

Constructing 3D compact sulfur host based on carbon-nanotube threaded defective Prussian blue nanocrystals for high performance lithium-sulfur batteries

Experimental section

Synthesis of Na-PB/CNTs and K-PB/CNTs

In a typical synthesis procedure, 100 mg multi-walled CNTs and 0.8 g PVP were dispersed in aqueous solution by ultra-sonication to form a homogeneous suspension. After adding 1 m mol $\text{Na}_4\text{Fe}(\text{CN})_6$ or $\text{K}_4\text{Fe}(\text{CN})_6$ in this suspension, the pH was then adjusted to 1.0 by hydrochloric acid (37%). The suspension was heated at 60 °C under vigorous stirring for 4 h to yield a black blue precipitation. The Na-PB/CNTs and K-PB/CNTs composites were collected by filtration, then washed by water and ethanol for three times, and dried under vacuum at 100 °C for 24 h.

Synthesis of S@Na-PB/CNTs and S@K-PB/CNTs

Typically, 35 mg of Na-PB/CNTs or K-PB/CNTs nanocomposites were first dispersed in 5.0 mL CS_2 by sonication. Then 65 mg sulfur was dissolved into this solution. The following CS_2 evaporation was performed at 40 °C under stirring. Then, the obtained powder was washed by distilled water and absolute ethanol several times and dried under vacuum at 60 °C for 12 h, which can be termed as S@Na-PB/CNTs and S@K-PB/CNTs, respectively.

Soluble lithium polysulfide adsorption tests

Li_2S_x was synthesized by dissolving 13.8 mg Li_2S and 67.3 mg sulfur in 50 mL mixtures of 1,2-dimethoxyethane and 1,3-dioxolane (DOL) under stirring for 12 h. 20 mg Na-PB/CNTs and K-PB/CNTs was soaked with 2 mL 6 mM Li_2S_x solution in an Ar-filled glovebox. The suspension was separated by filtration and the supernatant was characterized by UV-vis spectroscopy (UV-2600, Shimadzu). The sediments were dried naturally in Ar-filled glovebox to form Li_2S_x @Na-PB/CNTs and Li_2S_x @K-PB/CNTs for further X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi) characterizations using monochromatic Al $K\alpha$ radiation.

Structural Characterizations

X-ray diffraction patterns of the samples were measured by the Rigaku X-ray

diffractometer (XRD, Miniflex600, Rigaku Corporation) using $K\alpha$ radiation operated at 40 kV and 15 mA. The morphologies of as-prepared samples were characterized by the field-emission scanning electron microscopy (FESEM, MAIA3, TESCAN, with an accessory EDX spectrometer). Raman spectra of the samples were collected from a micro-Raman spectrometer (JobinYvon LabRAM HR-800). The chemical composition of PB-based composites was examined using the elemental analysis (Elementar Vario EL iii) for the C and N elements, and the inductively coupled plasma-mass spectrometry (ICP-MS, Spectro Blue SOP) for the Na, K, and Fe elements. To measure the conductivity of samples, the PB, CNTs, or PB/CNTs powders were first pressed into a pellet under various pressures, and then tested by the four-probe conductivity measurements (ST2722-SZ, JG Electronic).

Electrochemical measurements

The cathode was fabricated by mixing as-prepared S@Na-PB/CNTs or S@K-PB/CNTs composites, KJ-black (EC600J), and sodium alginate in distilled water with a weight ratio of 80:10:10. And then the slurry was cast onto aluminum foil current collector with a diameter of 12mm. Then, the electrodes were dried at 60 °C under vacuum for 12 h. The CR2032-type coin cells were assembled for electrochemical measurements in an argon-filled glovebox. The electrolyte was 1.0 M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) dissolved in a mixed solvent of DOL/DME (1:1/v:v) with 2.0 wt. % of LiNO_3 . The typical area sulfur mass loading of the cathode is in range of 1.5-3.0 mg cm^{-2} . Galvanostatic discharge/charge measurements were performed on a LAND system in a voltage window of 1.7-2.8 V (vs. Li^+/Li). Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) were performed on a CHI-760 electrochemical workstation. EIS analysis was performed with the frequency range from 100 kHz to 100 mHz. All the electrochemical data were measured at the stationary temperature of 25 °C.

