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# Introduction

Solid-state metathesis (SSM) reactions have been reported in the synthesis of many inorganic solids including metal borides, nitrides, and carbides.<sup>1-6</sup> These reactions exploit the intrinsic energy of the reactants to promote an exothermic exchange of ions under relatively mild conditions yielding the desired reaction product and a co-produced salt. As such, SSM reactions are well-suited for the preparation of thermally labile compounds. Since 2004 a large number of metal carbodiimide and cyanamide compounds have been prepared *via* SSM reactions between metal halides (MX<sub>n</sub>) and alkali–metal carbodiimides (A<sub>2</sub>(NCN), A = Li, Na).<sup>7-11</sup> More recently, the electrochemical and photochemical properties of this family have been explored with encouraging results.<sup>12-15</sup>

Somewhat simplified, metal carbodiimides may be regarded as pseudo-oxides or "divalent nitrides" and fre-

# Metathetic synthesis of lead cyanamide as a p-type semiconductor<sup>†</sup>

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Lead cyanamide PbNCN was synthesized by solid-state metathesis between PbCl<sub>2</sub> and Na<sub>2</sub>NCN in a 1:1 molar ratio, and its structure was confirmed from Rietveld refinement of X-ray data. Electronic-structure calculations of HSE06 density-functional type reveal PbNCN to be an indirect semiconductor with a band gap of 2.4 eV, in remarkable quantitative agreement with the measured value. Mott–Schottky experiments demonstrate PbNCN to be a p-type semiconductor with a flat-band potential of 2.3 eV vs. the reversible hydrogen electrode (RHE) which is commonly used to estimate the value of the valence band edge position. Moreover, thin films of powderous PbNCN were assembled into a photoelectrode for photoelectrochemical water splitting. On the example of p-type PbNCN, this study provides the first experimental evidence that MNCN compounds can be applied as photocathodes for reductive reactions in photoelectrochemical cells.

quently adopt layered structures in which metal cations alternate with symmetric  $D_{\infty h}$  carbodiimide or lower symmetry cyanamide forms depending on the nature of the bonding metal. These structures are often remarkably similar to those of their analogous oxides with a propensity for [NiAs] and [NaCl] derived motifs in which close-packed layers of NCN<sup>2–</sup> anions alternate with octahedrally coordinated metal cations.<sup>16,17</sup> However, the introduction of larger cations or those with specific coordination preferences yields alternate topologies that are often unique to solid-state NCN<sup>2–</sup> chemistry.<sup>18,19</sup>

This is also the case in lead cyanamide, PbNCN, which one might expect to crystallize in either an  $\alpha$ -SrNCN-type (*i.e.*, NaSCN) or a  $\beta$ -SrNCN-type rock-salt derived structure, given the similar ionic radii of Pb<sup>2+</sup> (r = 1.13 Å) and Sr<sup>2+</sup> (r = 1.19 Å).<sup>20</sup> The structure of PbNCN is, however, somewhat distinct and presents two structural features, which may imbue PbNCN with potential photochemical properties.<sup>21</sup> The first is the highly distorted square pyramidal coordination environment of PbN<sub>5</sub>, augmented by two more N atoms further apart, which is a long way from the regular PbS<sub>6</sub> octahedra seen in rock-salt PbS and more akin to the four-coordinate Pb environment in the PbO litharge structure.<sup>22</sup> This infers the presence of stereochemically active Pb 6s<sup>2</sup> lone pairs,<sup>23</sup> mediated by N 2p orbitals, which may help to promote hole conduction as in PbO.<sup>24</sup>

In addition, the cyanamide anion in PbNCN exhibits a significant deviation from the symmetric carbodiimide form, with distinct single (1.30(3) Å) and triple (1.16(3) Å) bonds, similar to those in molecular cyanamide  $(H_2NCN)$ .<sup>25</sup> This cyanamide character is also expressed in HgNCN and Ag<sub>2</sub>NCN

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binaries, which is attributed to the chemically soft acid-base nature of these cations that bind more covalently to one end of the NCN<sup>2-</sup> unit thereby engendering less symmetric N $\equiv$ C-N<sup>2-</sup> cyanamide forms.<sup>21,25</sup> In recent years, the photocatalytic properties of the n-type semiconductor Ag<sub>2</sub>NCN have been studied, revealing promising water photooxidation and photocurrent generation capabilities.<sup>26</sup> This has been attributed, in part, to the presence of localized dipoles on the asymmetric cyanamide anion, which promote the separation of electronhole pairs, thereby enhancing the photo-generation of carriers.

