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# Carbon nitride used as a reactive template to prepare mesoporous molybdenum sulfide and nitride†

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Carbon nitride  $C_3N_4$  has been used as a sacrificial template to prepare inorganic materials with hierarchical pore structure.  $C_3N_4$  impregnated with ammonium heptamolybdate was treated in reactive gas mixtures ( $H_2S/H_2$  or  $NH_3/H_2$ ). This approach allowed mesoporous molybdenum sulfide and molybdenum nitride materials to be obtained that replicate the morphology of the  $C_3N_4$  template. Advantageous catalytic properties have been demonstrated in the thiophene hydrosulfurization (HDS) and electrochemical hydrogen evolution reaction (HER). The highest rates in both reactions were observed for partially sulfidized  $Mo_2N$  solid.

## Introduction

Molybdenum is widely used in industrial catalytic processes such as hydrotreating,<sup>1–3</sup> and currently studied as a promising alternative for highly expensive platinum group metals in processes for producing sustainable energy and reducing environmental pollution.<sup>4–6</sup> Many recent works describe application of molybdenum sulphides or selenides, nitrides, carbides and phosphides (both supported and unsupported) in the reactions of hydrogen evolution,<sup>7–9</sup> oxygen reduction,<sup>10,11</sup> or carbon dioxide reduction.<sup>12</sup> For both electrochemical and catalytic reactions porous materials with hierarchical systems of interconnected macropores and mesopores are preferable because such structure facilitates diffusion of the reactants. In order to synthesize mesoporous Mo sulfides and nitrides versatile techniques have been proposed such as topotactic transformations of oxides<sup>13,14</sup> or of hybrid materials.<sup>15</sup> One of the most popular techniques to control the textural properties is template-based synthesis strategy. To prepare molybdenum sulfide and nitride, templating with silica,<sup>16,17</sup> polymers and MOFs<sup>18,19</sup> or biotemplating<sup>20,21</sup> have been applied. In the majority of templating methods the removal of template must be carried out at the final step, usually by etching. To avoid etching step the use of sacrificial templates is preferable. Carbon nitride has been first used as a sacrificial and reactive template by Antonietti and coll.<sup>22,23</sup> Upon heating of mesoporous  $C_3N_4$  impregnated with metal oxide species chemical reaction occurs that converts oxides to the corresponding nitrides (Al–Ga–N) and (Ti–V–N). Carbon nitride was also

applied as a template to obtain N-doped carbon layers with increased porosity by means of thermal treatment at 900 °C.<sup>24,25</sup> When a process using  $C_3N_4$  as a template is carried out in the inert atmosphere, the temperatures as high as 800–900 °C are required to fully transform metal oxide species to nitrides. While suitable to prepare nanoparticles of refractory nitrides, such temperatures are prohibitive for obtaining highly divided materials, because of advanced sintering.

In this work we demonstrate that in the reductive atmosphere carbon nitride can play a role of sacrificial reactive template at much lower temperatures. Moreover, the presence of a transition metal could further decrease the decomposition temperature of  $C_3N_4$ . This allows obtaining highly divided mesoporous materials, as demonstrated for the case study of  $MoS_2$  and  $Mo_2N$  materials with hierarchical porosity and advantageous catalytic properties in HDS and HER reactions.

## Experimental

### Materials preparation

To prepare carbon nitride ( $C_3N_4$ ), typically 30 g of urea was placed in a Pyrex tube, covered with a Pyrex cap and heated in static air for 2 h at 550 °C, with heating rate 10 °C min<sup>−1</sup>. Ammonium heptamolybdate (AHM) was supported onto carbon nitride by incipient wetness impregnation from aqueous solution (10% wt. AHM/ $C_3N_4$ ). To carry out the treatments in reductive atmosphere, weighted amount of 10% wt. AHM/ $C_3N_4$  (ca. 0.8 g) was placed in a Pyrex reactor and treated in a reactive gas mixture ( $NH_3/H_2$  or  $H_2S/H_2$ ) for 2 h at 550 °C with heating rate 5 °C min<sup>−1</sup>. The obtained samples are designated as  $Mo_2N$ -CN and  $MoS_2$ -CN, respectively. The solid obtained after heating of AHM/ $C_3N_4$  in pure nitrogen flow was also characterized as a reference.

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## Characterizations

Textural properties of the  $C_3N_4$  template and Mo-containing samples were studied by  $N_2$  adsorption-desorption volumetry at  $-196^\circ C$  on a Micrometrics ASAP 2010 device. Pore distributions have been calculated using BJH equation. The samples were outgassed before the measurements at  $400^\circ C$  for 2 h. Phase composition was studied by X-ray diffraction (XRD) on a Bruker D8 Advance A25 diffractometer with  $CuK\alpha$  emission. The phases were identified by comparison with JCPDS standards database. Phase composition was quantified using Rietveld refinement as implemented in the Philips XPert software. CHONS analysis was performed on a Thermo Fisher Flash 2000 device. Transmission Electron Microscopy (TEM) images were obtained on a JEOL 2010 instrument at 200 KV. TEM images were analyzed using Digital Micrograph Gatan program package. Temperature-programmed reduction (TPR) was carried out in a quartz reactor. The samples (*ca.* 0.01 g) were linearly heated under a hydrogen flow ( $50\text{ ml min}^{-1}$ ) from room temperature to  $1050^\circ C$  (heating rate  $5^\circ C\text{ min}^{-1}$ ). The gases evolved upon reduction were detected by means of Thermo Fischer quadrupole mass-spectrometer. Thermogravimetric analysis (TGA) was carried out on a SETARAM device. A weighted amount of sample powder (5–10 mg) was placed in an alumina crucible and heated in nitrogen flow from room temperature to  $800^\circ C$  at a  $10^\circ C\text{ min}^{-1}$  rate (NB: cyan and HCN released upon TPR and TGA experiments are toxic and should be neutralized at the reactor outlet).