Computational Methods

A first-principles approach based on density functional theory (DFT) was employed to understanding the interaction between LiPS and PB surfaces.[1, 2] All simulations were performed using the Vienna Ab-initio Simulation Package (VASP).[3] Electron-ion interactions were described by the projector augmented wave (PAW) method;[4] the electron exchange-correlation was described using the PBE functional.[5] The cut-off energy for the plane wave basis was set at 400 eV. The force convergence criteria for optimizing atom positions was set to $-0.02 \text{ eV}/\text{\AA}$. The 2×2

PB (001) surface cell, 2×1 with $1 \times 1 \times 1$ k-mesh were used for modeling the adsorption behavior of Li_2S_4 . The adsorption energy is calculated by

$$E_{ads} = E(PS + surf) - E(PS) - E(surf),$$

where $E(PS+surf)$ is the total energy of the entire system, $E(PS)$ is the energy of an isolated Li_2S_4 molecule, and $E(surf)$ is the energy of the clean surface. A more negative adsorption energy indicates a stronger binding force.

References

1. P. Hohenberg and W. Kohn, *Physical review*, 1964, **136**, B864-B871.
2. W. Kohn and L. J. Sham, *Physical review*, 1965, **140**, A1133-A1138.
3. G. Kresse and J. Furthmüller, *Physical review. B, Condensed matter*, 1996, **54**, 11169-11186.
4. P. E. Blochl and P. E. Blöchl, *Physical review. B, Condensed matter*, 1994, **50**, 17953-17979.
5. J. Perdew, K. Burke and M. Ernzerhof, *Physical review letters*, 1996, **77**, 3865-3868.

Table S1 Element contents of Na-PB/CNTs and K-PB/CNTs composites

	Na	K	Fe	C	N
Na-PB/CNTs	1.11 %		13.43%	69.94%	8.85%
K-PB/CNTs		2.55%	13.96%	69.16%	9.80%

Table S2. Summary of the electrochemical performance of S@CNTs threaded polar nanocrystal or Lewis acidic MOF cathode

Sulfur host	Initial capacity/mAh g ⁻¹	Rate/C	Cycles	Decay rate/%
MgAl-LDH@CNT ^[44]	1330	1.0	450	0.1
CNT/Co-NC ^[45]	884	1.0	500	0.067
CNTs-Co ₃ S ₄ NBs ^[46]	954	1.0	500	0.042
HKUST-1/CNTs ^[47]	1263	0.2	500	0.08
Mesoporous TiO ₂ -CNTs ^[48]	932	1.0	500	0.063
CNT/G-Al ₃ Ni ₂ ^[49]	885	1.0	800	0.055
ZIF-8-CNTs ^[50]	840	1.0	500	0.02
UiO-66/CNTs ^[51]	764	0.60	800	0.07
PB/PEDOT ^[29]	1101	0.1	100	0.15
PB ^[30]	1112	0.12	100	0.35
This work	1190	1.0	1000	0.052

Table S3. Summary of the electrochemical performance of MOF-based sulfur cathode using the conventional aluminum foil current collector

Sulfur host	Initial capacity/mAh g ⁻¹	Sulfur loading/mg cm ⁻²	Cycles	Capacity retention/%
MOF-525(Cu) ^[53]	1150 (0.5 C)	0.7	200	61.2
1,2,4-TMB ^[54]	1092 (0.1 C)	1.0	50	73.2
MIL-100 (V) ^[55]	849 (0.1 C)	0.9-1.0	200	64.8
Cu-TDPAT ^[56]	~1000 (0.5 C)	1.2	300	83.1
Mn cluster-based MOF ^[57]	1420 (0.2 C)	2.0	200	69.7
Cu(p-BDS)-(H ₂ O) ₄ /Sulfonic ^[58]	1190 (0.1 C)	1.5-2.0	100	87.7
This work	1000 (0.2 C)	3.0	200	69.0

