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Electronic Supplementary Information

Revealing Structure Evolution of PbS Nanocrystal Catalysts in the Electrochemical CO_2 Reduction Using *in situ* Synchrotron Radiation X-ray Diffraction

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Materials and Methods

Fig. S1 to S13

Table S1

Materials

Lead oxide (PbO, 99+%), bis(trimethylsilyl)sulfide (TMS, 95%), 1-octadecene (ODE, 90%), and ammonium thiocyanate (NH_4SCN, 99+%) were purchased from Acros Organics. Oleic acid (OAc, 90%) and potassium bicarbonate ($KHCO_3$, 99.7%) were obtained from Sigma-Aldrich.

Synthesis of PbS NCs

The PbS NCs were synthesized via an organic solution hot-injection approach, based on a previous publication with some modifications. To obtain 5.6 nm PbS NCs, 225 mg of PbO was first dissolved in 10 ml of OAc at 90 °C, and was then vacuumed using a typical Schlenk line technique to remove moisture and dissolved air. Next, the system was refilled with N_2 and heated to 150 °C. 105 µl of TMS dissolved in 5 ml of ODE was then quickly injected into the hot Pb solution. The reaction temperature was held for 30 seconds, followed by quenching with an ice bath. The as-synthesized NCs were washed and collected by the addition of isopropanol and subsequent centrifugation at 10000 rpm for 8 min. The product was washed of impurities twice more by the addition of hexanes and isopropanol, and then stored in hexanes for further applications.

The size of PbS NCs was controlled by adjusting the injection temperature and reaction duration. For example, with 30 seconds reaction duration, injecting the TMS/ODE solution at 130 °C led to 4.7 nm PbS NCs, while injecting at 180 °C yielded 11.8 nm NCs. If injecting TMS/ODE solution at 150 °C, a 50s reaction resulted in 7.0 nm NCs, while 60s generated 7.5 nm ones.

Preparation of PbS/C and surfactant removal

The as-synthesized NCs were sonicated with an appropriate amount of Vulcan 72R carbon black in hexanes, followed by centrifugation at 8000 rpm for 5 min to achieve a uniform distribution of PbS NCs over the carbon support. The carbon-supported PbS was then stirred in a NH_4SCN/acetone solution overnight to allow the bulky, surface-bound oleate ligands to be replaced by shorter SCN^-. The product was washed with copious amounts of acetone and dried under vacuum. Each catalyst material was named as PbS-T_i/C, where T_i is the injection temperature. The metal loadings of the PbS/C catalysts were determined by ICP-OES, which revealed that Pb composition was controlled at 33.3 wt% for PbS-150/C and 37.5 wt% for PbS-180/C.

Electrodeposition of Pb on glassy carbon electrodes

Electrodeposition was performed using a biologic VMP3 potentiostat/galvanostat with a glassy carbon electrode (GCE, 5 mm in diameter), a Ag/AgCl (sat'd KCl, -0.044 V vs. SCE) reference electrode, and a Pt gauze counter electrode. Pb electrodeposition was carried out by passing 0.6 C of charge through the freshly polished GCE at -0.6 V vs. Ag/AgCl in 0.1 M HCl containing 20 mM Pb^{2+}.

Electrochemical measurements and products analysis

The eCO_2RR measurements were conducted in 0.1 M $KHCO_3$ solution. To prepare the PbS/C working electrode, a catalyst ink was first prepared by uniformly dispersing a solution containing 90% PbS/C and 10% Nafion in isopropanol. The ink was then drop-cast onto a freshly polished GCE to achieve a PbS/C loading of 200 µg. Cyclic voltammograms were recorded in N_2- or CO_2-saturated 0.1 M $KHCO_3$ at 50 mV s^{-1}. Controlled potential electrolysis (CPE) was performed for 2 hours in a self-designed gas-tight H-type cell, the two compartments of which were separated by a Nafion-212 membrane. With 10 ml of electrolyte being charged to each compartment, CO_2 was purged through the catholyte for 30 min to achieve a steady state prior to electrolysis. During the electrolysis, CO_2 was steadily supplied to the cathode compartment at a rate of 10 sccm, and the gas phase effluent in the headspace of the cathode compartment was continuously introduced to the sampling loop of a Shimadzu gas chromatograph (GC 2014). The gaseous product stream was analyzed by a thermal conductivity detector (TCD) and a flame ionization detector (FID) equipped with a methanizer, using Argon as the carrier gas. The liquid phase products were analyzed using a Shimadzu high-performance liquid chromatograph (HPLC) equipped with a Bio-rad Aminex HPX-87H column, a photodiode array detector (PDA), and a reflective index detector (RID).