## Catalytic tests

The catalysts were tested in thiophene HDS right after their preparation: 40 mg of the sample was placed in a quartz reactor in continuous flow of  $H_2$  ( $50\text{ ml min}^{-1}$ ) passed through a bubbler with thiophene. HDS was studied at 320, 330,  $340^\circ C$ , respectively. The products were analyzed by gas chromatography on an Agilent 7820A device.

Electrochemical hydrogen evolution reaction (HER) was performed in a three electrode electrochemical cell in Ar-saturated 0.5 M  $H_2SO_4$  electrolyte at room temperature. Glassy carbon rotating electrode was used as a working electrode, saturated calomel electrode as a reference electrode and graphite rod as a counter electrode. 10 mg of catalyst was suspended in 400  $\mu\text{l}$  of Nafion (0.5%) and 800  $\mu\text{l}$  of EtOH and treated by ultrasound. 10  $\mu\text{l}$  of the obtained catalytic ink was spread on the working electrode and dried. Activity of the catalysts in HER was measured in the potential range from  $-800\text{ mV}$  to  $100\text{ mV}$ . LSV curves were obtained at  $5\text{ mW s}^{-1}$  rate. Tafel slopes were calculated *via* Tafel equation. Electrochemically active surface area (ECSA) was calculated from the non-faradaic parts of CV curves at sweep rates from 50 to  $300\text{ mV s}^{-1}$ .

## Results and discussion

### Reactivity of $C_3N_4$ vs. the nature of gas atmosphere and the presence of molybdenum

If heated under nitrogen flow, bare carbon nitride starts to decompose approximately at  $600^\circ C$  and the decomposition

completes at  $780^\circ C$  (Fig. S1†). The mass loss is nearly 100% (the solid completely disappears from the crucible). These results are in good agreement with previous reports of the TGA of  $C_3N_4$  carried out in nitrogen.<sup>26</sup> As shown by mass spectrometry,<sup>27</sup> gaseous CN and  $C_2N_2$  species and  $N_2$  are formed during the decomposition of  $C_3N_4$ . Addition of ammonium heptamolybdate (AHM) by impregnation results in the decrease of  $C_3N_4$  decomposition temperature by nearly  $100^\circ C$  (Fig. S1†). This suggests a chemical reaction between AHM and  $C_3N_4$  and probably a catalytic effect of formed Mo species on the decomposition. The mass loss is 92%; a solid residual was observed in the crucibles. Changing the gas flow from  $N_2$  to  $H_2$  leads to a further decrease of the onset temperature of decomposition (Fig. 1). For bare  $C_3N_4$  it shifts to  $500^\circ C$  and for the AHM/ $C_3N_4$  sample it becomes approximately  $450^\circ C$ . At the same time the nature of the released gases is modified: formation of  $NH_3$  and HCN occurs in hydrogen flow instead of cyan release previously observed in the inert atmosphere.

Therefore, both addition of Mo species and applying hydrogen flow lead to a decrease of the  $C_3N_4$  elimination temperature. Moreover, simultaneous application of  $H_2$  and addition of AHM provides a synergistic effect. Similar reaction onset temperature of  $450^\circ C$  is observed for AHM/ $C_3N_4$  sample in pure  $H_2$  (Fig. 1) and in the  $NH_3/H_2$  mixture (Fig. S2†).

### Properties of the solid products

We further collected the solid products of AHM/ $C_3N_4$  reactions in different atmospheres ( $N_2$ ,  $NH_3/H_2$  and  $H_2S/H_2$ ) and analyzed their properties. The XRD patterns are shown in Fig. 2 and S3.† In the  $N_2$  atmosphere highly divided  $\gamma\text{-Mo}_2N$  is formed at  $650^\circ C$  (Fig. S3†), but it is polluted with  $MoO_2$  oxide (13% vol. according to Rietveld analysis). However, observing  $Mo_2N$  as a major phase proves that  $C_3N_4$  plays the role of nitrogen source and therefore acts as a reactive template. Using  $NH_3/H_2$  and  $H_2S/H_2$  flows allows obtaining at  $550^\circ C$  almost pure phases of cubic  $\gamma\text{-Mo}_2N$  and hexagonal  $2H\text{-MoS}_2$  (Fig. 2), respectively (and small impurity of  $MoO_2$ , 2–4% vol).

In agreement with XRD, chemical analysis shows the S and N content values close to the theory values for the Mo sulfide and

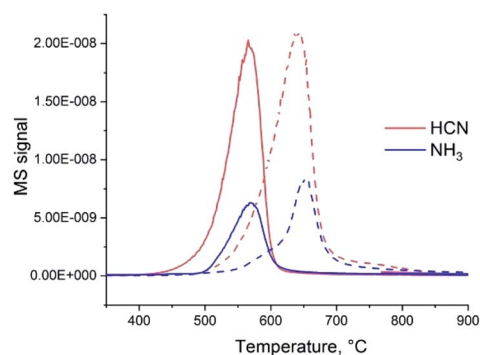


Fig. 1 MS signals of gases, released during heating in hydrogen of the  $C_3N_4$  and AHM/ $C_3N_4$  samples. The solid lines correspond to AHM/ $C_3N_4$  and dashed lines to bare  $C_3N_4$  (the intensity of MS signals was normalized).

