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13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. 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)					
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Results Dissemination:

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Honors and Awards:

Protocol Activity Status:

Technology Transfer:

INSIGHT INTO MULTIFUNCTIONAL REACTIVE ADSORBENTS

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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

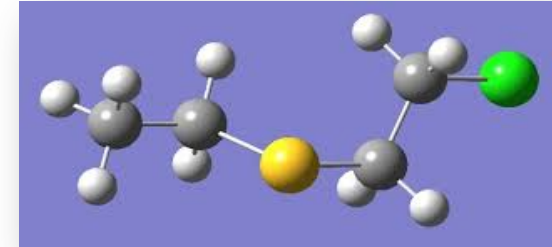
Motivation for the materials' choice

- ☑ 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

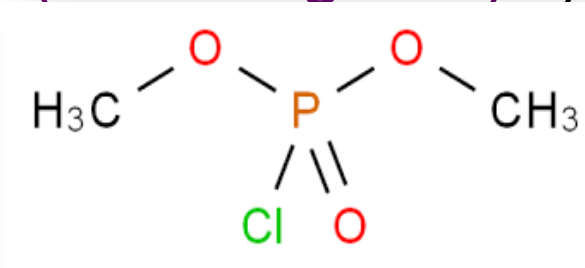
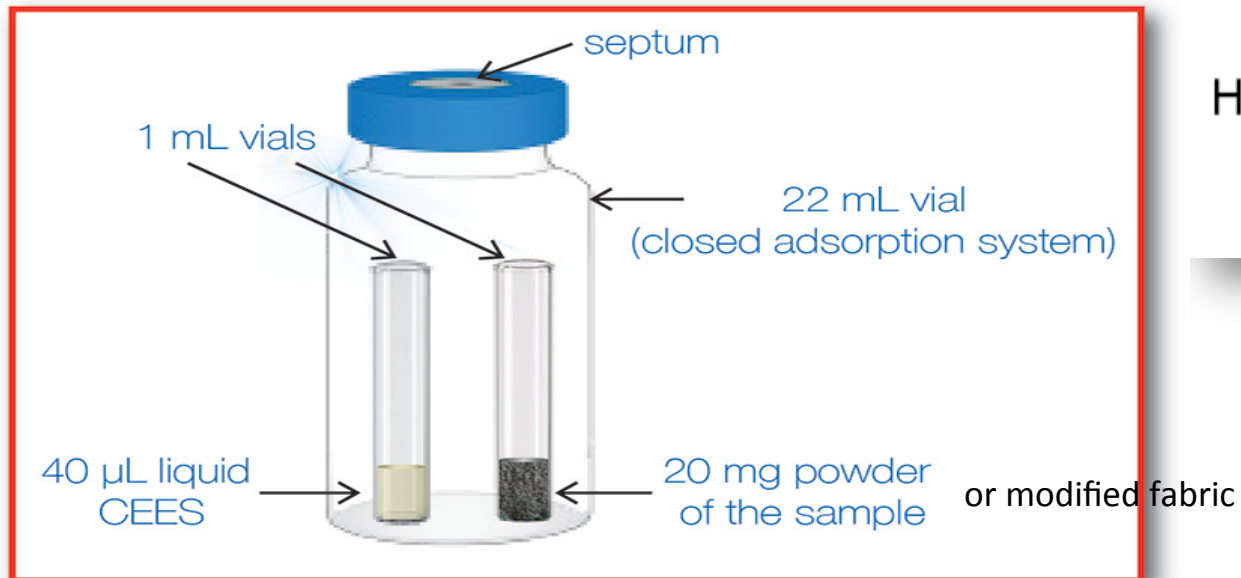
Testing CWA surrogate interactions

Surrogates:

- CEES- 2-chloroethyl ethyl sulfide (HD)



- DMCP- dimethyl chlorophosphate (nerve agents)X)



