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# A Versatile Self-Detoxifying Material Based on Immobilized Polyoxoniobate for Decontamination of Chemical Warfare Agent Simulants

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Abstract: A decontaminating composite, Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>, has been successfully prepared by immobilizing Lindqvist [H<sub>3</sub>Nb<sub>6</sub>O<sub>19</sub>]<sup>5-</sup> (Nb<sub>6</sub>) into Mg<sub>3</sub>Al-based layered double hydroxide (Mg<sub>3</sub>Al-LDH). To our knowledge, this represents the first successful approach to immobilize polyoxoniobate. As a versatile catalyst, Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> can effectively catalyze the degradation of both vesicant and nerve agent simulants via multiple pathways under mild conditions. Specifically, the sulfur mustard simulant, 2-chloroethyl ethyl sulfide (CEES), converts to the corresponding nontoxic 2-chloroethyl ethyl sulfoxide (CEESO) by selective oxidation; while the tabun (G-type nerve agent) simulant, diethyl cyanophosphonate (DECP), and the VX (V-type nerve agent) simulant, O,S-diethyl methylphosphonothioate (OSDEMP), are detoxified through hydrolysis and perhydrolysis, respectively. A possible mechanism was proposed according to control experiments and spectroscopic studies. The Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite exhibits remarkable robustness and can be readily reused for up to ten cycles with negligible loss of its catalytic activity. More importantly, a protective "self-detoxifying" material is easily constructed by integrating Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> onto textiles, which combines the flexible and permeable properties of textiles with the catalytic activity of polyoxoniobate and it removes 94% CEES in 1 h using nearly stoichiometric dilute H<sub>2</sub>O<sub>2</sub> (3%) as oxidant with 96% selectivity.

#### Introduction

Effective decontamination of chemical warfare agents (CWAs) is a vital scientific and humankind issue due to their unanticipated use in past wars and recent terrorist attacks.<sup>[1]</sup> Among all kinds of CWAs, nerve agents and vesicants are considered as the most nefarious and dangerous ones. Nerve agents, including Soman, Sarin, Tabun and VX, are organophosphorous compounds, which can be destructed by cleavage of the P-X bonds.<sup>[2]</sup> While vesicants such as sulfur mustard (also known as "King of the Battle Gases") is usually detoxified *via* selective oxidation approach.<sup>[3]</sup> Although homogeneous catalysts show excellent activities due to highly

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accessible catalytic active sites, from the practical point of view, the materials that can catalytically decompose CWAs with high robustness and excellent recyclability are more desirable. For example, a self-detoxifying material can be used to produce personal protective equipment by integrating into suits, gloves and boots.

Recently, several kinds of decontamination materials including metal-organic frameworks (MOFs),<sup>[4]</sup> metal oxides,<sup>[5]</sup> and supported polyoxometalates (POMs)<sup>[6]</sup> have been developed and investigated. A series of MOFs containing Lewis acidic Zr<sup>4+</sup> centers have been proven to be effective for the hydrolysis of nerve agents and/or their simulants. Metal oxides and supported POMs also exhibit satisfactory activities in the oxidative decontamination of sulfur mustard simulants. However, most previously reported catalytic materials can only decontaminate CWAs *via* single detoxification pathway (e.g. hydrolysis or oxidation), that causes limitations to the complicated scenarios containing multiple types of CWAs. Therefore, it is essential to develop a versatile and cost-effective material for the effective decontamination of various CWAs simultaneously.