In situ **synchrotron radiation X-ray diffraction (SR-XRD)**

The *in situ* synchrotron radiation X-ray diffraction (SR-XRD) measurements for PbS/C were performed at beamline 17BM ($\lambda = 0.24141$ Å) of Advanced Photon Source, at the Argonne National Laboratory. Illustrated in Fig. 3a, a self-designed electrochemical cell was used for each *in situ* measurement. The working electrode was prepared by airbrushing 4 mg of PbS/C with 10 wt% of Nafion over a carbon cloth with an active area of 1 cm^2, and it was positioned within the *in situ* electrochemical cell between two Kapton windows with a spacing of 0.5 mm. The two-dimensional diffraction patterns were collected with a PerkinElmer Si flat panel detector, which was set 700 mm behind the sample. The XRD data were processed with GSAS-II software to obtain plots of intensity vs. 2θ. During *in situ* experiments, fresh 0.1 M $KHCO_3$ was continuously pumped through the catalyst layer to maintain a thin liquid film at 1 ml min^{-1}. Meanwhile, cyclic voltammograms were collected at 100 mV min^{-1} using a Ag/AgCl reference electrode and a Pt wire counter electrode.

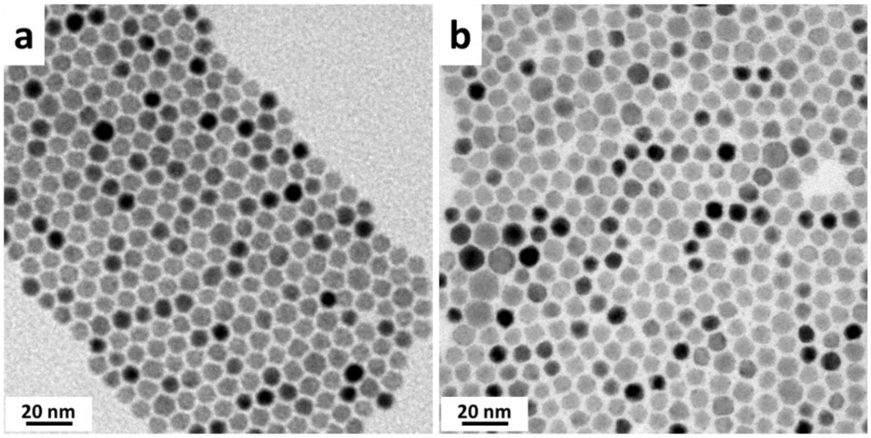

Figure S1. TEM image of PbS NCs prepared at 150°C for (a) 50 s and (b) 60 s.

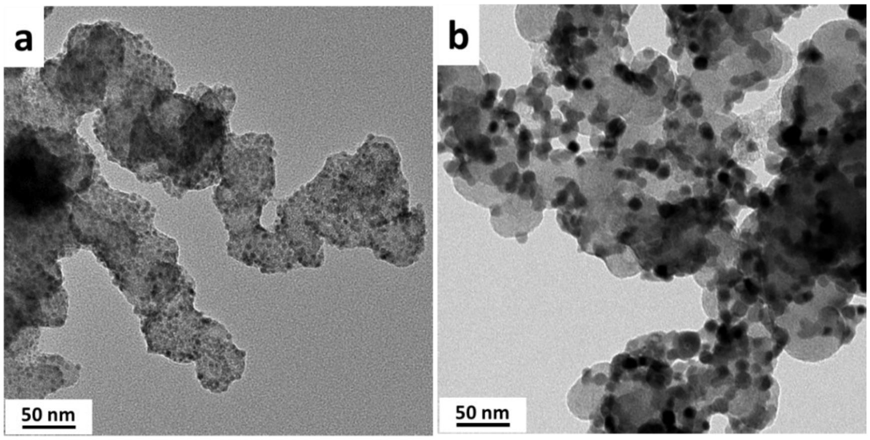

Figure S2. TEM image of carbon-supported (a) PbS-130 and (b) PbS-180.