Approaches to derive mechanisms

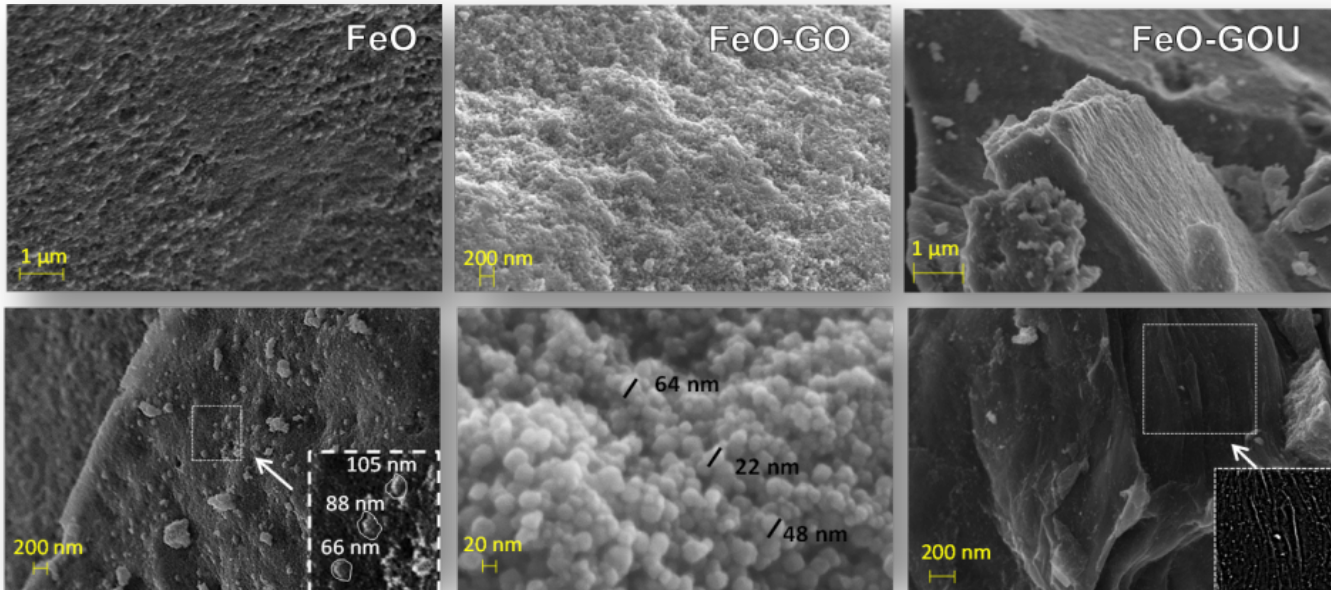
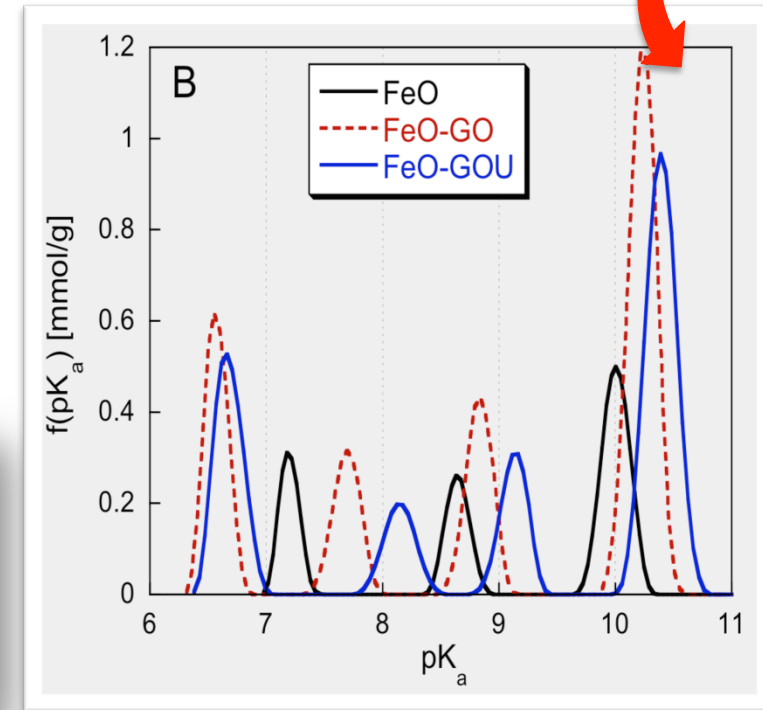
- ✓ Analysis of the surface of initial hydroxides and their composites (porosity, chemistry, microstructure, texture)(N₂, PT, FTIR, SEM, HRTEM..)
- ✓ Analysis of the surface of the exhausted samples (FTIR, TA-MS)
- ✓ Analysis of the surface extraction products (GC