As a special subclass of POMs, polyoxoniobates (PONbs) are a kind of potential versatile catalysts to accelerate the decontamination of CWAs. Hill and Nyman have reported that  $K_{12}[Ti_2O_2][XNb_{12}O_{40}]$  (X=Si or Ge)<sup>[7]</sup> and  $[Nb_6O_{19}]^{8-}$  [8] can catalyze the basic hydrolysis of nerve agent and their simulant in liquid and gas phase. Recently, we first found that a doubleanion complex,  $H_{13}[(CH_3)_4N]_{12}[PNb_{12}O_{40}(V^VO)_2(V^{IV}_4O_{12})_2]$ , are capable of activating H<sub>2</sub>O<sub>2</sub>, which can simultaneously catalyze the hydrolysis of nerve agent simulant and the selective oxidation of sulfur mustard simulant in homogeneous system.<sup>[9]</sup> However, the poor reusability restricts its practical application. Normally, immobilization is a preferred method to realize the heterogeneity of POMs as it provides dispersed and accessible active sites.<sup>[10]</sup> To our knowledge, the immobilization of PONbs is unexplored yet. The possible reasons include: (1) PONbs are highly basic and the immobilization methods based on acidic POMs are unsuitable for PONbs; (2) PONbs have higher charge-density (e.g. [Nb<sub>6</sub>O<sub>19</sub>]: 0.32, [SiNb<sub>12</sub>O<sub>40</sub>]: 0.30) and how to balance the negative charge is a challenge;<sup>[11]</sup> (3) The precursors of PONbs (e.g. K7HNb6O19 or Nb2O5·nH2O) have limited solubility in water and organic solvents.

Herein we report a novel approach to fabricate a decontaminating material,  $Mg_3AI$ -LDH-Nb<sub>6</sub>, by integrating active Lindqvist  $[H_3Nb_6O_{19}]^{5-}$  (Nb<sub>6</sub>) into  $Mg_3AI$ -based layered double hydroxide ( $Mg_3AI$ -LDH-NO<sub>3</sub>). The use of  $Mg_3AI$ -LDH as the host are based on the following considerations: (1) LDHs usually have good interlayer anion-exchange capability, (2) the charge density and acid/base property of LDH can be easily tuned by varying elemental compositions and molar ratios,<sup>[12]</sup> (3) the special interlayer structure of LDH allows the high exposure of

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catalytic active sites of Nb<sub>6</sub>, (4) the basicity of Mg<sub>3</sub>Al-LDH-NO<sub>3</sub> not only is compatible with the working pH region of Nb<sub>6</sub> but also might provide additional catalytic activity. Interestingly, the obtained Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite exhibits versatile catalytic capability for detoxification of different CWA simulants: selective oxidation for sulfur mustard (vesicant agent) simulant, basic hydrolysis for Tabun (G-type nerve agent) simulant. More importantly, such composite exhibits great potential for the preparation of portable, permeable, and economical self-detoxifying material by integrating them onto soft textiles.

#### **Results and Discussion**

#### Synthesis and Characterization of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>

The preparation of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite is illustrated in Figure 1. The Mg<sub>3</sub>Al-LDH-NO<sub>3</sub> was first prepared by the coprecipitation of Mg(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> solution with NaOH under N<sub>2</sub> atmosphere. After aging at 80 °C for 12 h, the precipitate was washed with deionized water and re-dispersed in deionized water to form a slurry. Hydrothermal treatment of TMA-Nb<sub>6</sub> and Mg<sub>3</sub>Al-LDH-NO<sub>3</sub> slurry at 100 °C for 24 h produces Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>. PXRD pattern of the Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> (Figure 2a and S1) reveals the characteristic diffraction peak of the (003) lattice plane for LDH splits into two peaks with a new peak emerging at lower angle region compared with that of Mg<sub>3</sub>Al-LDH-NO<sub>3</sub>, demonstrating that Nb<sub>6</sub> is partially intercalated into the host layers. According to the basal spacing of d(003) (11.1 Å), the calculated gallery height of 0.63 nm reveals that Nb<sub>6</sub> cluster is inserted with its  $C_2$  axis nearly parallel to the LDH layers. Furthermore, the (110) diffraction peak ( $2\theta = 60.9^{\circ}$ ) is unshifted, indicating that the structure of the LDH is retained after the intercalation of Nb<sub>6</sub>.<sup>[13]</sup> Based on the inductively coupled plasma atomic emission spectroscopy (ICP-AES) and CHN elemental analyses (Table S1), we concluded that around 58% of NO3<sup>-</sup> was exchanged by Nb6. The FT-IR absorption bands of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> at 865, 720 and 541 cm<sup>-1</sup> are attributed to the vibrations of Nb=Ot and Nb-Ob (t, terminal; b, bridging), respectively (Figure 2b). The characteristic peak of residual NO3is observed at 1383 cm<sup>-1</sup>, which is consistent with the result of PXRD.



Figure 1. The synthesis process of  $\mathsf{Mg}_3\mathsf{AI-LDH-Nb}_6$  by a hydrothermal ion-exchange method.

