**ABSTRACT**

The composites of a high porosity and of an increased number of terminal hydroxyl groups were prepared. The synthesized materials were exposed to CWA surrogate vapors (CEES or DMCP) at ambient conditions for various periods of time. The amounts adsorbed of either surrogates or their decomposition products were evaluated based on a weight gain. The products of surface reactions in the headspace or adsorbed on the surface were analyzed by MS. As a final step the active phase were deposited in fibers to create smart textile being able to protect and to detect CWA (based on the color change).

14. SUBJECT TERMS

CWA decontamination, multifunctional adsorbents, porosity, surface chemistry, photoactivity, composites

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INSIGHT INTO MULTIFUNCTIONAL REACTIVE ADSORBENTS

Teresa J. Bandosz

Department of Chemistry
The City College of New York
Objective

- Evaluation of the reactive adsorption capability for CWA surrogates of novel porous composite adsorbents consisting transition metals oxides, alone or in the mixed phase with the modified graphene phase, and with gold or silver nanoparticles.

- Understanding the basic science related to the activity of these materials as adsorbents and decontamination media.

- Materials engineering/deposition of the active phase on fabrics.
Materials: Past efforts

- Iron (hydr)oxide: FERRIHYDRITE
- Copper hydroxynitrate
- Zinc hydroxide

Composites
- With graphite oxide (GO)
- With aminated GO (GOU)
- With AgNP
Motivation for the materials’ choice

- Relatively high surface areas
- Oxygen vacancies as active sites
- Photoactive in UV-Vis
- Terminal OH groups
- GO
  - Enhances dispersion of inorganic phase
  - Provides electronic conductivity for redox reactions
  - (GOU) activates oxygen
  - Increases surface heterogeneity/defects
Testing CWA surrogate interactions

Surrogates:

- CEES- 2-chloroethyl ethyl sulfide (HD)
- DMCP- dimethyl chlorophosphate (nerve agents) X)

or modified fabric
Approaches to derive mechanisms

- Analysis of the surface of initial hydroxides and their composites (porosity, chemistry, microstructure, texture) (N\textsubscript{2}, PT, FTIR, SEM, HRTEM..)
- Analysis of the surface of the exhausted samples (FTIR, TA-MS)
- Analysis of the surface extraction products (GC-MS)
- Analysis of the headspace in the close system (GC-MS)
## Major Findings: texture and chemistry

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S^{\text{BET}} ) [m(^2)/g]</th>
<th>( V_T ) [cm(^3)/g]</th>
<th>( V_{\text{mic}} ) [cm(^3)/g]</th>
<th>( V_{\text{meso}} ) [cm(^3)/g]</th>
<th>( V_{\text{meso}}/V_{\text{mic}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>200</td>
<td>0.265</td>
<td>0.073</td>
<td>0.192</td>
<td>2.6</td>
</tr>
<tr>
<td>FeO-GO</td>
<td>243</td>
<td>0.304</td>
<td>0.087</td>
<td>0.217</td>
<td>2.5</td>
</tr>
<tr>
<td>FeO-GOU</td>
<td>288</td>
<td>0.312</td>
<td>0.102</td>
<td>0.210</td>
<td>2.1</td>
</tr>
</tbody>
</table>

![Graph showing distribution of \( f(pK_a) \) for different samples.](image)

**Arcibar Orozco et al. J. Mater. Chem. A 2015, 3, 17080-17090.**
Major Findings: Photoactivity

Major Findings: activity (copper hydroxynitrate)

- H$_3$PO$_4$ detection in the liquid
- NO$_2$ detection in the headspace

<table>
<thead>
<tr>
<th>Sample</th>
<th>NO$_2$ Concentration [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 h</td>
</tr>
<tr>
<td>CuON</td>
<td>1.3</td>
</tr>
<tr>
<td>CuONGO</td>
<td>15.9</td>
</tr>
</tbody>
</table>

Arcibar-Orozco, J. Advanced Materials Interfaces, 2015, 2, 1-9
**Major Findings: Reactive adsorption**

**HYDROLYSIS and OXIDATION**
- Both hydrolysis (EVS) and oxidation (CEESO) take place
- GO: increase the oxidation performance
- AgNPs: increase photo-reactivity/radical reaction (disulfides)

**HYDROLYSIS and DEGRADATION**
- The hydroxyl groups play a key role
- GO: increase the photocatalytic performance
- AgNPs: increased photo-reactivity/radical reaction (disulfides)

**HYDROLYSIS and OXIDATION**
- GO considerably accelerates the DMCP decomposition
- Hydroxyl groups: direct interactions with DMCP
- Nitrate groups: NOx formation

The mixed hydroxides are versatile and can detoxify CEES through dehydrohalogenation and DMCP through hydrolysis.