- ✓ -MS)

- ✓ Analysis of the headspace in the close system (GC-MS)

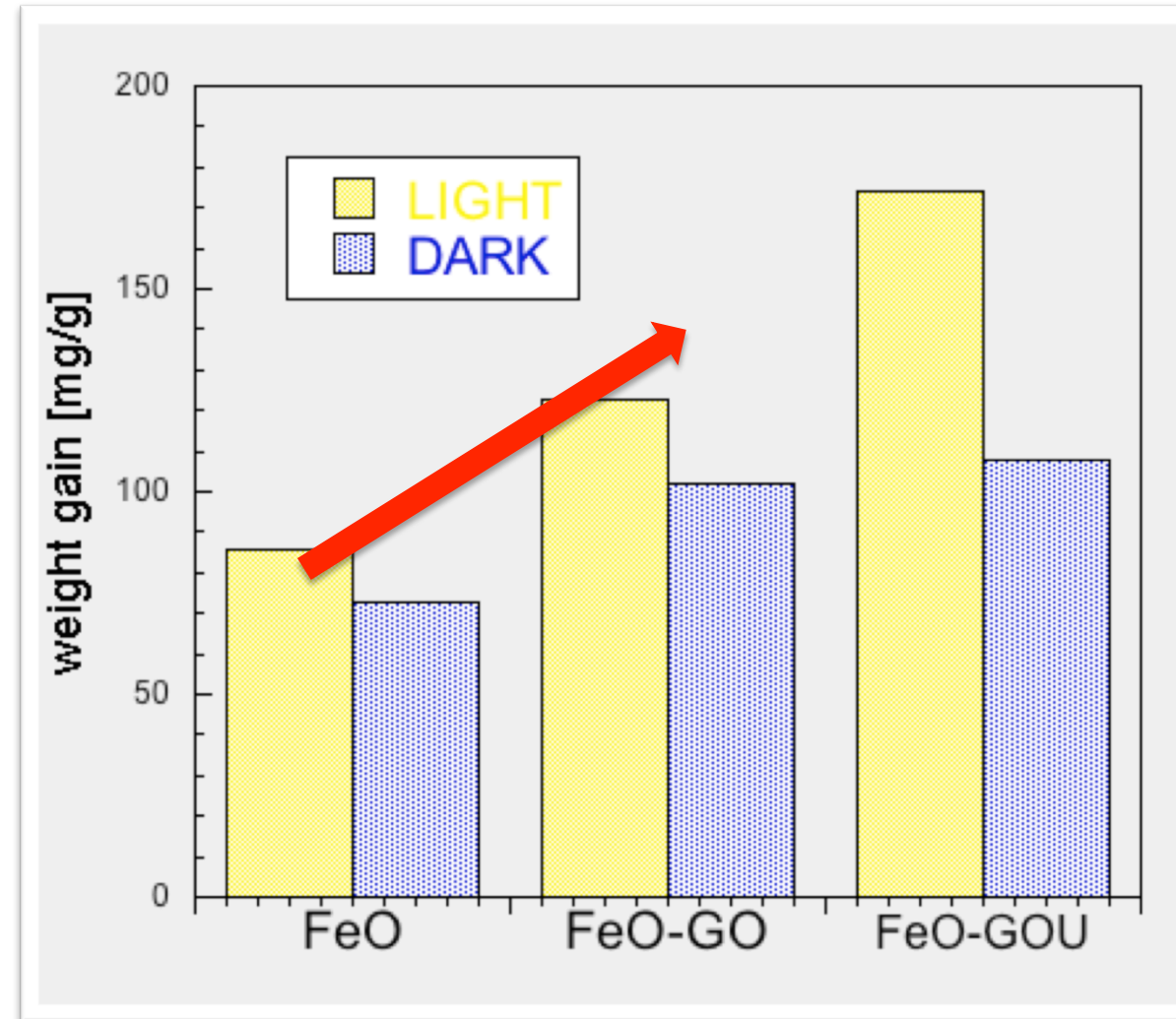
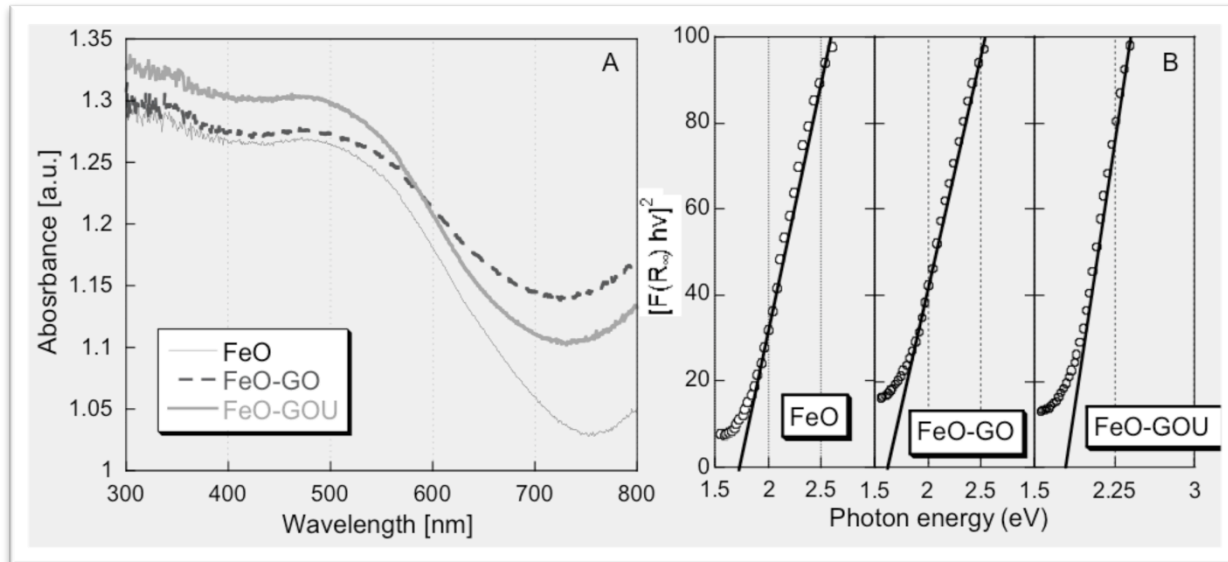
Major Findings: texture and chemistry

Sample	S^{BET} [$m^2 g^{-1}$]	V_T [$cm^3 g^{-1}$]	V_{mic} [$cm^3 g^{-1}$]	V_{meso} [$cm^3 g^{-1}$]	V_{meso}/V_{mic}
FeO	200	0.265	0.073	0.192	2.6
FeO-GO	243	0.304	0.087	0.217	2.5
FeO-GOU	288	0.312	0.102	0.210	2.1