Control experiments indicate that the loading amounts of Nb<sub>6</sub> can be regulated by tuning the amount of TMA-Nb<sub>6</sub> used in the hydrothermal reactions (Table 1) and a maximum loading amount of 28 wt% (corresponding to NO<sub>3</sub><sup>-</sup> exchanging rate of 58%) can be reached. In addition, K<sub>7</sub>HNb<sub>6</sub>O<sub>19</sub> was also used as Nb source under otherwise identical conditions, but the PXRD (Figure S2) suggests that [HNb<sub>6</sub>O<sub>19</sub>]<sup>7-</sup> could not be incorporated into Mg<sub>3</sub>Al-LDH. Such difference might be attributed to the higher charge-density of [HNb<sub>6</sub>O<sub>19</sub>]<sup>7-</sup> (0.28) compared to [H<sub>3</sub>Nb<sub>6</sub>O<sub>19</sub>]<sup>5-</sup> (0.20). Furthermore, we also found that the *in situ* formed Mg<sub>3</sub>Al-LDH-NO<sub>3</sub> slurry and the hydrothermal treatment are necessary to the synthesis of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>. No target product was obtained when using dried Mg<sub>3</sub>Al-LDH-NO<sub>3</sub> or performing the ion-exchange at ambient temperature.



Figure 2. (a) The XRD patterns of  $Mg_3AI-LDH-Nb_6$  and  $Mg_3AI-LDH-NO_3$ ; (b) FT-IR spectra of  $Mg_3AI-LDH-NO_3$ ,  $Mg_3AI-LDH-Nb_6$ , and TMA-Nb\_6.

SEM and TEM images show that the as-prepared Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> (Figure 3a-3c) exhibits typical nanosheet morphology of LDH with the sizes of 200 to 400 nm. Energy dispersive X-ray spectroscopy (EDS) (Figure S5) and elemental mapping measurements (Figure 3d) reveal that the composite contains

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Mg, Al, Nb, O and N elements, and Nb is evenly dispersed in the LDH layers. Figure S6 shows the BET measurements on the composite and the host. The N<sub>2</sub> adsorption-desorption isotherms of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> exhibit the type IV isotherm pattern with a clear hysteresis loop, indicating the presence of mesopores. It is worth mentioning that the surface area of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> (176.09 m<sup>2</sup>/g) is three times higher than that of Mg<sub>3</sub>Al-LDH-NO<sub>3</sub> (56.02 m<sup>2</sup>/g) (Table S2) and such increased surface area could facilitate the diffusion of substrates to the catalytic active centers and thus improve the decontamination efficiency.



Figure 3. (a) and (b) SEM images of  $Mg_3AI$ -LDH-Nb<sub>6</sub>; (c) TEM image of  $Mg_3AI$ -LDH-Nb<sub>6</sub>; (d) EDS elemental mapping of  $Mg_3AI$ -LDH-Nb<sub>6</sub>.

#### **Oxidative Decontamination of CEES**

Given the fact that Nb<sub>6</sub> can activate H<sub>2</sub>O<sub>2</sub> in homogeneous system<sup>[6e]</sup> and selective oxidation is the most promising pathway for sulfur mustard degradation,<sup>[14]</sup> the catalytic activity of Mg<sub>3</sub>Al-LDH-Nb6 was first evaluated in the oxidative decontamination of CEES, a sulfur mustard simulant (Figure 4a). In a typical reaction, CEES (0.5 mmol), 1,3-dichlorobenzene (internal standard, 0.25 mmol) and Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> (0.003 mmol) were dispersed in acetonitrile (4 mL). After 2 min of stirring at room temperature, 3 % aqueous H2O2 (0.525 mmol) was added to initiate the reaction. Figure 4b shows that 95% of CEES is converted in 2 h and the half-life (50% conversion of CEES) is about 15 min. In the oxidative degradation of sulfur mustard, the selectivity is a very important factor to consider as the nontoxic sulfoxide is more preferred than the highly toxic sulfone. In our experiment, the selectivity for CEESO exceeds 96%, which is much higher than most of the reported catalytic materials, such as saponite<sup>[15]</sup> (Sele.: 73%, oxidant: 30% aq. H<sub>2</sub>O<sub>2</sub>), nanosized metal oxidates  $^{[16]}$  (Sele.: 71%, oxidant: 30% aq.  $H_2O_2),$  and materials<sup>[5b]</sup> porous (Sele. 82%, oxidant: tert-butyl hydroperoxide). In addition, our catalytic system is more environmentally benign due to the use of nearly stoichiometric, diluted  $H_2O_2$  (3%) as oxidant.