Florent, M. et al., submitted
Ferrihydrite on cotton

Loose Fibers
7.1% Iron

Swatch from TW
10.2% Iron

Swatch from TS
4.8% Iron
Active Ferrihydrite phase on cotton: CEES

I. t-shirt
- Maximum loading
- First loading

II. towel
- Maximum loading

Weight uptake / g/g of Fe

<table>
<thead>
<tr>
<th></th>
<th>7d g/g</th>
<th>7d g/g Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>FHYD</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>TW-Fe</td>
<td>0.15</td>
<td>0.8</td>
</tr>
<tr>
<td>TS-Fe</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>LF-Fe</td>
<td>0.05</td>
<td>0</td>
</tr>
</tbody>
</table>

Images showing structural changes and iron content over dip-and-dry cycles.
Active Ferrihydrite phase on cotton: extract analysis

TS-Fe
- CEES: 98.5%
- surface reaction products: 1.5%

LF-Fe
- CEES: 98.4%
- surface reaction products: 1.6%
- ACE-CI: 8.9%
- THR: 13.7%
- EVS: 10.8%
- EES: 6.0%

TW-Fe
- CEES: 96.2%
- surface reaction products: 3.8%
- ACE-CI: 22.3%
- THR: 8.3%
- EVS: 6.3%
- EES: 7.3%
- DEDS: 15.1%

1.6 mg FHYD
- CEES: 99.4%
- surface reaction products: 0.6%
- ACE-CI: 25.1%
- THR: 57.9%
- EVS: 17.0%

2.4 mg FHYD
- CEES: 99.0%
- surface reaction products: 1.0%
- ACE-CI: 82.6%
- THR: 7.2%
- EVS: 10.2%

3.5 mg FHYD
- CEES: 98.7%
- surface reaction products: 1.3%
- ACE-CI: 86.3%
- THR: 8.0%
- EVS: 5.7%
Active copper phase on cotton

Swatch from Towel
Copper (hydr)oxide

Swatch from T-shirt
Copper (hydr)oxide
Washed with water

<2 % CuO

Washed with base

TA in air:
5 % CuO

Copper oxide

Copper oxide
Active copper phase on cotton fibers-DMCP

Weight uptake [mg/g]

Copper content < 2 %
Active copper phase on carbon fibers

Types of Carbon

Graphite fiber swatch

Fibers from swatch

Carbon swatch

Graphite lattice formation

Amorphous Carbon

Graphite

Source: Marsh 1991
Active copper phase on graphitic carbon fibers

<table>
<thead>
<tr>
<th>Material</th>
<th>DMCP adsorption mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 day</td>
</tr>
<tr>
<td>GrF+CuOH</td>
<td>69.1</td>
</tr>
<tr>
<td>GrF-NS+CuO</td>
<td>57.1</td>
</tr>
</tbody>
</table>

+ 20 %

< 3 % CuO

![Graph showing DMCP adsorption mg/g for different materials and time periods]
Active copper phase on carbon fibers-Cu-BTC

3 μm
Sensing capability

Swatch from T-shirt, Cu(OH)$_2$, base washed

Swatch from Towel, CuO

initial

24 hours

DMCP

3 hours

3 hours

CF-SN+CuON

CF-SN+CuO
ZnO$_2$ activity: EES conversion - Extracts analysis

Pie charts showing the percentage distribution of different extracts among ZnO$_2$, Zn130, Zn200, Zn300, and Zn400 samples.

- EES
- HEMS
- ES
- EESO
- EESO$_2$
- DEDS

Graphs illustrating the change in concentration of EES, EESO, and DEDS across different samples.

Inset graph showing the percentage change in H$_2$O$_2$ under light conditions.
Cu-BTC/g-C$_3$N$_4$ composites: Activity- DMCP

Cu-BTC/g-C$_3$N$_4$ composites: Porosity

General decontamination mechanism

A: $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3 + \cdot\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\cdot + \text{CH}_3\text{CH}_2\text{S}\cdot \text{CHCH}_3$
- $\beta$-carbon radical thioether
- $\alpha$-carbon radical thioether

B: $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\cdot + \cdot\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\cdot + \text{H}_2\text{O}$
- hydroxyethyl ethyl sulfide

C: $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\cdot \rightarrow \text{CH}_3\text{CH}_2\cdot + \text{CH}_2\cdot\text{CH}_3$
- $\text{H}^+$
- hydroxyethyl methyl sulfide

D: $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\cdot + \cdot\text{OH} \rightarrow \text{CH}_3\text{CH}_2\cdot + \text{CH}_2\cdot\text{CH}_3$
- hydroxyethyl sulfide

E: $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\cdot + \cdot\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\cdot + \text{H}_2\text{O}$
- $\text{H}^+$
- diethyl disulfide
- 1,2-bis(ethylthio) ethane
- Defects in the catalytic phase of metal (hydr)oxide promote reactivity towards CWA
- Addition of GO increases the surface heterogeneity and thus activity
- Deposition of active phase on fibers results in synergist effect related to the surface distribution of active phase and defects
- The color change of the active phase/fabrics might be an indicative of the exhaustion level of the protection layers
- High surface area of carbon cloths/textiles and electrical conductivity make them potential candidates for smart and reactive fabrics
Why Modified Carbon fibers as a support for an active phase?

- Their surface can be chemically modified to create a site for active phase strong/covalent attachment.
- On the interface new chemistry beneficial for the decontamination can be formed.
- The surface reaction products can be adsorbed in the developed pore system enhancing adsorption of organic molecules.
- The conductivity of carbon phase may promote redox/oxidation reactions.
- The support is light, breathable, durable, and environmentally stable.
- Possibility to integrate sensing of the exhaustion level.
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Dr. Christopher Karwacki (ECBDC)