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# Effect of GO phase in $Zn(OH)_2$/GO composite on the extent of photocatalytic reactive adsorption of mustard gas surrogate

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## ABSTRACT

Composites of zinc hydroxide with various contents of graphite oxide (GO) were synthesized with a controlled precipitation rate. They were used at ambient conditions as adsorbents of a mustard gas surrogate, 2-chloroethyl ethyl sulfide (CEES). The samples' surface features were characterized by various physical and chemical methods. The materials acted as photocatalysts upon light irradiation, degrading CEES to less- or no-toxic compounds. Exposure to visible light and the presence of GO in the composites improved the performance. The results indicated a paramount role of terminal OH groups as well as the porosity in the reactive adsorption process. The enhanced performance is linked to an increase in the degree of chemical and structural heterogeneity upon addition of GO. The surface characteristics strongly depend on the amount of the carbonaceous phase and 10 wt% was found as an optimal content. The CEES degraded mainly to ethyl vinyl sulfide by dehydrohalogenation and to hydroxyethyl ethyl sulfide via a hydrolysis pathway. The irradiation under visible light led to further transformation to vinyl vinyl sulfide and methyl vinyl sulfide through radical's reaction. The presence of GO promotes the electrons transfer and oxygen activation.

## 1. Introduction

One of the most widely used chemical warfare agents (CWA) is mustard gas also referred to as sulfur mustard (HD), which is a highly toxic blistering agent. Its toxicity to humans, similar to phosgene and hydrocyanic acid, is associated with the ability to alkylate proteins. It rapidly penetrates through a membrane into a living cell, releasing HCl after hydrolysis [1].

Because of the extremely high toxicity of HD, the simulant 2-chloroethyl ethyl sulfide or half mustard gas (CEES), which is less toxic, is often used for research studies focused on the development of decontamination technologies [2]. CEES contains the same $ClCH_2CH_2S$- group as HD does. This moiety is responsible for its toxicity. In general, the CEES degradation pathways can be through the cleavage of C—S or C—Cl bonds and through the photocatalytic degradation/oxidation, where hydroxyl radicals are usually the main oxidizing species [3].

Metal oxides/hydroxides are considered as suitable reactive/photoactive adsorbents for the catalytic decontamination of a variety of organic contaminants [4–6]. This is due to their large number of highly reactive terminal groups, thermal stability, enhanced reactivity, high surface area, and adsorption capability [7–9]. The efficiency of the catalytic and photocatalytic activity depends on a chemical nature, particle size, crystallinity and the surface area of a particular metal oxide/hydroxide.

There are studies on the adsorption of CWA or their surrogates on metal oxides, but mostly from solutions or by a direct contact of the materials with the liquid phase of CWA [10–15]. There are also some studies addressing CEES removal/deactivation from vapor phase. Mawhinney et al. studied in details the interactions of CEES with $Al_2O_3$ at different temperatures in a special IR cell [16,17]. Adsorption of CEES in $N_2$ atmosphere on carbon-coated porous magnesium oxide was studied by Vu et al. [18]. In all research where the adsorption from vapor phase was addressed, hydroxyl groups were indicated as playing a crucial role in surface interactions. Nevertheless, there are limited studies for the removal of vapors from the gas-phase at ambient conditions (ambient pressure, temperature and moisture content) [19,20]. Since those are the conditions of the potential use of CWA, there is a need for the research on the development of novel highly efficient and low cost materials, capable of totally detoxify CEES vapors. Employing photoactivity in visible light, in order to increase the efficiency of a catalytic degradation to less or nontoxic compounds, would be an advancement,

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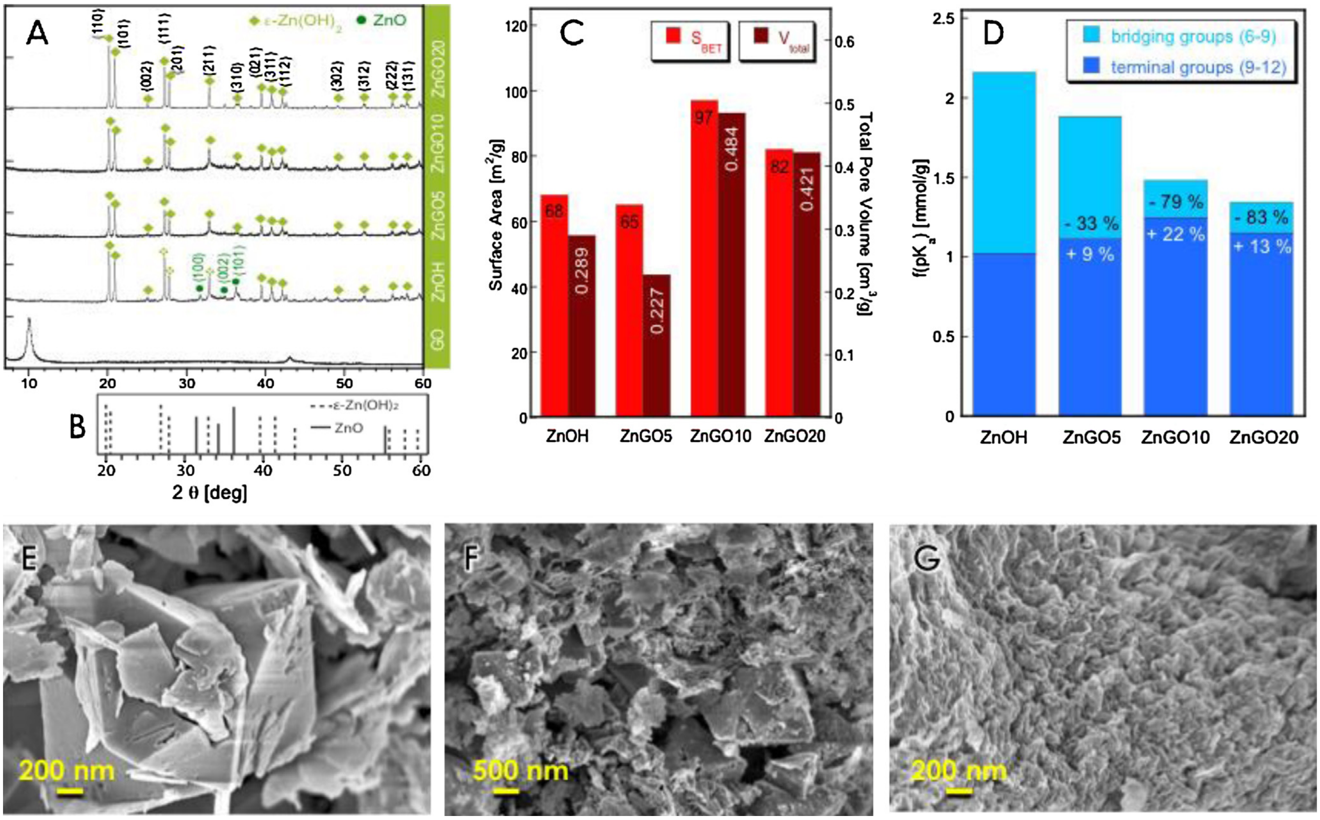