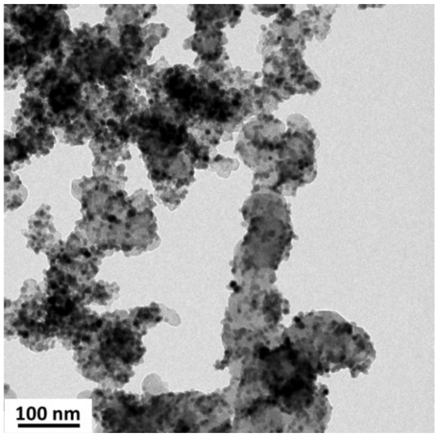

Figure S3. TEM image of PbS-150/C (after ligand exchange).

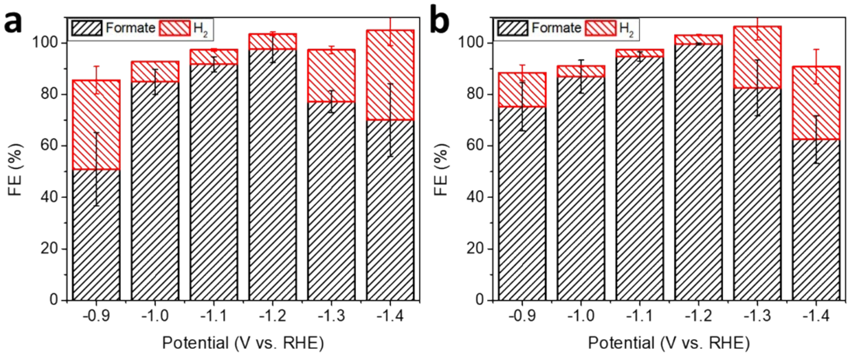

Figure S4. FE to formate and H_2 obtained on (a) PbS-150/C and (b) PbS-180/C at different potentials.

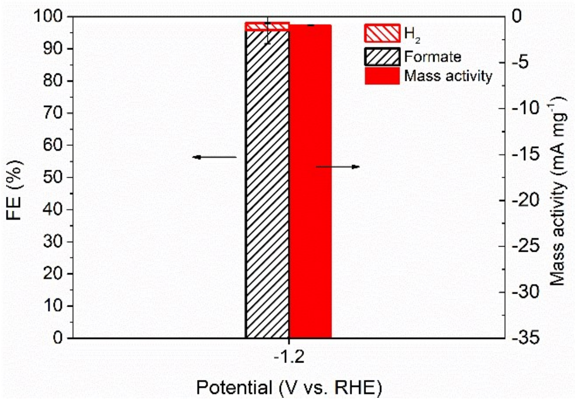

Figure S5. eCO_2RR results on electrodeposited Pb.

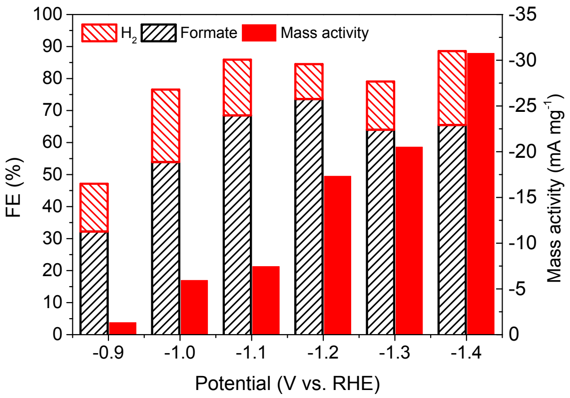

Figure S6. eCO_2RR results on as-deposited PbS-150/C without ligand exchange.

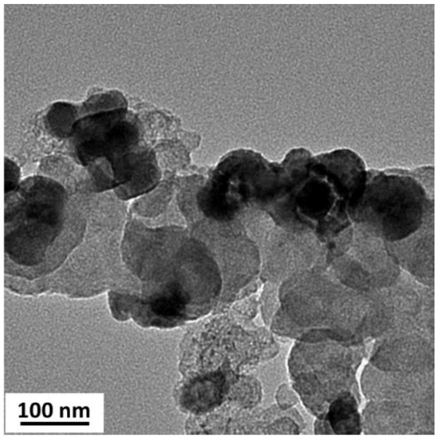

Figure S7. TEM image of PbS-180/C after two potential cycles in CO_2-saturated 0.1 M $KHCO_3$.