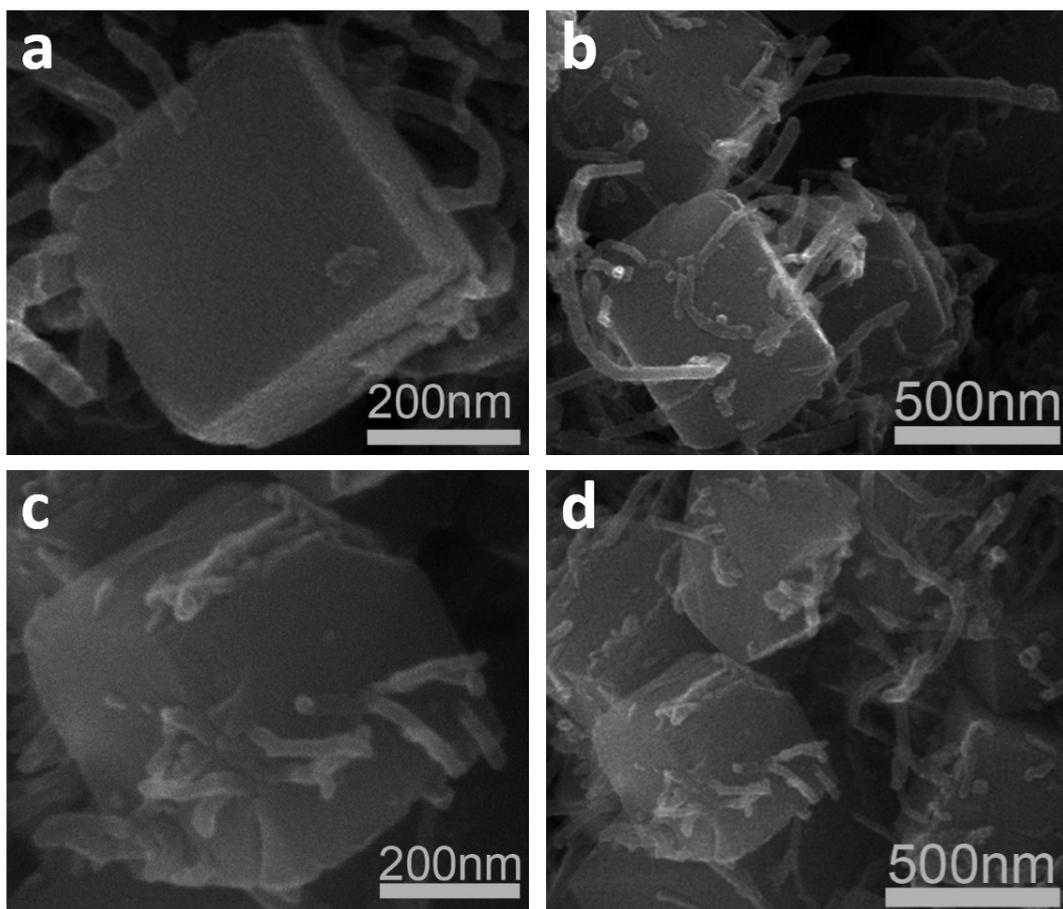


Figure S1 SEM images of S@Na-PB/CNTs (a, b) and S@K-PB/CNTs (c, d) composites

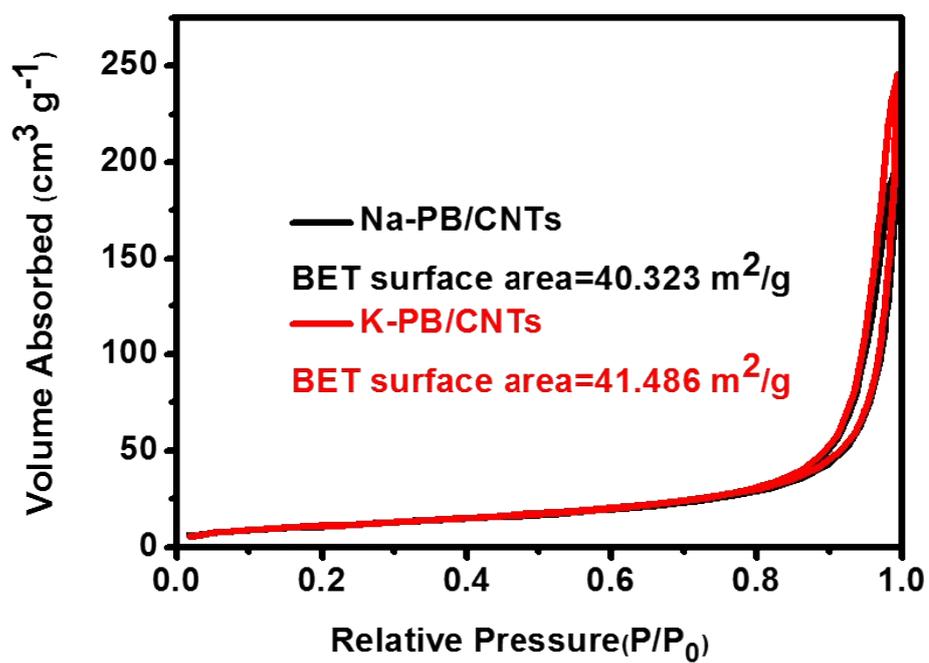


