Supporting information

Metathetic synthesis of lead cyanamide as a new p-type semiconductor photoelectrocatalyst

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Table S1 Crystallographic data and fractional coordinates for PbNCN. Standard deviations are given in parentheses. The thermal displacement parameters of C and N were constrained to be equal.

Atom	Wyckoff site	*x*	*y*	*z*	U_{iso} (Å^2)
Pb1	4*c*	0.39296(21)	¼	0.63469(15)	0.0246(5)
N1	4*c*	0.3329(26)	¼	0.4394(13)	0.001(3)
N2	4*c*	0.9248(26)	¼	0.3655(18)	"
C1	4*c*	0.1148(25)	¼	0.4051(15)	"

Orthorhombic, *Pnma* (No. 62), $Z = 4$, $a = 5.5514(2)$ Å, $b = 3.8609(1)$ Å, $c = 11.7103(4)$ Å; $R_{wp} = 2.51\%$, $R_p = 1.61\%$, 32 variables.

Table S2 Comparison of bond lengths from this work, single-crystal data and calculated ones by electronic-structure theory (PBE functional). Note that DFT is notoriously unreliable to correctly model the single-/triple C–N bond distances.

Bond lengths (Å)	this work	single crystal	DFT calculation
C1−N1	1.15(3)	1.16(3)	1.227
C1−N2	1.28 (3)	1.30(3)	1.248
Pb1−N1 (–*x*+½, –*y*, *z*+½)	2.311(16)	2.31(2)	2.379
Pb1−N1 (*x*+½, *y*, –*z*+½)	2.607(10)	2.620(13)	2.645
Pb1−N2	2.615(10)	2.622(11)	2.583