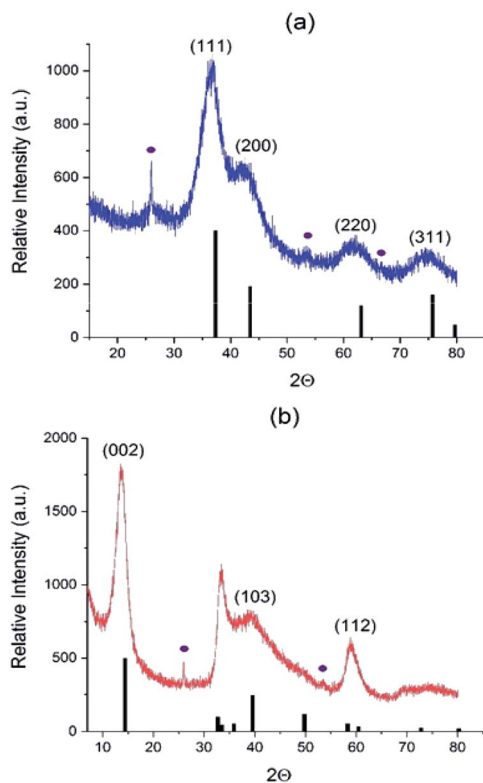


Fig. 2 Diffraction patterns of (a)  $\text{Mo}_2\text{N-CN}$  (b)  $\text{MoS}_2\text{-CN}$ . Black bars correspond to (a)  $\text{Mo}_2\text{N}$  phase (00-025-1366) and (b)  $2\text{H-MoS}_2$  phase (03-065-0160); violet circles correspond to  $\text{MoO}_3$  impurity (01-078-1070).

nitride, respectively (Table 1). Carbon is almost completely removed from the  $\text{MoS}_2\text{-CN}$  sample, but is still present in the  $\text{Mo}_2\text{N-CN}$  (probably as amorphous matter not detected by XRD). Small amount of oxygen in both samples is probably due to partial surface oxidation and due to a contribution from minor  $\text{MoO}_3$  impurity.

Therefore, the use of the reactive gas mixtures ( $\text{NH}_3/\text{H}_2$  or  $\text{H}_2\text{S}/\text{H}_2$ ) allowed us to obtain at  $550^\circ\text{C}$  the materials containing molybdenum nitride or sulfide as major components. We further studied the morphology and the catalytic properties of these materials.

The  $\text{C}_3\text{N}_4$  template has the specific surface area ( $S_{\text{BET}}$ )  $157\text{ m}^2\text{ g}^{-1}$  and pore volume  $0.87\text{ cm}^3\text{ g}^{-1}$  (Table 2). The isotherm shape corresponds to type II (IUPAC classification) which is characteristic of the macroporous materials (Fig. 3a). Pore size distribution is broad and has a polymodal shape (Fig. 3b), the pores with diameters between 30 and 50 nm being the most abundant

Table 1 Results of CHONS analysis

Element, wt% sample	N	C	H	S	O
$\text{C}_3\text{N}_4$	62.1	35.3	1.55	0	0.91
$\text{Mo}_2\text{N-CN}$	6.6	8.4	0.72	0	2.09
$\text{MoS}_2\text{-CN}$	1.7	0.43	0.25	29.0	3.9

Table 2 Textural properties of the samples

Sample	$S_{\text{BET}}, \text{m}^2\text{ g}^{-1}$	Pore volume, BJH, $\text{cm}^3\text{ g}^{-1}$
Bare $\text{C}_3\text{N}_4$	157	0.87
$\text{Mo}_2\text{N-CN}$	96	0.32
$\text{MoS}_2\text{-CN}$	64	0.31

ones. The amount of micropores is rather low; the narrow peak at pore radius *ca.* 2 nm is an artifact caused by cavitation-induced evaporation (Fig. 3b).

The isotherms of  $\text{Mo}_2\text{N-CN}$  and  $\text{MoS}_2\text{-CN}$  have similar shape to that of the parent  $\text{C}_3\text{N}_4$  material, but the pore volumes and the specific surface areas are smaller, obviously because of higher density of the corresponding molybdenum compounds (Table 2). Comparison of isotherms and BJH pore size distributions suggests that  $\text{Mo}_2\text{N-CN}$  and  $\text{MoS}_2\text{-CN}$  replicate the main features of the pore structure of  $\text{C}_3\text{N}_4$  template and possess hierarchical mesoporosity. This is an important finding since mesoporous materials of this type are highly demanded and not readily available. Indeed, both  $\text{Mo}_2\text{N}$  and  $\text{MoS}_2$  obtained by conventional solid-gas reaction techniques are microporous. Bulk  $\text{Mo}_2\text{N}$  prepared *via* widely used Volpe and