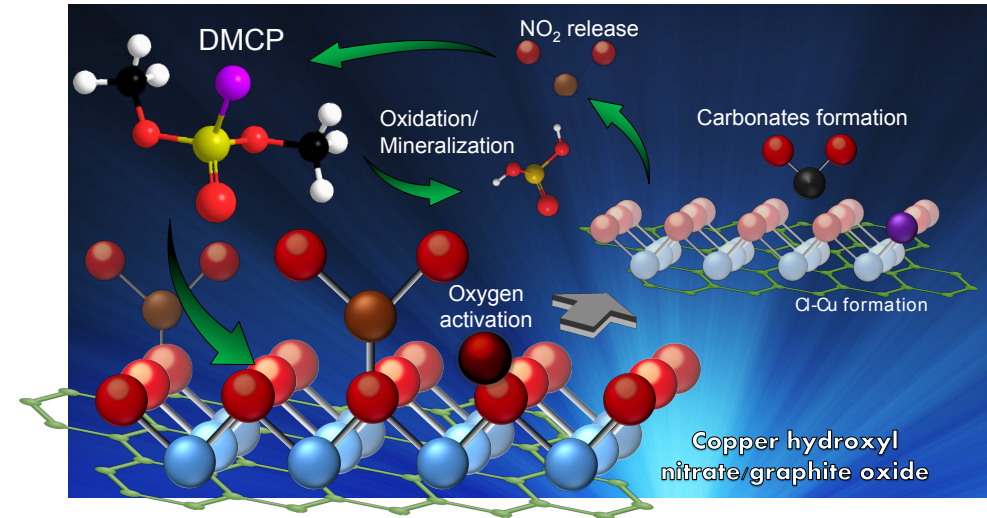
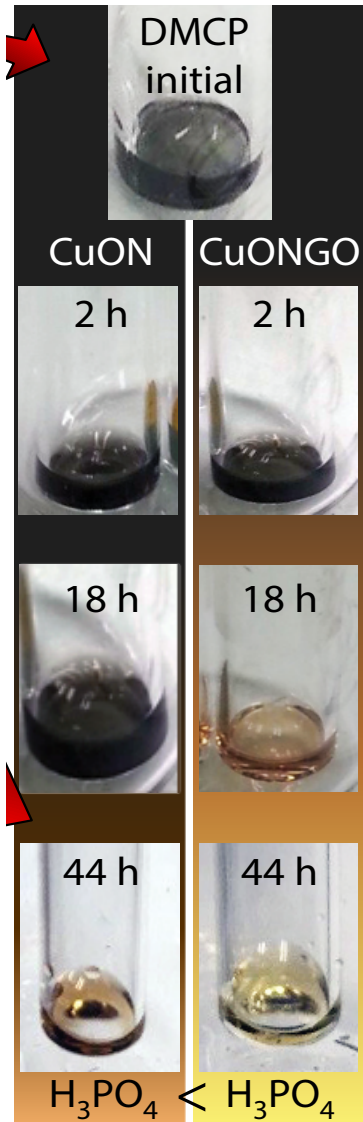


Arcibar Orozco et al. *J. Mater. Chem. A* 2015, 3, 17080-17090.