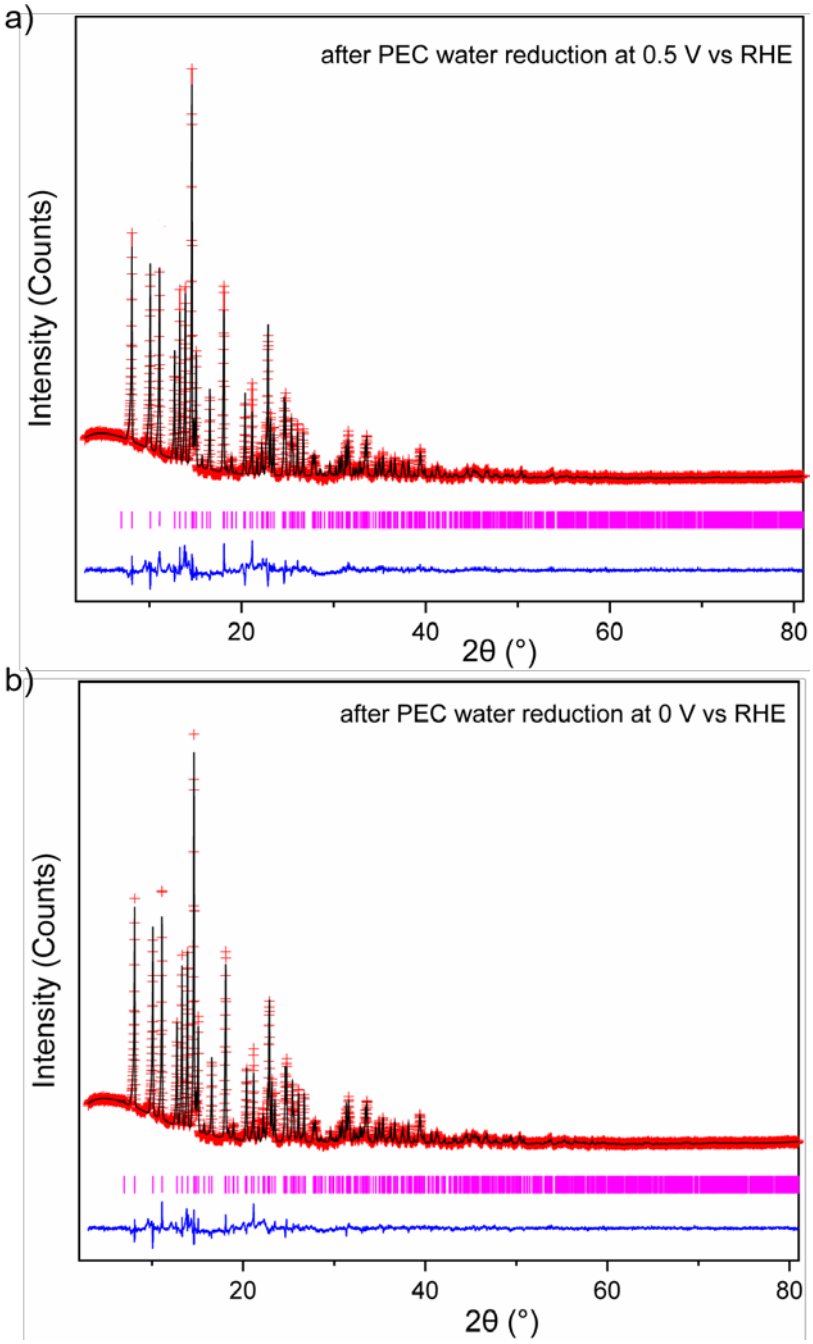

Figure S1 Rietveld refinements of experimental powder XRD patterns of PbNCN photoelectrodes after PEC water reduction at a) 0.5 V vs RHE and b) 0 V vs RHE for 1 h.

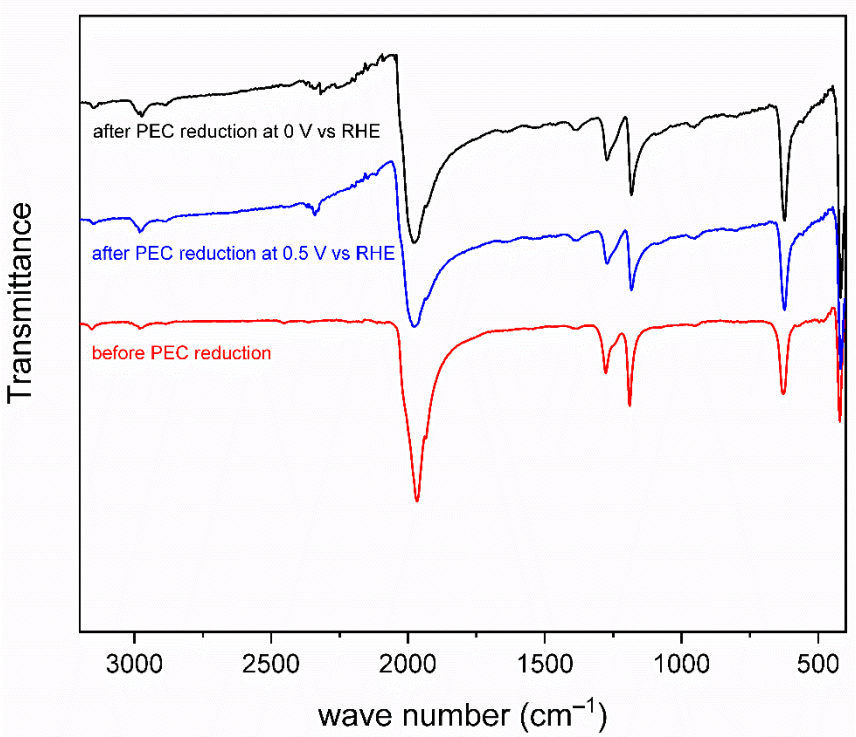

Figure S2 Experimental IR spectrum of separate PbNCN photoelectrodes after PEC water reduction at 0.5 V vs RHE and 0 V vs RHE for 1h comparing with original PbNCN.