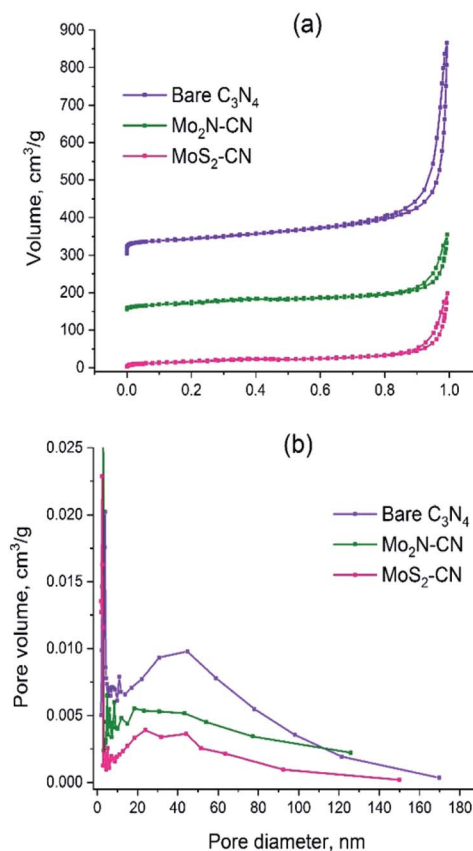


Fig. 3 (a)  $\text{N}_2$  adsorption-desorption isotherms for  $\text{C}_3\text{N}_4$ ,  $\text{Mo}_2\text{N-CN}$  and  $\text{MoS}_2\text{-CN}$ ; (b) BJH pore distributions for  $\text{C}_3\text{N}_4$ ,  $\text{Mo}_2\text{N-CN}$ ,  $\text{MoS}_2\text{-CN}$ .



Boudart TPR method possesses high specific surface area (around  $200 \text{ m}^2 \text{ g}^{-1}$ ), but pore size smaller than  $30 \text{ \AA}$ , fully lying in the microporosity range.<sup>28,29</sup> Similarly,  $\text{MoS}_2$  synthesized by conventional techniques such as ammonium thiomolybdate (ATM) decomposition possesses low pore volume and considerable microporosity.<sup>30</sup>

Transmission electron microscopy (TEM) study corroborates the results of other characterizations and provides additional insights into the morphology of the solids. Low-magnification TEM reveals lamellar morphology of the  $\text{C}_3\text{N}_4$  template (Fig. 4a and S5†). The layers of carbon nitride are randomly bent, having a rag-like aspect. The morphology of the reaction products  $\text{Mo}_2\text{N}-\text{CN}$  and  $\text{MoS}_2-\text{CN}$  bears a significant similarity to the parent template. Lamellar morphology and open porosity with convex macropores were observed (Fig. 4b and c; see also video in the ESI†).

At higher magnifications stacked layers of  $\text{MoS}_2$  become visible in the  $\text{MoS}_2-\text{CN}$  sample (Fig. 5b) and several nm-size  $\text{Mo}_2\text{N}$  particles were observed in the  $\text{Mo}_2\text{N}-\text{CN}$  solid (Fig. 5a).

Interplanar distances  $0.205 \text{ nm}$  and  $0.242 \text{ nm}$  correspond respectively to the  $(2\ 0\ 0)$  and  $(1\ 1\ 1)$  planes of  $\gamma\text{-Mo}_2\text{N}$ . In the  $\text{MoS}_2-\text{CN}$  sample the measured interplanar distance is  $0.67 \text{ nm}$ , corresponding to the theory value for  $(0\ 0\ 2)$  plane of  $\text{MoS}_2$  ( $0.62 \text{ nm}$ ) and to the measured XRD peak position ( $0.65 \text{ nm}$ ). Note that because of the slabs bending and stacking defects, the measured interplane distance in the nanoscopic  $\text{MoS}_2$  samples is often greater than in the bulk molybdenite.<sup>31</sup>

Overall, the obtained mesoporous  $\text{Mo}_2\text{N}$  and  $\text{MoS}_2$  materials replicate the hierarchical porous structure and lamellar morphology of the template.  $\text{Mo}_2\text{N}-\text{CN}$  and  $\text{MoS}_2-\text{CN}$  were further tested in the model reactions of gas-phase thiophene HDS and liquid-phase HER.

### Catalytic properties

Thiophene HDS rates are shown in Fig. 6 in comparison with the benchmark ATM- $\text{MoS}_2$  reference. The  $\text{Mo}_2\text{N}-\text{CN}$  sample demonstrates one of the highest HDS activities reported for the non-promoted Mo catalysts, being at least five times more active than the ATM- $\text{MoS}_2$  bulk reference and also much more active than bulk  $\text{MoS}_2$  solids from our previous works that were tested in the HDS reaction under the same conditions.<sup>32</sup> (Fig. 6a).

The evolution of HDS activity *versus* time was significantly different for sulfide and nitride samples. At  $320^\circ\text{C}$  the nitride catalyst loses 50% of its activity during the first hour on-stream, whereas  $\text{MoS}_2-\text{CN}$  sulfide was deactivated much less (Fig. 6b). The  $\text{Mo}_2\text{N}-\text{CN}$  solid after the HDS test preserved opened porous morphology (Fig. 6c). However, at high resolution short ( $1\text{--}3 \text{ nm}$ )  $\text{MoS}_2$  single slabs were observed. Therefore, partial sulfidation of molybdenum nitride occurred at the surface of pores. Steady state HDS activity can be attributed to these slabs, very short due to confinement in the pores of  $\text{Mo}_2\text{N}$  matrix. In agreement with our findings, it was reported earlier that the initial thiophene HDS activity of  $\gamma\text{-Mo}_2\text{N}/\text{Al}_2\text{O}_3$  is high, but during the reaction rapid sulfidation of the surface occurs and the steady state activity is defined by the  $\text{MoS}_2$  slabs formed on the surface.<sup>33</sup>