Figure 4. (a) Catalytic decontamination of CEES; (b) Concentration timecourse plots for CEES oxidative transformation using  $Mg_3AI-LDH-Nb_6$ ; (c) Recycle test for CEES decontamination using  $Mg_3AI-LDH-Nb_6$ . Reaction conditions: CEES (0.5 mmol),  $Mg_3AI-LDH-Nb_6$  (0.003 mmol) and 1,3dichlorobenzene (internal standard, 0.25 mmol), 3% aqueous  $H_2O_2$  (0.525 mmol) and acetonitrile (4 mL) at room temperature.

To evaluate the role of Nb<sub>6</sub> and Mg<sub>3</sub>Al-LDH to the degradation reaction, a series of control experiments were conducted. No appreciable conversion of CEES was observed in the absence of catalyst (Table 1, entry 7). Under otherwise identical conditions, Mg<sub>3</sub>Al-LDH-NO<sub>3</sub> only catalyzes 12% conversion of CEES (Table 1, entry 1), while the precursor TMA-Nb<sub>6</sub> in homogeneous system decontaminates 100% CEES within 15 min (Table 1, entry 2). The activity of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> with different loading amounts was also investigated (Table 1, entry 3-6). The conversion of CEES increases with the loading amount of Nb<sub>6</sub>. Above analyses suggest that the intercalated Nb<sub>6</sub> clusters work as main catalytic active sites. The Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>-28% was used in the following decontamination reactions.

Table 1. Decontamination of CEES using different catalysts. <sup>[a]</sup>						
Entry	Catalyst	Time (h)	Conv. (%)	Selec. (%)		
1	Mg <sub>3</sub> Al-LDH-NO <sub>3</sub>	2	12	99		
2	TMA-Nb6 <sup>[b]</sup>	0.25	100	98		

3	Mg <sub>3</sub> AI-LDH-Nb <sub>6</sub> -13%	2	31	99
4	Mg <sub>3</sub> Al-LDH-Nb <sub>6</sub> -20%	2	68	97
5	Mg <sub>3</sub> Al-LDH-Nb <sub>6</sub> -25%	2	81	96
6	Mg <sub>3</sub> Al-LDH-Nb <sub>6</sub> -28%	2	95	97
7	Blank	2	0	0

[a] Reaction conditions: CEES (0.5 mmol), catalyst (0.003 mmol) and 1,3-dichlorobenzene (internal standard, 0.25 mmol), 3% aqueous  $H_2O_2$  (0.525 mmol) and acetonitrile (4 mL) at room temperature; [b] TMA-Nb\_6 catalyzes CEES decontamination in homogeneous system.

According to previous investigations, radical process might be involved in the oxidation reaction using  $H_2O_2$  as oxidant. To understand the mechanism, radical scavengers, such as pbenzoquinone (for  $\bullet O_2^{-}/\bullet O_2H$ ), *tert*-butyl alcohol and diphenylamine (for •OH),<sup>[17]</sup> were chosen and used in the CEES oxidation reaction. As shown in Figure 5a, after adding scavengers the conversion of CEES remains unchanged and so we can rule out any radical species responsible for the selective oxidation of CEES. As POMs tend to form peroxo-metal species in the presence of  $H_2O_2$ ,<sup>[18]</sup> we proposed a possible non-radical reaction mechanism. As shown in Figure 5c, the intercalated hexaniobates may interact with  $H_2O_2$  to form active peroxo species (side-on peroxo or end-on hydroperoxo), which subsequently oxidize the accessible CEES. Such speculation is supported by Raman spectra of H<sub>2</sub>O<sub>2</sub>-treated TMA-Nb<sub>6</sub> solution, where a peak at 867 cm<sup>-1</sup> attributed to the O-O stretch is observed (Figure 5b), proving the existence of active peroxo species.