On the basis of the above considerations PbNCN appears an excellent model compound for photocatalytic investigations. However, whilst the preparation of lead cyanamide reported by Liu *et al.*, which utilizes the reaction of cyanamide with a solution of lead acetate in the presence of ammonia,<sup>21</sup> does yield single crystals, powder samples are prone to significant contributions from a secondary PbO·xH<sub>2</sub>O phase. Here, we report a new SSM routine to synthesize monophasic polycrystalline PbNCN that avoids the formation of such by-products. We then go on to characterize PbNCN as a new p-type semiconductor, with an indirect band gap of 2.4 eV, that can be assembled into a photoelectrochemical cell<sup>27</sup> for water splitting.

## **Experimental section**

#### Synthesis

All synthetic steps were performed in an argon-filled glove box.  $PbCl_2$  (Alfa) and  $Na_2NCN^{28}$  were reacted in a 1:1 stoichiometric ratio, according to eqn (1). The reactants were mixed and ground using an agate pestle and mortar, and the reaction mixture was loaded into a glass ampoule. The ampoule was then placed in a tube furnace under flowing argon and heated to 400 °C for 12 h, with heating and cooling rates of 2 °C min<sup>-1</sup>. The resulting yellow powder was subsequently airexposed and then washed using water to remove excess reactants and the NaCl metathesis salt.

$$PbCl_2 + Na_2NCN \rightarrow PbNCN + 2NaCl$$
 (1)

#### **PXRD** analysis

Powder X-ray diffraction (PXRD) data were collected on a washed sample of lead cyanamide, PbNCN, at room temperature using a calibrated STOE STADI-MP powder diffractometer with a flat sample holder (Mo K<sub>a1</sub>, linear PSD,  $2\theta$  range from 0–85° with individual steps of 0.015°). Rietveld analysis was undertaken using the Rietveld refinement suite GSAS2,<sup>29</sup> using the *Pnma* structural model of PbNCN described by Liu *et al.* as a starting point.<sup>21</sup> In the final cycles of least-squares refinement, atomic positions and isotropic thermal displacement parameters were refined.

#### Infrared and Raman measurements

The infrared spectrum of PbNCN was measured on a washed powder sample with no further pre-treatment using an ALPHA II FT-IR-Spectrometer (Bruker). The Raman spectroscopy was performed on a WITec alpha 300R confocal Raman microscope setup using a 532 nm diode pumped solid state laser. The Raman spectrum was recorded on powder samples on glass slides.

#### SEM

Scanning electron microscopy (SEM) images were acquired on a Leo Supra 35VP SMT (Zeiss).

#### X-ray photoelectron spectroscopy (XPS)

XPS analysis was done in a hemispherical VG SCIENTA R3000 analyzer with a monochromatized aluminum source Al  $K_{\alpha}$  (E = 1486.6 eV) at constant pass energy of 100 eV. The adventitious C 1s line at 284.6 eV was used as a charge-referencing standard. A fitting of high resolution spectra was obtained through the Casa XPS software.

#### Density-functional theory (DFT) calculations

The Vienna *Ab initio* Simulation Package (VASP) code<sup>30</sup> and the Perdew–Burke–Ernzerhof<sup>31</sup> functional in the generalized gradient approximation<sup>32</sup> was adopted to calculate the electronic structure within the framework of density-functional theory (DFT). In addition, the hybrid Heyd–Scuseria–Ernzerhof (HSE06) functional<sup>33,34</sup> was used to obtain a more accurate band gap. The pseudopotentials were constructed by means of the augmented plane-wave method with  $5d^{10}6s^26p^2$ ,  $2s^22p^2$ and  $2s^22p^3$  treated as the valence electrons of the Pb, C and N atoms, respectively. A cutoff energy of 800 eV was adopted.

#### UV-Vis spectroscopy measurements

UV-Vis spectra were collected using a Shimadzu UV-2600 spectrophotometer. The band gap was determined from a Tauc plot by means of the Kubelka–Munk function  $F(R) = (1 - R)^2/2R^{.29}$ 

#### Photoelectrochemical (PEC) characterization

The PbNCN photoelectrode was fabricated *via* an electrophoretic deposition (EPD) process.<sup>35</sup> In short, a uniform suspension was made by sonicating the mixture of 30 mg PbNCN powder and 10 mg iodine in 30 ml acetone. Two precleaned conductive fluorine-doped tin oxide (FTO) slides were immersed in the above suspension with 1 cm distance, and a potential of 30 V was applied between them for 5 min. PbNCN particles were deposited on the electrode. The electrodes were dried at 333 K for 12 hours.