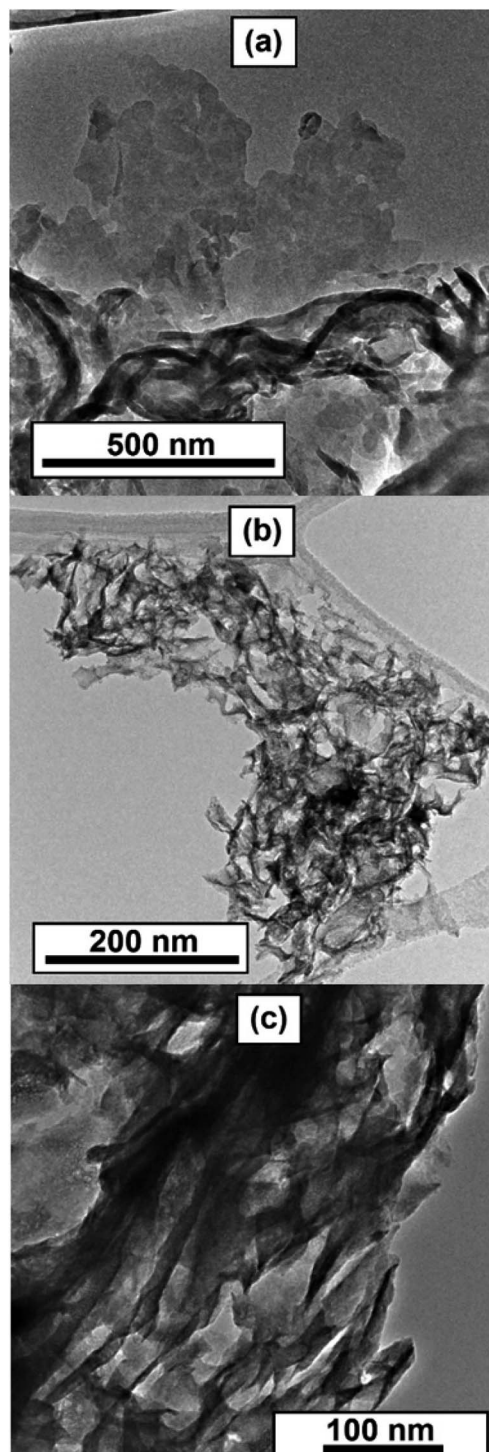


Fig. 4 Low magnification TEM images of (a)  $\text{C}_3\text{N}_4$ , (b)  $\text{Mo}_2\text{N}-\text{CN}$ , (c)  $\text{MoS}_2-\text{CN}$ .

Formation of  $\text{MoS}_2$  occurs *via* sulfidation of the passivating surface oxide layer rather than a direct nitride-to-sulfide transformation.<sup>34</sup> Exceptionally high apparent HDS rate during the initial period might be due to high intrinsic activity of  $\text{Mo}_2\text{N}$ , but might be also related to the sulfur uptake by nitride.



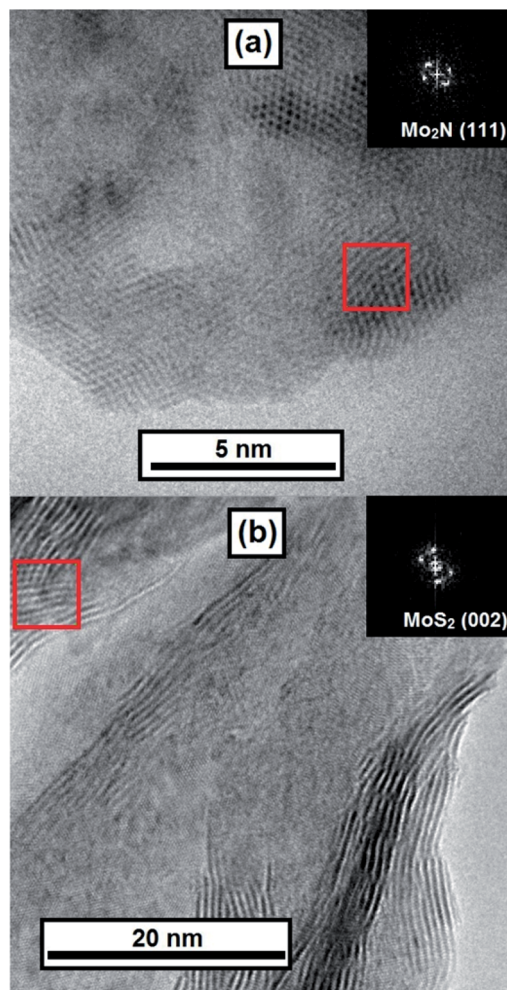


Fig. 5 TEM images of (a)  $\text{Mo}_2\text{N-CN}$  and (b)  $\text{MoS}_2\text{-CN}$ ; insets – digital diffraction for zones marked by red squares.

The  $\text{MoS}_2\text{-CN}$  sample demonstrates lower HDS activity than the  $\text{Mo}_2\text{N-CN}$  one, but still higher than the ATM- $\text{MoS}_2$  reference (Fig. 6a). Indeed, on the TEM images of  $\text{MoS}_2\text{-CN}$ , extended (>5 nm) and stacked layers of  $\text{MoS}_2$  are mostly present (Fig. 5b). Lower dispersion of  $\text{MoS}_2$  slabs and therefore lower amount of the active edge structures explains its lesser activity in comparison with  $\text{Mo}_2\text{N-CN}$ . The selectivity distributions of HDS products are similar to those observed earlier for the non-promoted Mo sulfide catalysts (Fig. S6†).<sup>30,32</sup> Beside  $\text{C}_4$  HDS products, small amounts of methane were detected. Production of methane might be due to partial surface oxidation of  $\text{Mo}_2\text{N}$  and  $\text{MoS}_2$  with formation of Mo oxide species that possess acidic sites, able to perform cracking.

