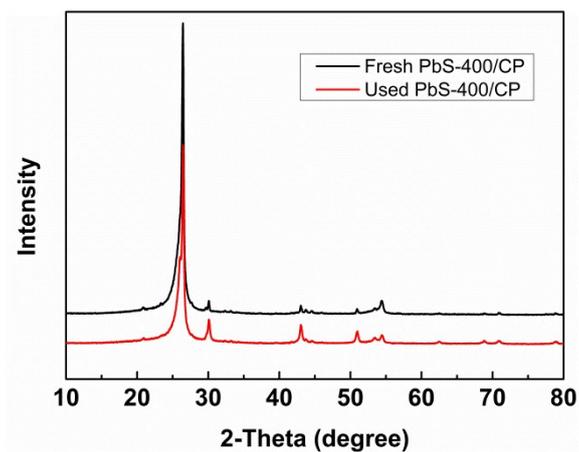


Fig. S15. XRD patterns of the fresh and used PbS-400/CP electrode

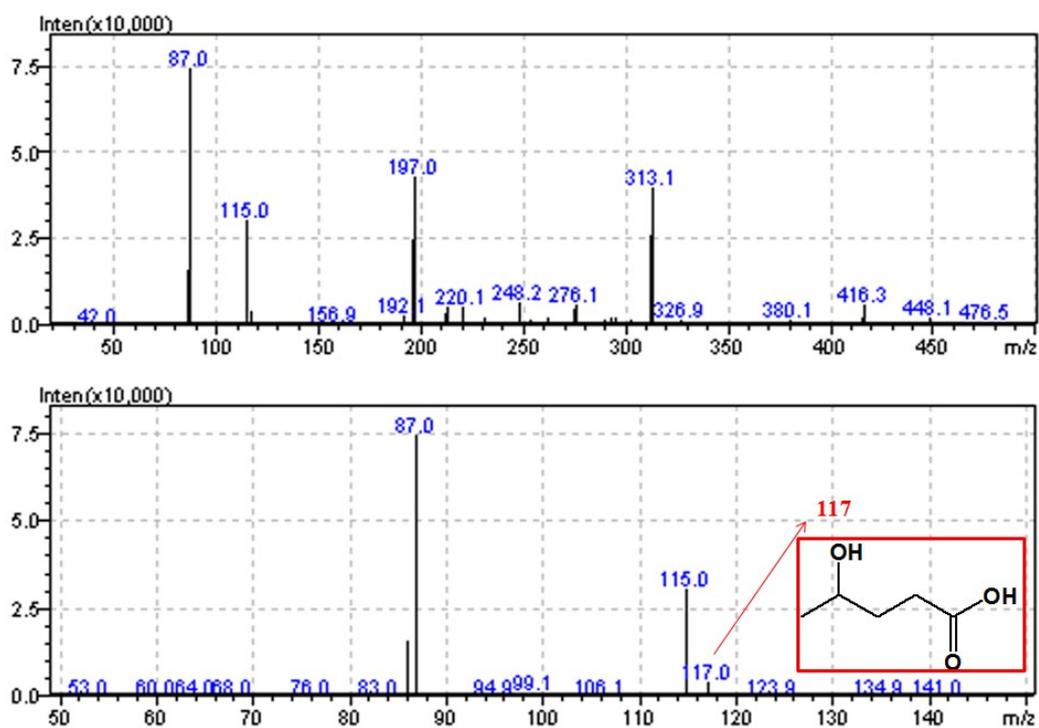


Fig. S16. MS spectra of the electrolyte after electrolysis for the electrochemical reduction of LA using PbS-400/CP in [Bmim]BF₄ (1.8 wt%)-MeCN-H₂O (1.8 wt%) at -2.15 V vs. Ag/Ag⁺ for 4 h.