Figure S2 N₂ adsorption–desorption isotherms of Na-PB/CNTs and K-PB/CNTs composites.

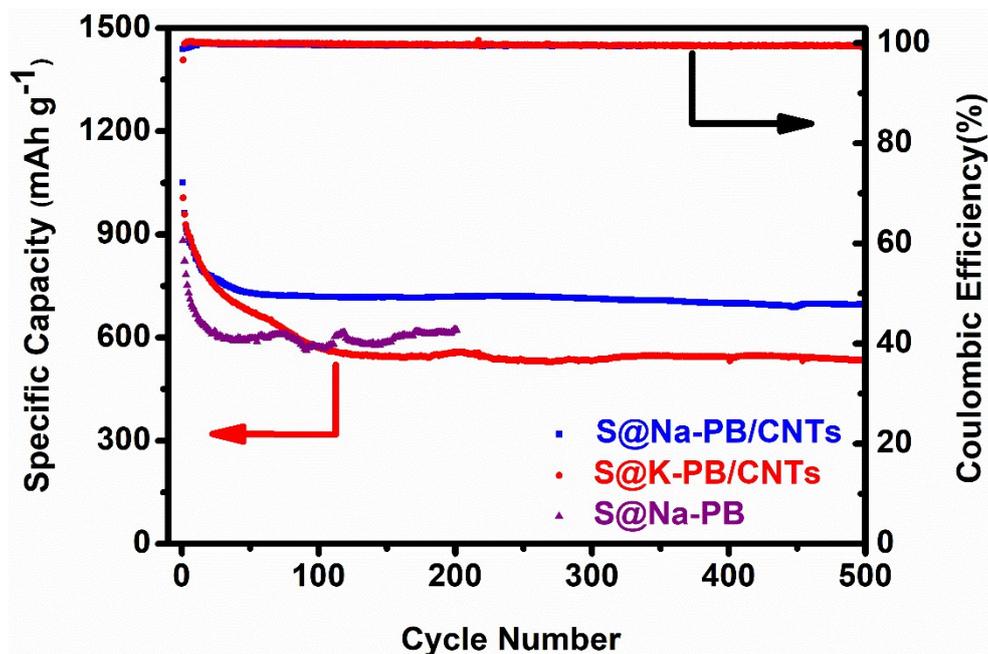


Figure S3 Cycle performances of S@Na-PB, S@Na-PB/CNTs, and S@K-PB/CNTs cathodes at 0.5 C.