**Fig. 1.** X-ray diffraction patterns for the initial samples (A); JCPDS standard diffraction patterns for würtzite and wülfingite (B); parameters of porous structure calculated from the nitrogen adsorption isotherms (C); amounts of terminal OH groups detected from potentiometric titration experiments (D); SEM images of ZnOH (E); ZnGO5 (F) and ZnGO10 (G).

since 46% of the solar spectrum consists of irradiation in the visible light range [21].

Zinc oxides and hydroxide have attracted researchers' attention owing to their suitability for applications as gas sensors, varistors, in the fabrication of optical devises, and as gas adsorbents. As a well-known semiconductor, zinc (hydr) oxide has a wide band gap (3.0–3.3 eV) leading to the photoactivity in the visible range of violet spectrum (375.7–413.3 nm) [22–25]. Similar activity has been indicated for titanium dioxide ($TiO_2$) [26]. Upon exposure to visible light irradiation, both $Zn(OH)_2$ and $TiO_2$ can promote photocatalytic reactions, which can lead to the degradation of various organic pollutants [27–29].

It has been shown that zinc hydroxide, owing to the presence of OH groups, has a higher reactivity toward a CEES degradation in visible light than has zinc oxide [20]. An alteration in experimental conditions of sodium hydroxide addition to zinc chloride can lead to differences in the properties of precipitates [30,31]. The nucleation and growth of $Zn(OH)_2$ instead of ZnO is favorable at a low basicity ($pH < 10$) at room temperature, since the hydroxide phase is chemically and structurally stable [20,32]. At higher pH values, the hydroxide phase can be transformed to oxide [20,33].

Recent advances in materials science have led to the development of new efficient and photoactive adsorbents and catalysts containing graphene. It has been shown that the texture, the surface chemistry and the physicochemical properties of the metal oxide/hydroxide change dramatically after a GO addition [34–37]. Recently, the composites of zinc (hydr) oxide with graphite oxide have been reported as efficient reactive adsorbents of TICs such as $H_2S$ [38,39] and $SO_2$ [40] at ambient conditions. The improvement in the performance was linked to an increase in the number of OH groups and in their surface dispersion. These groups were found to participate in oxidation reactions and in the formation of superoxide ions via the photochemical path with the contribution of a GO phase [41].

Based on the above, the objective of this paper is the evaluation of the composites consisting of GO and $Zn(OH)_2$ ($Zn(OH)_2/GO$) as photocatalytic reactive adsorbents with an intended application for CEES decomposition. The performance is studied under ambient light exposure, solar light irradiation (simulator) and in the dark. Since it was found that the high number of OH surface groups enhances the chemical reactivity [20], we target the composites with a increased amount of terminal active groups and with a higher surface area and total pore volume, compared to those of $Zn(OH)_2$. Moreover, the presence of GO may contribute to a faster electrons transfer and may improve oxygen activation. All of the aforementioned parameters would be of a paramount importance for the detoxification of CEES vapors.

## 2. Experimental

### 2.1. Materials

Zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH) with a purity higher than 99% and deionized water were used in this study. Graphite oxide (GO) was synthesized by oxidation of commercial graphite (Sigma-Aldrich) following the Hummers method [42]. Details of a GO preparation are presented elsewhere [39,43]. All materials were synthesized following a typical precipitation procedure at room temperature [20,38].

The composites of zinc hydroxide with GO were prepared by dispersing GO (5, 10 and 20% wt. of the final mass of the composite) in 0.5 L of a zinc chloride solution (0.05 M) and maintained under vigorous stirring for 2 h. Than the stoichiometric amount of NaOH (1L, 0.05 M) was added at a rate of 2.0 mL/min. The pH during synthesis