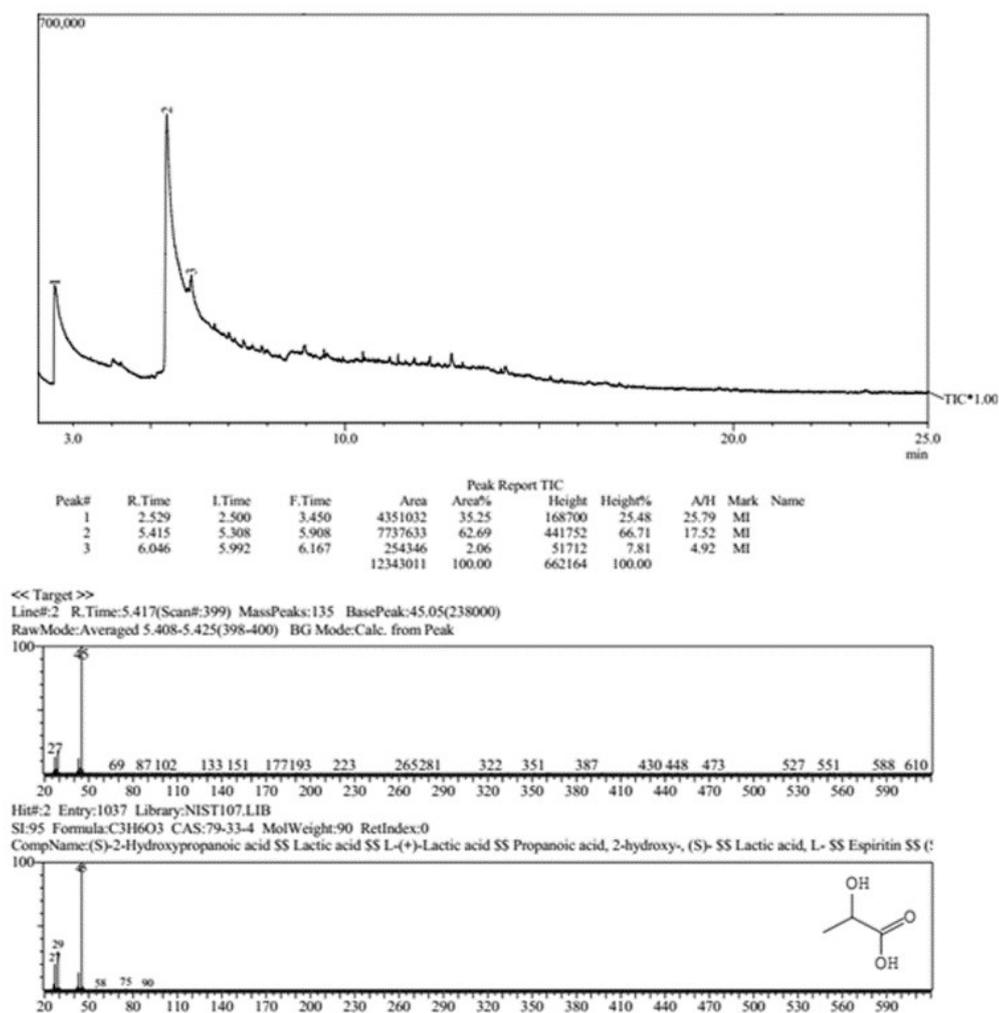
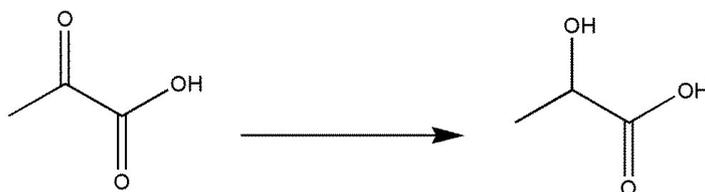


Fig. S17. GC-MS spectra of the electrolyte after electrolysis of pyruvic acid using PbS-400/CP in the electrolyte of [Bmim]BF₄ (1.8 wt%)-MeCN-H₂O (1.8 wt%) at -2.15 V vs. Ag/Ag⁺ for 4 h.



Scheme S1. Electrochemical reduction of pyruvic acid over PbS-400/CP electrode in the electrolyte of [Bmim]BF₄ (1.8 wt %)-MeCN-H₂O (1.8%).

Table S1. The chemical composition of the PbS-X.

Materials	The determined elements content from ICP-AES		Composition
	Pb (wt%)	S (wt%)	
PbS	86.54	12.69	PbS
PbS-300	85.81	13.04	(PbS) _{28.06} /PbSO ₄
PbS-400	80.38	11.80	(PbS) _{2.45} /PbSO ₄
PbS-500	70.42	10.26	(PbS) _{0.16} /PbSO ₄
PbS-600	68.25	9.79	PbSO ₄

The theoretical contents of Pb in PbS and PbSO₄ are 86.6 wt% and 68.3 wt%, respectively. The theoretical contents of S in PbS and PbSO₄ are 13.4 wt% and 10.57 wt%, respectively.