Figure 5. (a) Decontamination of CEES catalyzed by Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> without adding radical scavengers (red); with adding diphenylamine (blue), *p*-benzoquinone (pink), and *t*-butanol (green) as radical scavengers; (b) Raman spectra of TMA-Nb<sub>6</sub> before and after adding 3% aqueous H<sub>2</sub>O<sub>2</sub>; (c) Possible reaction mechanism of CEES decontamination.

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To verify the heterogeneity of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite, leaching test was performed. The catalyst was filtered off when the conversion reached about 30%. The solution was kept running under the same conditions for another 1.5 h, but negligible conversion of CEES was observed (Figure S12). Moreover, ICP-AES (detection limit ca. 1 ppm) reveals that no detectable niobium exists in the filtrate. The above results confirm that Mg<sub>3</sub>Al-LDH is an effective and stable host for Nb<sub>6</sub> cluster. In addition, we also evaluated the recyclability and stability of such Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite. The activity of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> shows negligible decrease after ten cycles (Figure 4c) and also no obvious change is observed from the PXRD patterns and IR spectra before and after the recycle experiment (Figure S13 and S14). The stability of our Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite outperforms that of the reported organicinorganic hybrids.<sup>[19]</sup> More importantly, during each recycle the selectivity maintains above 95%. The robustness and recyclability of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite makes it a promising catalytic material for effective decontamination of sulfur mustard.

#### Hydrolytic decontamination of DECP

Given the catalytic performance of hexaniobate in basic hydrolysis of nerve agents,<sup>[8]</sup> we examine the activity of the Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> towards hydrolysis of the tabun simulant, DECP (Figure 6a). Using Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> as catalyst, 97% of DECP is converted into the nontoxic product, diethyl hydrogen phosphate (DEHP), in 30 min with a half-life of ~5 min in the absence of extra organic base such as N-ethylmorpholine that is commonly used in MOF-catalyzed decontaminating system<sup>[4]</sup> (Figure 6b). In contrast, the blank test shows only 20% DECP decontamination in 30 min. Furthermore, the control experiments support that both Nb<sub>6</sub> and Mg<sub>3</sub>Al-LDH do catalyze the basic hydrolysis reaction: conversions are 100% and 40%, respectively and this displays that Mg<sub>3</sub>Al-LDH not only acts as a good supporter but also provides additional catalytic activity (Figure 6c).



**Figure 6.** (a) Catalytic hydrolysis of DECP; (b) Concentration time-course plots for DECP transformation with Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> and without catalyst; (c) DECP decontamination using different catalysts. Reaction conditions: DECP (20 µL), catalyst (0.003 mmol), nitrobenzene (internal standard,  $3.25 \times 10^{-2}$  mmol), H<sub>2</sub>O (100 µL), DMF (1200 µL) at room temperature for 30 min.

#### Perhydrolytic decontamination of OSDEMP

In addition, we also evaluated the activity of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite towards detoxifying V-type nerve agent, O-ethyl-S-[2-(diisopropylamino)ethyl]-methylphosphono-thioate (VX), that is more potent than Sarin with lethal dose of 0.0096 mg/m<sup>3</sup>. Hydrolysis of VX under basic conditions leads to the cleavage of both P-S and P-O bonds: the product of P-S cleavage is the nontoxic EMPA (ethyl methylphosphonic acid) while P-O cleavage yields the toxic EA-2192.[20] In contrast, the perhydrolysis of VX in the presence of H<sub>2</sub>O<sub>2</sub> is a more attractive route due to the exclusive cleavage of P-S bond and fast reaction rate.<sup>[21]</sup> The low toxic simulant, OSDEMP, was used to investigate the activity of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> (Figure 7a) and the extent of decontamination is monitored by <sup>31</sup>P NMR. Under mild conditions, the Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite removes 90% of OSDEMP within 5 h while the blank control experiment only yields a conversion of 15%. More importantly, only the product of P-S cleavage, nontoxic EMPA ( $\delta$ = 26.5 ppm), is detected (Figure 7b). Generally, the perhydrolysis proceeds in strong alkali solution, where the in situ generated peroxy anions (OOH)