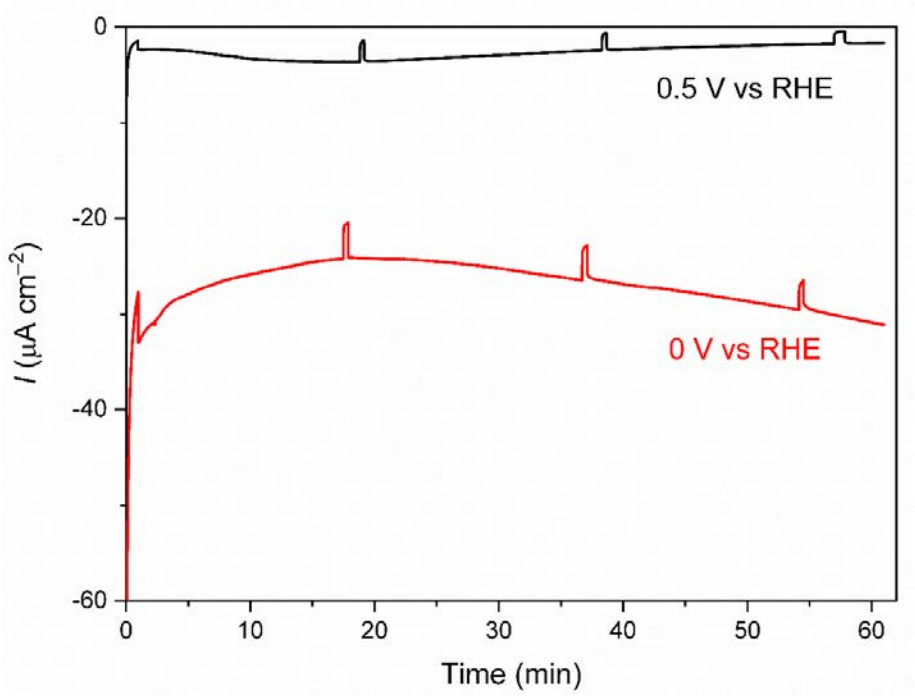

Figure S3 CA of separate PbNCN photoelectrodes at 0.5 V and 0 V vs RHE in 0.1 M kPi electrolyte (pH = 7) under chopped AM 1.5G illumination (100 mW cm^{-2}).

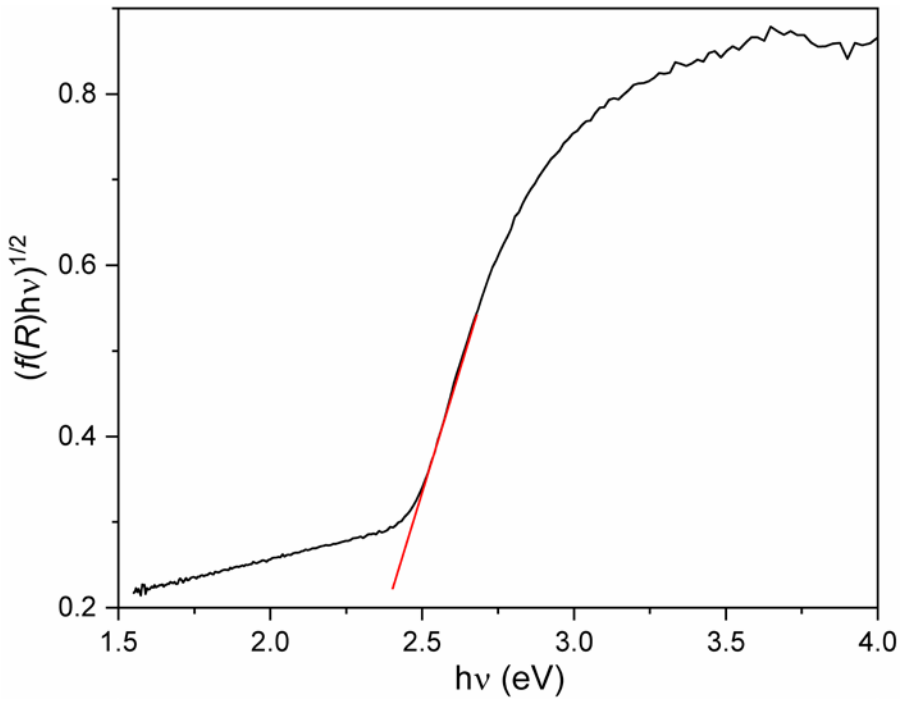

Figure S4 Tauc plot for the PbNCN electrode showing the electronic band gap.