A conventional three-electrode configuration PEC cell (WAT Venture) was used to carry out the measurements. The prepared PbNCN, platinum wire and a 1 M Ag/AgCl electrode were used as working, counter and reference electrodes, respectively. All current values of the photoelectrodes were recorded *versus* 1 M Ag/AgCl and converted *vs*. RHE according to  $E_{\rm RHE} = E_{\rm 1MAg/AgCl}^{\theta} + 0.059$  pH +  $E_{\rm Ag/AgCl}$ . 0.1 M potassium phosphate (KP<sub>i</sub>) buffer at pH 7 was used as supporting electrolyte for all experiments. The electrolyte was prepared with Milli-Q water (18.3  $\Omega$  cm).

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Linear sweep voltammetry (LSV) with a scan rate of 10 mV s<sup>-1</sup> and chronoamperometry (CA) curve at different constant bias *versus* RHE were recorded with a potentiostat (PalmSens4, PalmSens BV). The photoelectrodes were illuminated from the back side with 100 mW cm<sup>-2</sup> simulated visible light (AM 1.5G), which was generated by a solar light simulator (class-AAA 94023A, Newport) equipped with an ozone-free 450 W xenon short-arc lamp. Mott–Schottky measurements were conducted using the Gamry INTERFACE 1010 T Potentiostat/Galvanostat/ZRA workstation in a dark setting at ac amplitude of 5 mV and a frequency of 1000 Hz.

### **Results and discussion**

#### Structural characterization of PbNCN

The surface morphology of PbNCN is shown in Fig. 1. The scanning electron microscopy images reveal that PbNCN's crystallites are in the micrometer range and strongly resemble flowers petal.

The PXRD pattern of PbNCN was indexed to an orthorhombic unit cell with lattice parameters ( $a \approx 5.54$  Å,  $b \approx$ 3.86 Å,  $c \approx 11.72$  Å) in good agreement with those reported by Liu *et al.*<sup>21</sup> This *Pnma* model of PbNCN was therefore used as a starting point for Rietveld analysis, with additional C–N bond and N–C–N angle restraints for a more stable refinement based on the superior single-crystal data.<sup>21</sup> This resulted in an excellent agreement between the observed and calculated intensities (Fig. 2), and a chemically sensible model with reasonable agreement factors (Table S1†).

The resultant structural model is very close to that reported by Liu *et al.*, characterized by corrugated double layers of NCN<sup>2-</sup> anions and Pb<sup>2+</sup> cations (Fig. 3). The divalent Pb cation is coordinated by five terminal nitrogen atoms with one short apical Pb–N1 bond of 2.311(16) Å almost parallel to the *c* axis and four longer basal bonds (2× Pb–N1 = 2.607(10) Å; 2× Pb–N2 = 2.615(10) Å) in a distorted square-pyramidal environment, augmented by two nonbonding Pb–N distances of 3.472(17) Å. This reflects the presence of stereochemically active 6s<sup>2</sup> lone pairs that are orientated away from the PbN<sub>5</sub> polyhedra into the interlayer voids, as seen in litharge PbO.<sup>17</sup> A comparison of the derived bond lengths from this work and those from the single-crystal analysis and DFT calculations is given in Table S2.<sup>†</sup>



Fig. 2 Rietveld fit of PbNCN to Mo  $K_{\alpha 1}$  PXRD data, showing observed (red), calculated (black), and difference (blue) intensities. Bragg positions of PbNCN (pink) are denoted by vertical markers.



**Fig. 3** Projection of (a) the crystal structure of PbNCN along *b*, (b) the coordination environment of  $Pb^{2+}$  with dashed bonds representing the nearest contact towards the neighboring double layer, and (c) the crystal structure of PbNCN along *c*.





Fig. 1 SEM micrograph of PbNCN powder with different magnification.

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Fig. 4 Infrared and Raman spectra of PbNCN.

imide anions.<sup>7,36,37</sup> The asymmetric and deformation vibrations are observable in the Raman spectra (Fig. 4), while the symmetric vibrations are extremely weak.