Because of the relatively low electronic conductivity of Na-PB host, the initial discharge capacity of S@Na-PB cathode is only 870 mAh g⁻¹. However, as result of strong chemical interaction between Na-PB and lithium polysulfide, the high Coulombic efficiency almost reach 100% and excellent cycling stability (capacity retention of 70.4 % after 200 cycles) can be achieved in S@Na-PB cathode.

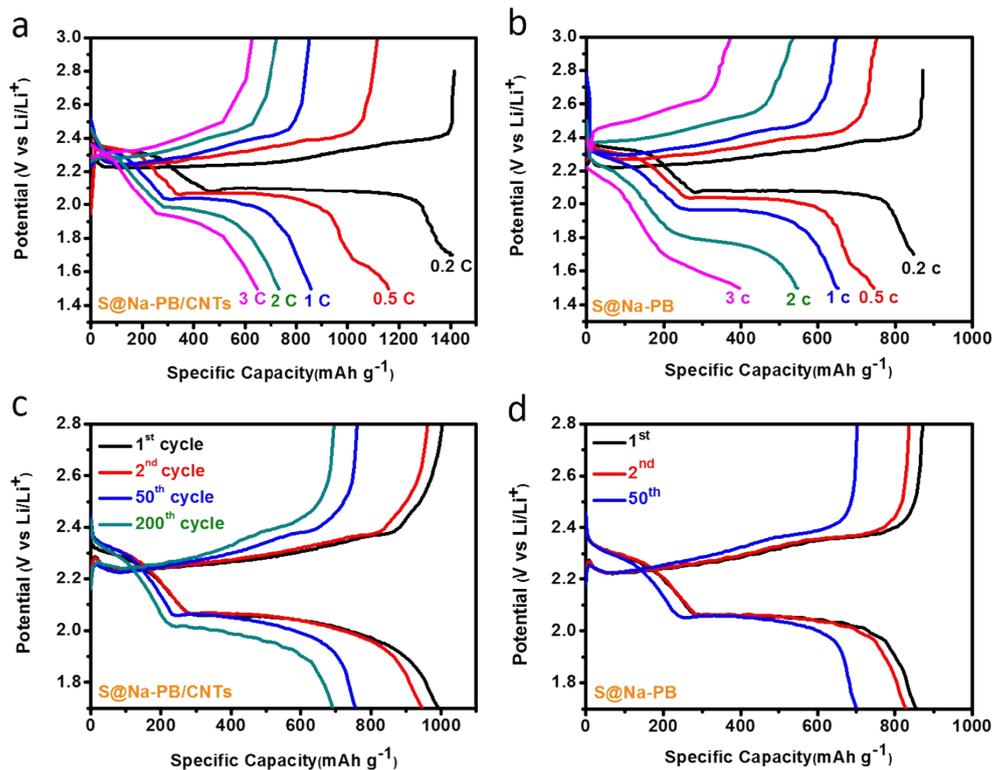


Figure S4 Voltage profiles of (a) S@Na-PB/CNTs and (a) S@Na-PB cathode at various current rates from 0.2 to 3 C; (c) S@Na-PB/CNTs and (d) S@Na-PB cathode with high sulfur areal loading about 3.0 mg cm⁻² at 0.2 C in different cycles.

Specially, the potential gap between the charge and discharge profiles of S@Na-PB cathode increases more quickly than that of S@Na-PB/CNTs cathode as the rate gradually increases from 0.2 to 3 C. It is important to note that the second discharge plateau disappears in voltage profile of S@Na-PB cathode at high rate of 3 C. All these phenomena indicate a better kinetics of S@Na-PB/CNTs electrode.