To access the potential of electrochemical applications,  $\text{Mo}_2\text{N-CN}$  (fresh and after HDS test) and  $\text{MoS}_2\text{-CN}$  were tested in the electrochemical HER in 0.5 M  $\text{H}_2\text{SO}_4$ . The  $\text{MoS}_2\text{-CN}$  material demonstrates poor HER activity, in accordance with its moderate HDS catalytic performance (Fig. 7a). Low activity of bulk 2H- $\text{MoS}_2$  was previously reported in the literature.<sup>35</sup> The  $\text{Mo}_2\text{N}$  based samples demonstrate good activity, the sample taken after HDS being more active than the initial nitride. The

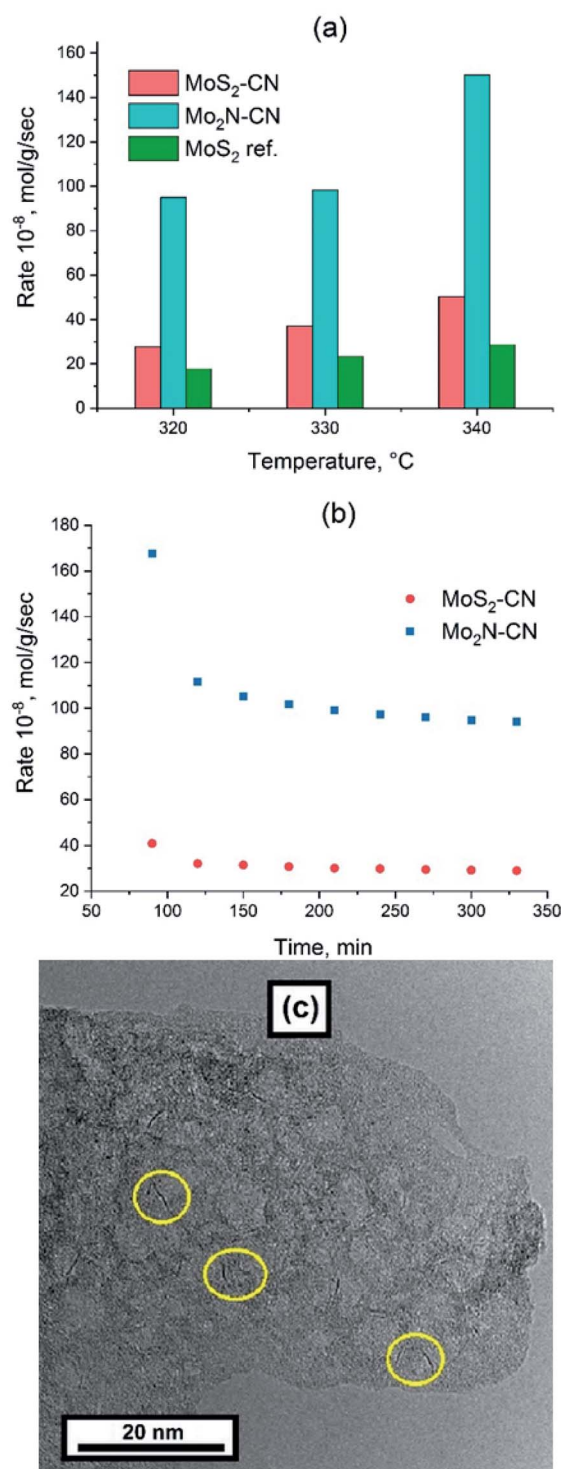


Fig. 6 (a) Steady state thiophene conversion rate vs. temperature for  $\text{Mo}_2\text{N-CN}$ ,  $\text{MoS}_2\text{-CN}$  and  $\text{MoS}_2$  bulk reference; (b) time dependence of thiophene conversion rate at 320 °C for  $\text{Mo}_2\text{N-CN}$  and  $\text{MoS}_2\text{-CN}$ ; (c) TEM image of  $\text{Mo}_2\text{N-CN}$  after HDS, yellow circles indicate the  $\text{MoS}_2$  slabs.

overpotential for  $\text{Mo}_2\text{N-CN}$  after HDS at  $10 \text{ mA cm}^{-2}$  is much lower (239 mV) than that of the initial nitride sample (390 mV) (Fig. 7a). The calculated Tafel slopes for three tested samples





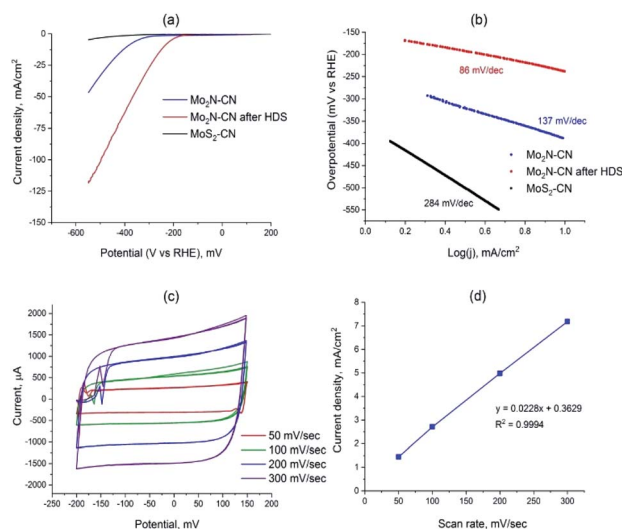


Fig. 7 (a) LSV curves of Mo<sub>2</sub>N-CN, Mo<sub>2</sub>N-CN after HDS and of MoS<sub>2</sub>-CN; (b) Tafel slopes for Mo<sub>2</sub>N-CN, Mo<sub>2</sub>N-CN after HDS and MoS<sub>2</sub>-CN; (c) cyclic voltammograms (CV) for Mo<sub>2</sub>N-CN after HDS, measured at the scan rates 50, 100, 200, 300 mV s<sup>-1</sup>; (d) linear dependence between the current density and the scan rates.