To investigate the stability of PbNCN to the PEC water reduction process, XRD and IR measurements were performed on a portion of separate PbNCN photoelectrodes removed from the thin film after PEC at 0.5 V *vs.* RHE and 0 V *vs.* RHE for 1 h in potassium phosphate electrolyte at pH 7, respectively. The Rietveld refinements shown in Fig. S1<sup>†</sup> indicate the phase purity of PbNCN and its structural bulk stability during PEC water reduction. Furthermore, the IR spectrum of PbNCN after PEC water reduction is consistent with that of the asmade product (Fig. S2<sup>†</sup>), confirming that the cyanamide character is also maintained. Fig. S3<sup>†</sup> illustrates the CA at 0.5 V *vs.* RHE and 0 V *vs.* RHE recorded for 1 h.

#### **Electronic structure**

The optical band gap of a yellow PbNCN powder was determined by means of UV-vis spectroscopy, yielding a value of 2.4 eV (Fig. S4†) with the slope of the Tauc plot fitting well for the exponent r = 2, indicating an indirect transition.<sup>38</sup> This value is similar to the experimental indirect band gaps of 1.9 eV, 2.8 eV and 2.0 eV as determined for  $\alpha$ -PbO,  $\beta$ -PbO and PbO<sub>2</sub>, respectively.<sup>39,40</sup>

In order to furnish more details of the electronic structure of PbNCN, the band structure was calculated (Fig. 5). The DFT calculation yields an indirect zero-temperature band gap of approximately 2.4 eV between VBM (at -0.14 eV) and CBM (at 2.26 eV) located at (0.154, 0, 0) and  $U(\frac{1}{2}, 0, 0)$ , respectively. This value is practically identical with that determined from UV-Vis measurements, see above.

The band structure analysis clarifies that the levels occupied by the Pb 6s electrons are the dominant contribution in the region between approximately -11 eV and -8 eV. The region above, between -8 eV and 0 eV, is primarily composed of N 2p levels. Additionally, in the vicinity of the VBM,





**Fig. 5** Band structure of PbNCN with orbital contributions of C 2s, C 2p, N 2s, N 2p, Pb 6s, and Pb 6p represented by green, blue, light blue, orange, black and red colours, respectively.

between -4 eV and 0 eV, the N 2p levels dominate, with a little admixture of dispersed Pb 6s and Pb 6p levels, while the CBM consists of emptied Pb 6p levels. This picture is reminiscent of that in litharge PbO,<sup>23</sup> and alludes to an (antibonding) interaction between the Pb 6s and N 2p orbitals or, in an alternative wording, indicates the formation of a stererochemically active  $6s^2$  lone pair, which may be beneficial to hole conduction.<sup>41</sup>

#### Photoelectrochemistry

In order to verify or falsify the above expectations, photoelectrochemical experiments were performed on as-deposited PbNCN thin film electrodes prepared from PbNCN powder *via* an electrophoretic deposition (EPD) process. The Mott– Schottky (MS) plot was performed at 1000 Hz frequency in the dark, Fig. 6(a). The curve exhibits a negative slope, indicating



**Fig. 6** (a) The Mott–Schottky (M–S) plot of the PbNCN photocathode at 1000 Hz in the dark and (b) band-edge positions of PbNCN.

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lead cyanamide to be a p-type semiconductor. This is exceptional, the second report only of p-type semiconductivity in a solid-state metal cyanamide or carbodiimide after NiNCN,<sup>42</sup> with n-type behavior typically predominating, as in analogous metal oxides.<sup>8,26</sup> NiNCN as a p-type semiconductor has been previously integrated into a p-type dye-sensitized solar cell. It should be noted that PbO, structurally and chemically related to the pseudo-oxide PbNCN, has been reported as a p-type semiconducting behavior by photocurrent measurements.<sup>43</sup> Although PbO could show anodic photocurrent (n-type behavior) at relative higher potential, the surface of PbO will be oxidized to higher oxides, *i.e.* PbO<sub>2</sub> or intermediates due to photogenerated holes.<sup>44</sup>

The flat-band potential was estimated from the extrapolation of the MS plot to be about 2.3 eV relative to RHE, which is commonly used to estimate the VBM position in p-type semiconductors. It should be noted that the absolute values of the VBM are generally negative, *ca.* 0.1–0.3 V from the flat band potential. The VBM of PbNCN was estimated between 2.2 and 2.0 eV, and the CBM position was estimated to be between -0.2 and -0.4 eV on the RHE scale, Fig. 6(b). The CBM position and p-type behavior would render PbNCN a possible candidate for photoelectrochemical water reduction. Furthermore, we note that the conduction band and valence band positions straddle the water redox potentials, indicating the potential of splitting water without external bias.<sup>45</sup>