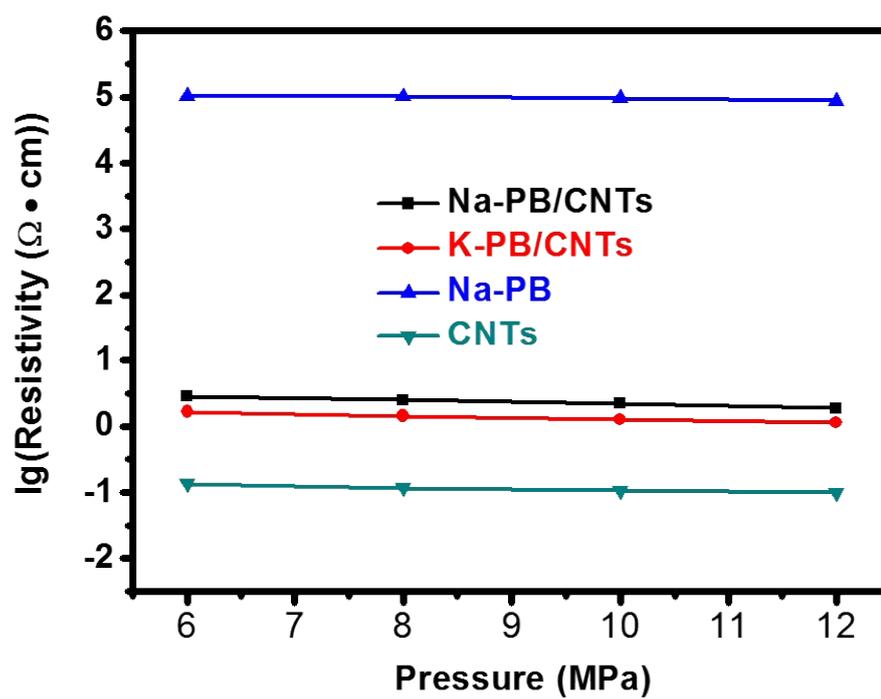


Figure S5 The resistivity of Na-PB, raw CNTs, Na-PB/CNTs, and K-PB/CNTs composites at different pressures.