are 86 mV dec<sup>-1</sup> for Mo<sub>2</sub>N-CN after HDS, 137 mV dec<sup>-1</sup> for Mo<sub>2</sub>N-CN and only 284 mV dec<sup>-1</sup> for MoS<sub>2</sub>-CN (Fig. 7b). The obtained values of Tafel slopes for Mo<sub>2</sub>N based catalysts indicate that HER reaction follows Volmer-Heyrovsky mechanism. For the sample Mo<sub>2</sub>N-CN collected after HDS test, that shows the highest HER performance, the electrochemical surface area (ECSA) calculated from the non-faradaic CV at different scan rates is 136 m<sup>2</sup> g<sup>-1</sup> (Fig. 7c and d). This value is close to the BET surface area and attests good availability of the surface for the electrochemical reaction.

The superior HER catalytic performance of the Mo<sub>2</sub>N-CN sample after HDS test might be associated with high activity of short MoS<sub>2</sub> slabs on the surface of Mo<sub>2</sub>N, formed during the HDS reaction due to sulfidation of the catalyst surface by the released H<sub>2</sub>S. Oppositely to the metallic Mo<sub>2</sub>N, 2H-MoS<sub>2</sub> is a semiconductor, so it possesses relatively low electric conductivity<sup>36</sup> and, therefore, lower activity in HER, whereas the active sites for these two materials are similar (MoS<sub>2</sub> slabs edges). It appears that mesoporous Mo<sub>2</sub>N decorated with MoS<sub>2</sub> fringes provides optimal structure for an efficient HER catalyst. Thus in ref. 37 it was suggested that if MoS<sub>2</sub> edges are in a tight contact with the surface of Mo<sub>2</sub>N, then the electronic structure of Mo sites located at the interface could be tuned, boosting HER catalytic performance. Recently, in the same lines, for chemically similar W sulfide it was shown that metallic W particles surrounded with WS<sub>2</sub> show high HER activity.<sup>38</sup> The interface between MoS<sub>2</sub> n-type semiconductor, and Mo<sub>2</sub>N would create ohmic or Schottky contact, depending on the difference between the work functions of two materials. For the similar Mo-MoS<sub>2</sub> contact, low Schottky barrier was observed that potentially provides easy charge injection from current collector to the catalyst sites.<sup>39</sup> For the Mo<sub>2</sub>N-MoS<sub>2</sub> interface, both experiment and DFT analysis show that an electric field is

created at the interface between Mo<sub>2</sub>N and MoS<sub>2</sub> that facilitates charge transfer.<sup>40</sup>

## Conclusions

Mesoporous MoS<sub>2</sub> and Mo<sub>2</sub>N materials replicating the hierarchical mesoporous morphology of C<sub>3</sub>N<sub>4</sub> were prepared using a simple topotactic solid-gas reaction. Due to the advantageous morphology these solids are well adopted for the applications in the heterogeneous catalysis and in the electrocatalysis. The most active catalyst in both HDS and HER reactions is mesoporous molybdenum nitride decorated at the surface by small MoS<sub>2</sub> fringes. The HDS performance of this sample is one of the highest ever reported for the non-promoted Mo systems.

Due to application of the reactive gases, our synthetic approach extends the potential use of C<sub>3</sub>N<sub>4</sub> as a template towards considerably lower temperatures and to the materials other than nitrides. The advantage of this method is its utter simplicity. Indeed, carbon nitride support is impregnated with ammonium heptamolybdate according to the standard procedure, commonly applied for the preparation of heterogeneous catalysts. Further activation with H<sub>2</sub>S/H<sub>2</sub> or NH<sub>3</sub>/H<sub>2</sub> is also carried out by following the standard procedures that are used to prepare sulfide and nitride catalysts. Unlike in many other template-based techniques there is no template leaching steps. Obviously, mesoporous sulfides and nitrides of other metals (such as V, W, Cr) and their combinations could be prepared using this approach under relatively soft conditions. By the same token, preparation of mesoporous phosphides or borides could be considered, by means of the reductive treatment of phosphates or borates supported on C<sub>3</sub>N<sub>4</sub>. Beside catalysis, other applications could be considered in the fields where materials with open porosity are demanded, such as pseudo capacitors, electrodes or sensors.

## Author contributions

DR: writing, materials preparation, catalytic tests, PA: conceptualising, materials characterizations, writing.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 H. Topsøe, B. S. Clausen and F. E. Massoth, *Hydrotreating Catalysis, Catalysis: Science and Technology*, Springer, Berlin, Heidelberg, 1996.
- 2 R. R. Chianelli, *Catal. Rev.*, 1984, **26**, 361–393.