react with VX.<sup>[21]</sup> As both the Mg<sub>3</sub>AI-LDH and the intercalated Nb<sub>6</sub> are basic, one might speculate that the activity of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> comes from its alkalinity. To better understand the catalytic process, a control experiment using 2 equivalents NaOH as homogeneous catalyst was performed under otherwise identical conditions. Surprisingly, only 33% of OSDEMP was converted (Figure 7b and S15) which is much lower than that of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>-catalyzed system (90%), indicating that alkalinity is not the main factor to accelerate the perhydrolysis reaction. In other control experiments (Figure S16), the host itself, Mg<sub>3</sub>AI-LDH-NO<sub>3</sub>, converts only 42% of OSDEMP in 5 h, while TMA-Nb<sub>6</sub> in homogeneous system decomposes 100% of OSDEMP in 30 min. Therefore, we speculate that the intercalated Nb<sub>6</sub> plays a key role in the perhydrolysis process and the interactions between Nb<sub>6</sub> and H<sub>2</sub>O<sub>2</sub> are responsible for its catalytic performance. To our knowledge, the reported Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> represents the first material that can simutaneously decontaminate vesicant, G-type nerve agent, and V-type nerve agent.



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**Figure 7.** (a) Two pathways of OSDEMP degradation; (b) <sup>31</sup>P spectra of OSDEMP decontamination using Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> (red) and NaOH (blue), and without catalyst (black) after 5 h. Reaction conditions: OSDEMP (5 µL), D<sub>2</sub>O (500 µL), acetonitrile (200 µL), catalyst (0.008 mmol for Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> and 0.016 mmol for NaOH) and 30% aqueous H<sub>2</sub>O<sub>2</sub> (700 µL) at room temperature.

Decontaminaiton of CEES by the Mg\_Al-LDH-Nb\_based Material

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Furthermore, we have investigated the potential practical application of such Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite in fabricating protective materials. Recently, several MOF-based selfdetoxifying materials towards CWAs have been reported.<sup>[22]</sup> Given the excellent activity, high robustness and recyclability of our Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite, we initiatively construct a selfcleaning clothing by incorporating Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> onto carbon cloth (CC) substrate. Typically, a so-called "catalyst ink" was first prepared by dispersing freshly-prepared Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> into the DMF solution of polyvinylidene fluoride. Then, a piece of carbon cloth was soaked in the "catalyst ink" under ultrasonic conditions to obtain the carbon cloth-supported Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> (Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>-CC) (Figure 8a). The SEM images and optical photographs demonstrate that Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> is well-dispersed on the carbon cloth (Figure 8b-c and S7): the integrated composite maintains the typical plate-like morphology of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> without obvious aggregation and the flexibility of the textile (Figure 8d). It is noted that such supporting substrate can also be extended to other textiles; the purpose of using carbon cloth is to



Figure 8. (a) Procedure for preparing Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>-CC; (b) and (c) SEM images of the carbon cloth fibers; (d) Optical photograph of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>-CC under twisted state; (e) PXRD patterns of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>-CC, Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> and CC.

obtain high-quality SEM images. Furthermore, XRD patterns confirm that the structure of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> keeps unchanged (Figure 8e). When a solution containing CEES and H<sub>2</sub>O<sub>2</sub> was absorbed by such cloth (Figure 9a), without further treatment 94% CEES was decontaminated in 1 h and the selectivity for CEESO reaches 96% (Figure 9b). After the first catalytic run, we recycled the "self-cleaning clothing" by simply washing with H<sub>2</sub>O and acetonitrile, and reused for the next run. Even after three catalytic runs, the activity and selectivity is still comparable to that of the first run (Figure 9c), indicating the high robustness of such Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>-CC composite.





Figure 9. (a) Decontamination of CEES on  $Mg_3AI-LDH-Nb_6-CC$ ; (b) Concentration time-course plots for the CEES oxidative transformation on  $Mg_3AI-LDH-Nb_6-CC$ ; (e) Recycle test for CEES decontamination on  $Mg_3AI-LDH-Nb_6-CC$ .