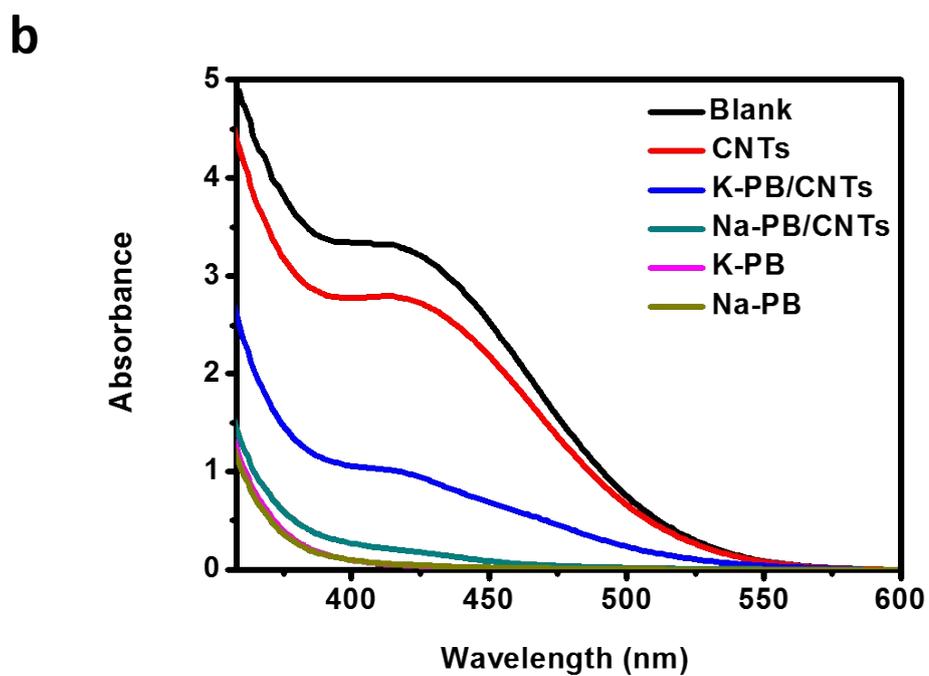
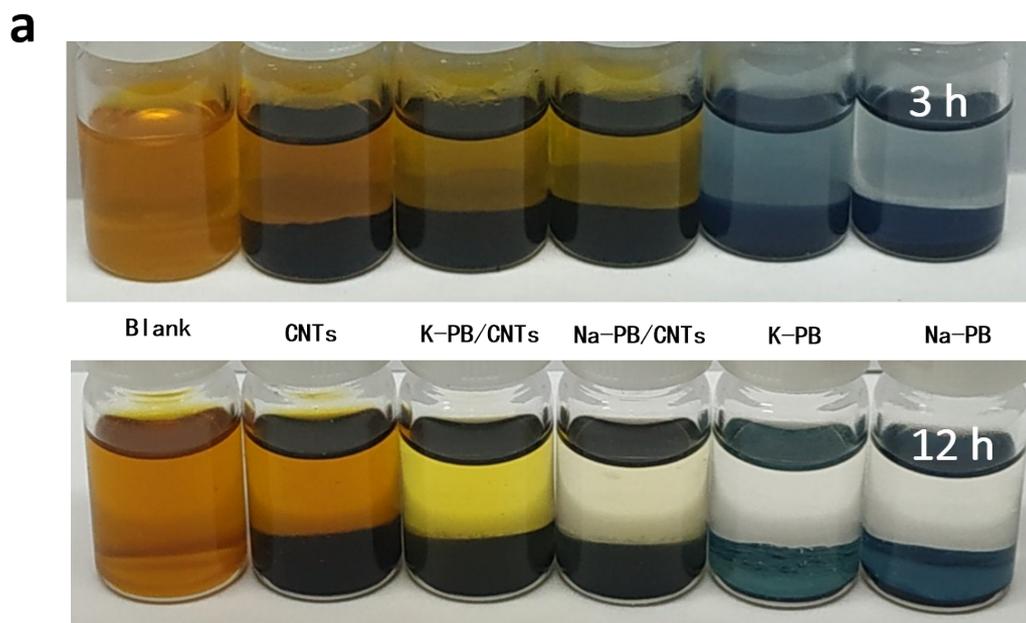


Figure S6 (a) Photographs of static adsorption experiment after 3h and 12 h; (b) UV-visible spectra of L_2S_x solution soaked with CNTs, K-PB/CNTs, Na-PB/CNTs, K-PB and Na-PB for 12 h.

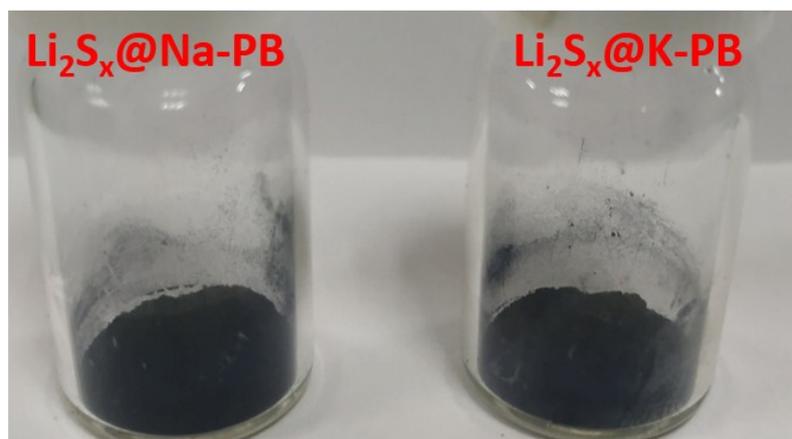


Figure S7 Photo of the PB nanocrystals exposed in the Li_2S_x solution after evaporating the solvents.