- 3 E. J. M. Hensen, P. J. Kooyman, Y. van der Meer, A. M. van der Kraan, V. H. J. de Beer, J. A. R. van Veen and R. A. van Santen, *J. Catal.*, 2001, **199**, 224–235.
- 4 C. G. Morales-Guio, L.-A. Stern and X. Hu, *Chem. Soc. Rev.*, 2014, **43**, 6555.
- 5 S. Zaman and K. J. Smith, *Catal. Rev.*, 2012, **54**, 41–132.
- 6 M. Führer, T. van Haasterecht and J. H. Bitter, *Catal. Sci. Technol.*, 2020, **10**, 6089–6097.
- 7 Z. Liang, Y. Xue, X. Wang, Y. Zhou, X. Zhang, H. Cui, G. Cheng and J. Tian, *Chem. Eng. J.*, 2021, **421**, 130016.
- 8 Z. Liang, X. Meng, Y. Xue, X. Chen, Y. Zhou, X. Zhang, H. Cui and J. Tian, *J. Colloid Interface Sci.*, 2021, **598**, 172–180.
- 9 P. Xiao, M. A. Sk, L. Thia, X. Ge, R. J. Lim, J.-Y. Wang, K. H. Lim and X. Wang, *Energy Environ. Sci.*, 2014, **7**, 2624–2629.
- 10 B. Cao, J. C. Neufeind, R. R. Adzic and P. G. Khalifah, *Inorg. Chem.*, 2015, **54**, 2128–2136.
- 11 A. Arunchander, S. G. Peera and A. K. Sahu, *J. Power Sources*, 2017, **353**, 104–114.
- 12 M. Asadi, B. Kumar, A. Behranginia, B. A. Rosen, A. Baskin, N. Repnin, D. Pisasale, P. Phillips, W. Zhu, R. Haasch, R. F. Klie, P. Král, J. Abiade and A. Salehi-Khojin, *Nat. Commun.*, 2014, **5**, 4470.
- 13 C. Oumahi and P. Afanasiev, *J. Alloys Compd.*, 2018, **768**, 824–829.
- 14 P. Afanasiev, *Catal. Today*, 2015, **250**, 134–144.
- 15 P. Qin, D. Yi and J. Hao, *Adv. Powder Technol.*, 2021, **32**, 1594–1601.
- 16 L. Jing, G. Lian, S. Han, J. Sun, C. Sun, Q. Wang, H. Jiang and D. Cui, *J. Alloys Compd.*, 2019, **801**, 367–374.
- 17 L. Su, L. Luo, J. Wang, T. Song, W. Tu and Z. Wang, *Catal. Sci. Technol.*, 2021, **11**, 1292–1297.
- 18 J. Dai, J. Li, Q. Zhang, M. Liao, T. Duan and W. Yao, *Mater. Lett.*, 2019, **236**, 483–486.
- 19 S. Wang, C. An and J. Yuan, *Materials*, 2010, **3**, 401–433.
- 20 P. Afanasiev, C. Geantet, I. Llorens and O. Proux, *J. Mater. Chem.*, 2012, **22**, 9731–9737.
- 21 G. Zhao, Y. Cheng, P. Sun, W. Ma, S. Hao, X. Wang, X. Xu, Q. Xu and M. Liu, *Electrochim. Acta*, 2020, **331**, 135262.
- 22 A. Fischer, M. Antonietti and A. Thomas, *Adv. Mater.*, 2007, **19**, 264–267.
- 23 A. Fischer, J. O. Müller, M. Antonietti and A. Thomas, *ACS Nano*, 2008, **2**, 2489–2496.
- 24 F. Pan, B. Li, W. Deng, Z. Du, Y. Gang, G. Wang and Y. Li, *Appl. Catal., B*, 2019, **252**, 240–249.
- 25 Q. Li, X. Tian, W. Yang, L. Hou, Y. Li, B. Jiang, X. Wang and Y. Li, *Appl. Surf. Sci.*, 2020, **530**, 147298.
- 26 Y. Cao, Z. Zhang, J. Long, J. Liang, H. Lin, H. Lin and X. Wang, *J. Mater. Chem. A*, 2014, **2**, 17797–17807.
- 27 M. Elshafie, S. A. Younis, P. Serp and E. A. M. Gad, *Egypt. J. Pet.*, 2020, **29**, 21–29.
- 28 L. Volpe and M. Boudart, *J. Solid State Chem.*, 1985, **59**, 332–347.
- 29 G. Ranhotra, *J. Catal.*, 1987, **108**, 24–39.
- 30 P. Afanasiev, *J. Catal.*, 2010, **269**, 269–280.
- 31 H. Liu, D. Su, R. Zhou, B. Sun, G. Wang and S. Z. Qiao, *Adv. Energy Mater.*, 2012, 1–6.
- 32 P. Afanasiev, *Appl. Catal., B*, 2018, **227**, 44–53.
- 33 Z. Wu, C. Li, Z. Wei, P. Ying and Q. Xin, *J. Phys. Chem. B*, 2002, **106**, 979–987.
- 34 Z. B. Z. Wei, P. Grange and B. Delmon, *Appl. Surf. Sci.*, 1998, **135**, 107–114.
- 35 H. Tributsch and J. C. Bennett, *J. Electroanal. Chem. Interfacial Electrochem.*, 1977, **81**, 97–111.
- 36 T. Okamoto, T. Shimizu, K. Takase, T. Ito and S. Shingubara, *Micro Nano Eng.*, 2020, **9**, 100071.
- 37 K. Ojha, S. Saha, S. Banerjee and A. K. Ganguli, *ACS Appl. Mater. Interfaces*, 2017, **9**, 19455–19461.
- 38 L. Ji, H. Cao, W. Xing, S. Liu, Q. Deng and S. Shen, *J. Mater. Chem. A*, 2021, **9**, 9272–9280.
- 39 J. Kwon, C. J. Delker, D. B. Janes, C. T. Harris and S. R. Das, *Phys. Status Solidi A*, 2020, **217**, 1900880.
- 40 S. Yang, Y. Zhang, S. Wang, J. Shi, X. Liu and L. Li, *J. Mater. Chem. A*, 2019, **7**, 23886–23894.