Two additional separate electrodes were used to carry out LSV measurements in different scan direction to avoid any reduction or oxidation of Pb affecting the photocurrent response. The results are depicted in Fig. 7. A cathodic photocurrent was observed when sweeping negatively and positively, thereby confirming the p-type nature of PbNCN inferred from Mott–Schottky measurements. When sweeping in different directions, a similar net photocurrent was achieved. The noticeable dark current could be caused by the large crystal size of PbNCN, which is inadequate to fully block the underlying FTO substrates.

The periodic on/off photocurrent response of the PbNCN electrode is depicted in Fig. 8. Just like the LSV curves, the CA curves also develop a cathodic current at 0.5 V *vs.* RHE. It reconfirms the p-type character of semiconducting PbNCN. The PEC performance demonstrates that PbNCN is a promising photo-active material which is worthy of further investigation.

#### X-ray photoelectron spectroscopy (XPS) analysis

The surface of a PbNCN photocathode after PEC water reduction at 0 V vs. RHE for 1 h was analyzed by XPS (Fig. 9). The obtained results clearly confirm the stability of the PbNCN phase. In the Pb 4f region, two dominant components at 138.4 eV (Pb 4f<sub>7/2</sub>) and 143.2 eV (Pb 4f<sub>5/2</sub>) are observed, corresponding to Pb<sup>2+</sup> (PbNCN and PbO).<sup>46</sup> No metallic lead was formed during the photoelectrochemical operation. Some part of the active surface, however, was covered by phosphate species as evidenced by the low intense doublet at 139.8 eV and 144.5 eV and additionally confirmed by the P 2p<sub>3/2</sub> peak at



Fig. 7 LSV curves of a PbNCN photocathode in 0.1 M KP<sub>i</sub> electrolyte (pH = 7) at a scan rate of 10 mV s<sup>-1</sup> under chopped AM 1.5G illumination (100 mW cm<sup>-2</sup>). The difference between (a) and (b) is the scan direction.



Fig. 8 Periodic on/off photocurrent response of a PbNCN electrode in 0.1 M KP<sub>i</sub> electrolyte (pH = 7) at 0.5 V vs. RHE under chopped AM 1.5G illumination (100 mW cm<sup>-2</sup>).

132.8 eV in the survey spectrum (not shown). On the other hand, in the high-resolution XPS C 1s spectrum, apart from the typical C–C component at 284.6 eV, two peaks at 285.8 eV and 287.8 eV appear, which are attributed to C–N and C $\equiv$ N



Fig. 9 XPS Pb 4f and C 1s spectra of a PbNCN photocathode after PEC water reduction at 0 V vs. RHE for 1 h.

species, respectively, typical of cyanamide.<sup>47</sup> Unfortunately, this discussion cannot be additionally supported by the analysis of the N 1s region, as it overlaps with the Pb 4d photoemission. The calculated value of the molar ratio of  $Pb^{2+}$  species to carbon atoms in C–N and C=N moieties is *ca.* 3.5, showing that a large part of Pb has formed an oxide phase (PbO) on the outermost surface.

# Conclusions

Lead cyanamide, PbNCN, has been prepared by an SSM route and structurally characterized through PXRD and IR measurements. Electronic structure calculations indicate an indirect band gap of 2.4 eV, in excellent agreement with the measured value from UV-vis spectroscopy. Mott-Schottky experiments demonstrate PbNCN to be a p-type semiconductor with a CBM position theoretically suitable for application as a photocathode for photochemical water reduction. The photoelectrochemical measurements developed cathodic photocurrent for water reduction. The bulk stability of PbNCN in the given potential range has been confirmed by means of XRD and IR. The complementary XPS analysis reveals that the surface composition differs from the bulk, similar to non-oxidic materials used as photoelectrodes. Interestingly, no metallic Pb could be detected in the surface region. Although it is clear from the environmental perspective that the commercial application of Pb-containing materials for solar energy conversion is unrealistic, this study provides the first experimental evidence that MNCN compounds can be applied as photocathodes for reductive reactions in photoelectrochemical cells. These findings on photoactive properties encourage further exploration of cyanamide compounds as novel functional materials for solar energy applications.

# Conflicts of interest

There are no conflicts to declare.

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