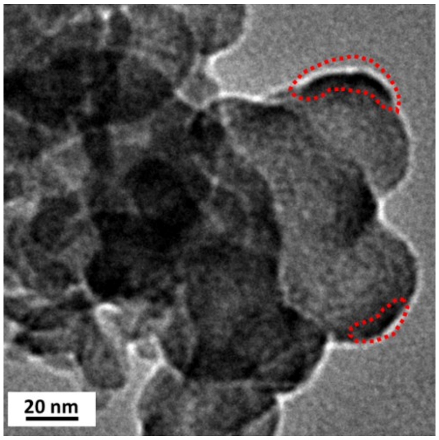

Figure S8. TEM image of PbS-150/C after two potential cycles in CO_2-saturated 0.1 M $KHCO_3$ with the thin film structures clearly highlighted within the red circles.

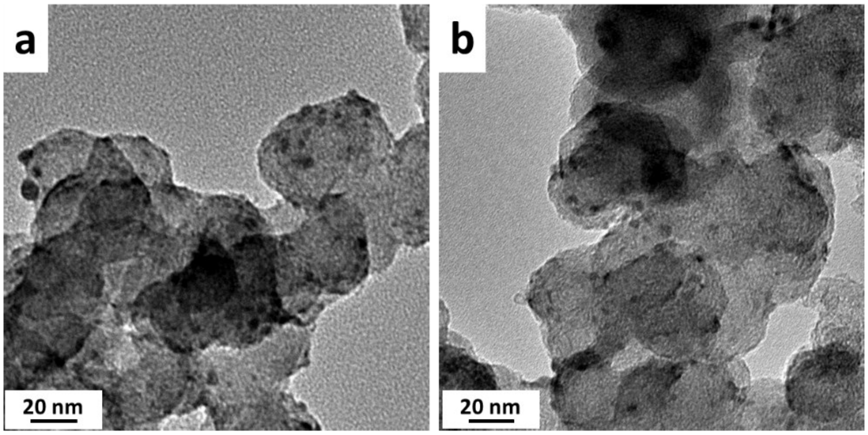

Figure S9. TEM images of (a) PbS-150/C and (b) PbS-180/C after two hours of CPE at -1.2 V vs. RHE in CO_2-saturated 0.1M $KHCO_3$.

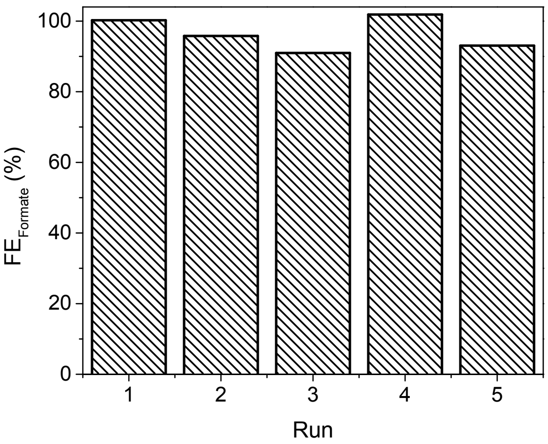

Figure S10. Catalytic stability of PbS-150/C for CO_2 reduction in CO_2-saturated 0.1 M $KHCO_3$ at -1.2 V vs. RHE.

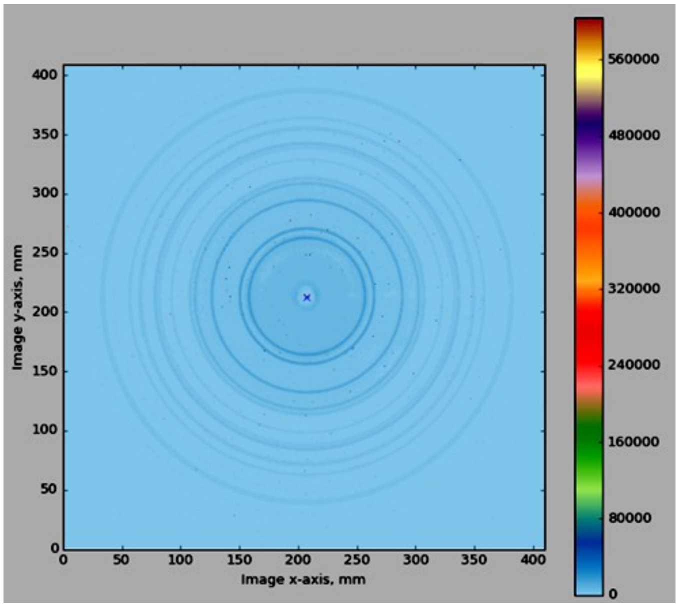

Figure S11. Typical 2D diffraction pattern of PbS-150/C.