#### Conclusions

In summary, the active hexaniobate cluster has been successfully intercalated into Mg<sub>3</sub>Al-LDH to form an immobilized Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>. As a versatile catalyst, Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> can effectively decontaminate three CWA simulants through the optimal pathway of each: selectively oxidizing sulfur mustard simulant (CEES), hydrolyzing a G-type nerve agent simulant (DECP), and perhydrolyzing a V-type nerve agent simulant (OSDEMP). As an all-inorganic material, such Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite exhibits excellent stability and recyclability for continuous catalytic runs. Importantly, a self-detoxifying cloth is fabricated by integrating Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> onto textiles that can remove 94% of CEES without stirring in 1 h in the presence of nearly stoichiometric 3%  $H_2O_2$ . The reported Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite catalyst not only represents a novel and effective



decontaminating material but also offers a new opportunity in making portable, permeable, and economical protective selfdetoxifying clothing (e.g. protective suits, gloves, and boots, etc.) against chemical warfare agents.

### **Experimental Section**

#### Materials and Methods

All reagents and other starting materials were obtained commercially and used as received.  $K_7HNb_6O_{19}^{[23]}$  and  $[(CH_3)_4N]_5[H_3Nb_6O_{19}]$  (TMA-Nb<sub>6</sub>)<sup>[24]</sup> were prepared using the literature methods. 2-chloroethyl ethyl sulfide (CEES) was purchased from Aladdin Industrial Corporation. Diethvl cyanophosphonate (DECP) and О, S-diethylmethyl phosphonothioate (OSDEMP) were purchased from Alfa Aesar (China) Chemicals Co., Ltd.. Caution: the simulants of CWAs (CEES, DECP, OSDEMP) are highly toxic and must be handled only by trained personnel using applicable safety procedures in a closed system or in a hood under good ventilation. Powder X-ray diffraction (PXRD) data on samples were recorded on a Bruker instrument equipped with graphitemonochromatized Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm; scan speed = 5° min<sup>-1</sup>; 20 = 5-70°) at room temperature. IR spectra were collected (as KBrpressed pellets) on a Nicolet 170SXFT-IR spectrophotometer in the range 400-4000 cm<sup>-1</sup>. The X-ray photoelectron spectrum (XPS) analysis was conducted on an ESCALAB 250 spectrometer using an Al K $\alpha$ radiation as the X-ray source (1486.7 eV) with a pass energy of 30 eV and the pressure inside the analyzer was maintained at 10-9 Torr. Elemental analyses (C, H and N) were conducted on an ElementarVario EL cube Elmer CHN elemental analyzer; Mg, Al and Nb were determined by a ThermoiCAP 6000 atomic emission spectrometer. TGA of the sample was performed using a Shimadzu DTG-60AH thermal analyzer under air with a heating rate of 10 °C min-1. The morphology and microstructure of the samples were observed by scanning electron microscopy (SEM, JEOLS-4800) and transmission electron microscopy (TEM, JEOL JEM-2010). The Brunauer-Emmett-Teller (BET) specific surface areas were performed at 77 K in a Belsorp-max surface area detecting instrument. The GC analyses were performed on Shimadzu GC-2014C with a FID detector equipped an HP-5 ms capillary column. <sup>31</sup>P NMR spectra were determined on a Bruker 400 MHz instrument in  $D_2O_2$ , and all the chemical shifts were referenced to aqueous  $H_3PO_4$ solution (85%). Raman spectra were obtained on SNFT-SRLab1000 equipped with an excitation wavelength of 785 nm.

#### Synthesis of Mg<sub>3</sub>AI-LDH-Nb<sub>6</sub> Composite

A 10 mL solution containing 6 mmol of Mg(NO<sub>3</sub>)<sub>2</sub> and 2 mmol of Al(NO<sub>3</sub>)<sub>3</sub>, and an aqueous solution of NaOH (0.2 M) were simultaneously dropped into a 250 mL three-necked flask with vigorous stirring under N<sub>2</sub> at room temperature. The relatively adding rate of two solutions was adjusted to keep the final pH value of the mixture to ~10. After aging at 80 °C for 12 h, the precipitate was washed with water for 3 times and redispersed in 8 mL water preparing Mg<sub>3</sub>Al-LDH-NO<sub>3</sub> slurry. Then, 2 mL Mg<sub>3</sub>Al-LDH-NO<sub>3</sub> slurry and 8 mL TMA-Nb<sub>6</sub> aqueous solution (containing 0.1 g TMA-Nb<sub>6</sub> for Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>-13%; 0.4 g TMA-Nb<sub>6</sub> for Mg<sub>3</sub>Al-LDH-Nb6-20%; 0.8 g TMA-Nb6 for Mg3Al-LDH-Nb6-25% and 1.0 g TMA-Nb6 for Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>-28%) were mixed and stirred for 20 min under N<sub>2</sub> at room temperature. Then the mixture was transferred to a Teflon-lined stainless steel autoclave (23 mL), kept in an oven at 100 °C for 24 h and left to cool down to room temperature. A white solid of Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> composite was obtained after washing with water for 3 times and drying at 80 °C for 12 h under vacuum.