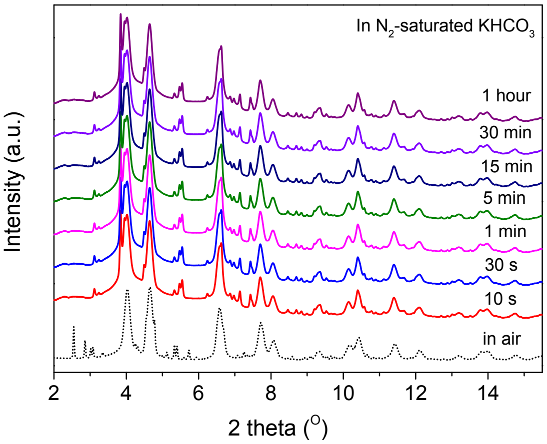

Figure S12. SR-XRD patterns of PbS-150/C under OCP in N_2-saturated 0.1 M $KHCO_3$ for different durations, compared with that in air (dashed line).

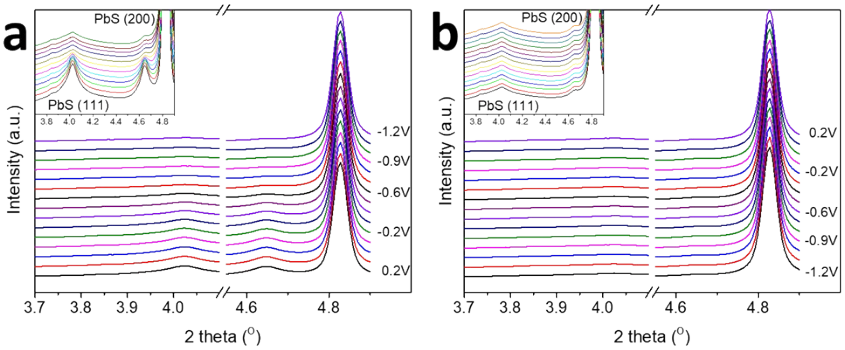

Figure S13. *In situ* SR-XRD patterns from 3.7° to 4.9° of PbS-150/C collected during (a) the second cathodic scan and (b) the second anodic scan. The inset figures are magnified along the y axis in order to show that the PbS is stabilized at potentials ≤ -0.7 V.

Table S1. List of typical diffraction peaks identified in SCPDs.

PbS		$Pb(SCN)_2$		$PbCO_3$		Pb	
2θ	hkl	2θ	hkl	2θ	hkl	2θ	hkl
4.032	111	2.548	110	3.118	110	4.828	111
4.657	200	2.859	200	3.244	020	5.578	200
6.571	220	3.018	-111	3.844	111	7.888	220
7.715	311	3.081	111	3.946	021	9.256	311
8.067	222	3.352	002	4.486	002	9.670	222
10.212	331	4.258	112	5.326	200	12.178	331
10.455	420	4.318	-202	5.470	112	14.496	420
11.422	422	4.550	021	5.548	130		
12.119	511	4.783	310	6.238	220		
13.162	440	5.009	-311	6.502	040		
13.818	531	5.128	311	6.880	041		
14.003	442	5.331	-221	6.976	202		
14.751	620	5.402	221	7.144	132		
		5.587	-113	7.426	113		
		5.736	400	8.464	311		
		5.945	312	8.704	241		
		6.499	130	8.848	150		
		6.696	-131	9.190	223		
		7.077	-223	9.364	330		
		7.256	223				
		7.363	421				
		7.471	510				
		7.804	-331				
		8.585	-423				
		8.925	240				
		9.098	042				
		9.390	134				
		9.664	-531				
		9.765	-225				
		10.671	-712				