#### Synthesis of Mg<sub>3</sub>AI-LDH-Nb<sub>6</sub>-CC

60 mg wet Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub> sample was dispersed in 2 mL DMF under ultrasonic conditions for 10 min in a vial. 1 mL polyvinylidene fluoride (PVDF) solution (20 mg) was then added to the suspension. The combined Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>/PVDF suspension was sonicated for additional 10 min, resulting in a catalyst "ink". A piece of carbon cloth (CC) was immersed in the catalyst "ink" under ultrasonic conditions for 10 min and then dried under vacuum at 70 °C for 12 h.

# Catalytic oxidation of 2-chloroethyl ethyl sulfide (CEES) with $Mg_3Al\-LDH-Nb_6$

The selective oxidation (decontamination) of CEES using different catalysts were performed as follows. Catalyst (0.003 mmol) was dispersed in acetonitrile (4 mL) and to this solution CEES (0.5 mmol) and 1,3-dichlorobenzene (internal standard, 0.25 mmol) were added. After stirring for 2 minutes at room temperature, 3% aqueous  $H_2O_2$  (0.525 mmol) was added dropwise. The reaction was monitored by gas chromatography at various time intervals and the products were qualitatively analyzed by GC-MS.

# Catalytic hydrolysis of diethyl cyanophosphonate (DECP) with $Mg_{3}Al\text{-LDH-Nb}_{6}$

The hydrolysis of DECP with various catalysts were performed as follows. Catalyst (0.003 mmol) was added to the mixture of H<sub>2</sub>O (100  $\mu$ L) and DMF (1200  $\mu$ L), followed by addition of DECP (0.12 mmol) and nitrobenzene (internal standard, 3.25×10<sup>-2</sup> mmol). The reaction was monitored by gas chromatography at various time intervals.

# Catalytic Perhydrolysis of O,S-diethyl methylphosphonothioate (OSDEMP) with Mg\_3Al-LDH-Nb\_6

The perhydrolysis of OSDEMP using different catalysts were conducted as follows. Catalyst (0.008 mmol) was dispersed in the mixture of D<sub>2</sub>O (500 µL) and acetonitrile (200 µL). After stirring for 2 min at room temperature, OSDEMP (5 µL) and 30% aqueous H<sub>2</sub>O<sub>2</sub> (700 µL) was added to initiate the reaction. The mixture was monitored by <sup>31</sup>P NMR at various time intervals.

#### Catalytic Decontamination of CEES with Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>-CC

The degradation of CEES using Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>-CC were conducted as follows. CEES (0.1 mmol), 1,3-dichlorobenzene (internal standard, 0.05 mmol) and 3% aqueous H<sub>2</sub>O<sub>2</sub> (0.105 mmol) were mixed in acetonitrile (400  $\mu$ L) to produce a "toxic solution". The above prepared "toxic solution" was absorbed by the cloth (Figure 9a) and the degradation experiment was performed under ambient conditions without other treatment. To detect the products, at various time intervals, the cloth was washed with acetonitrile (500  $\mu$ L) and the extract was monitored by gas chromatography. The catalytic data in Figure 9b are from four parallel experiments.

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**Keywords:** chemical warfare agents • self-detoxifying material • heterogeneous catalysis • decontamination • polyoxoniobates

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A novel decontaminating material, Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>, was prepared by immobilizing hexaniobate into layered double hydroxide. As a versatile catalyst, Mg<sub>3</sub>Al-LDH-Nb<sub>6</sub>, effectively degrades a sulfur mustard simulant by selective oxidation, a G-type and a Vtype nerve agent simulants by hydrolysis and perhydrolysis, respectively. Furthermore, such catalyst can be integrated onto textiles to construct a portable and permeable self-detoxifying clothing.



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