Major Findings: Photoactivity



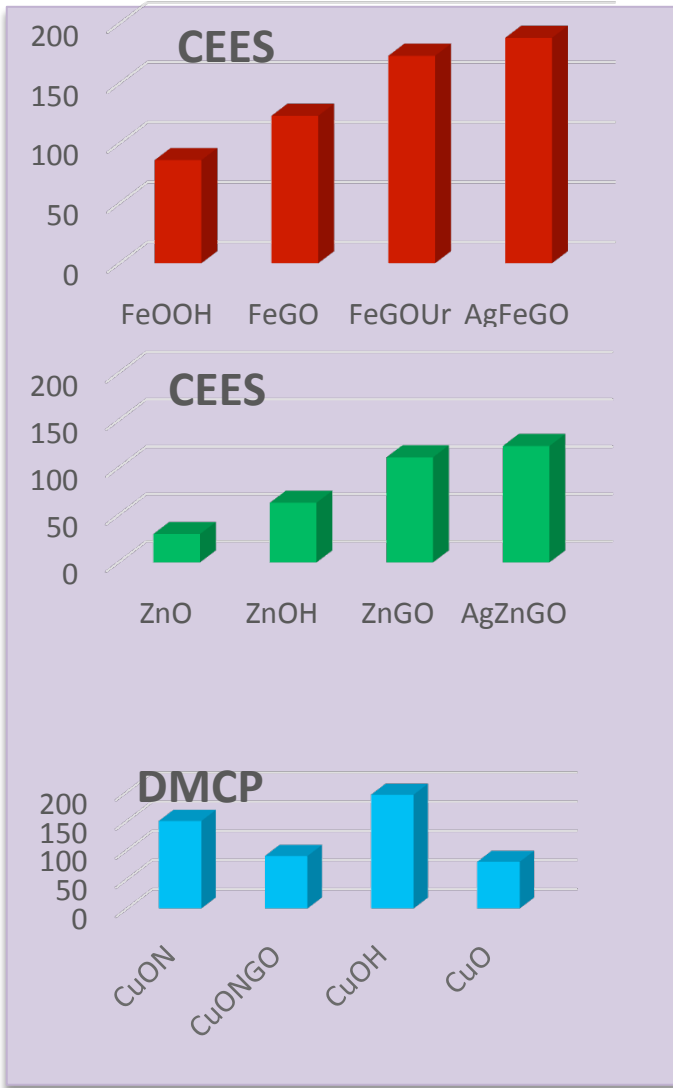
Major Findings: activity (copper hydroxynitrate)



- ✓ H_3PO_4 detection in the liquid
- ✓ NO_2 detection in the headspace

Sample	NO_2 Concentration [ppm]	
	24 h	48 h
CuON	1.3	27.0
CuONGO	15.9	57.6

Major Findings: Reactive adsorption



HYDROLYSIS and OXIDATION

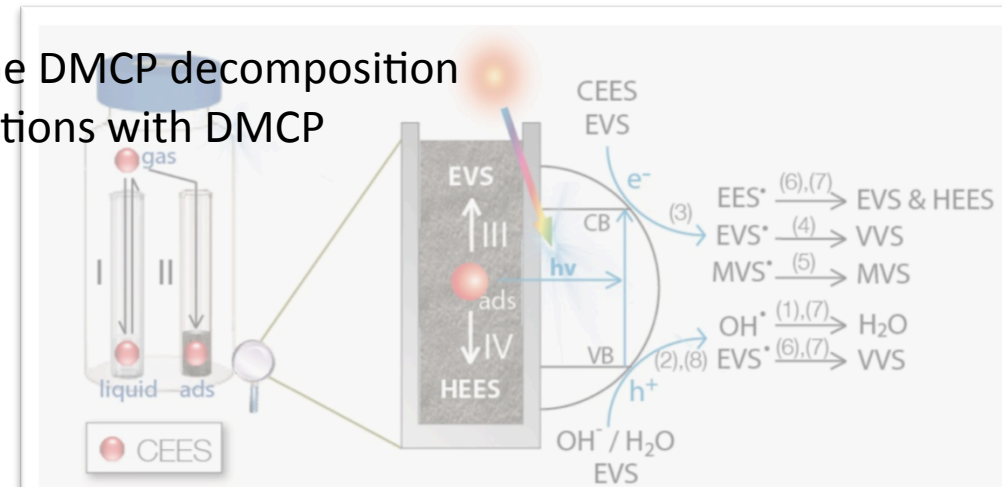
- Both hydrolysis (EVS) and oxidation (CEESO) take place
- GO: increase the oxidation performance
- AgNPs: increase photo-reactivity/radical reaction (disulfides)

HYDROLYSIS and DEGRADATION

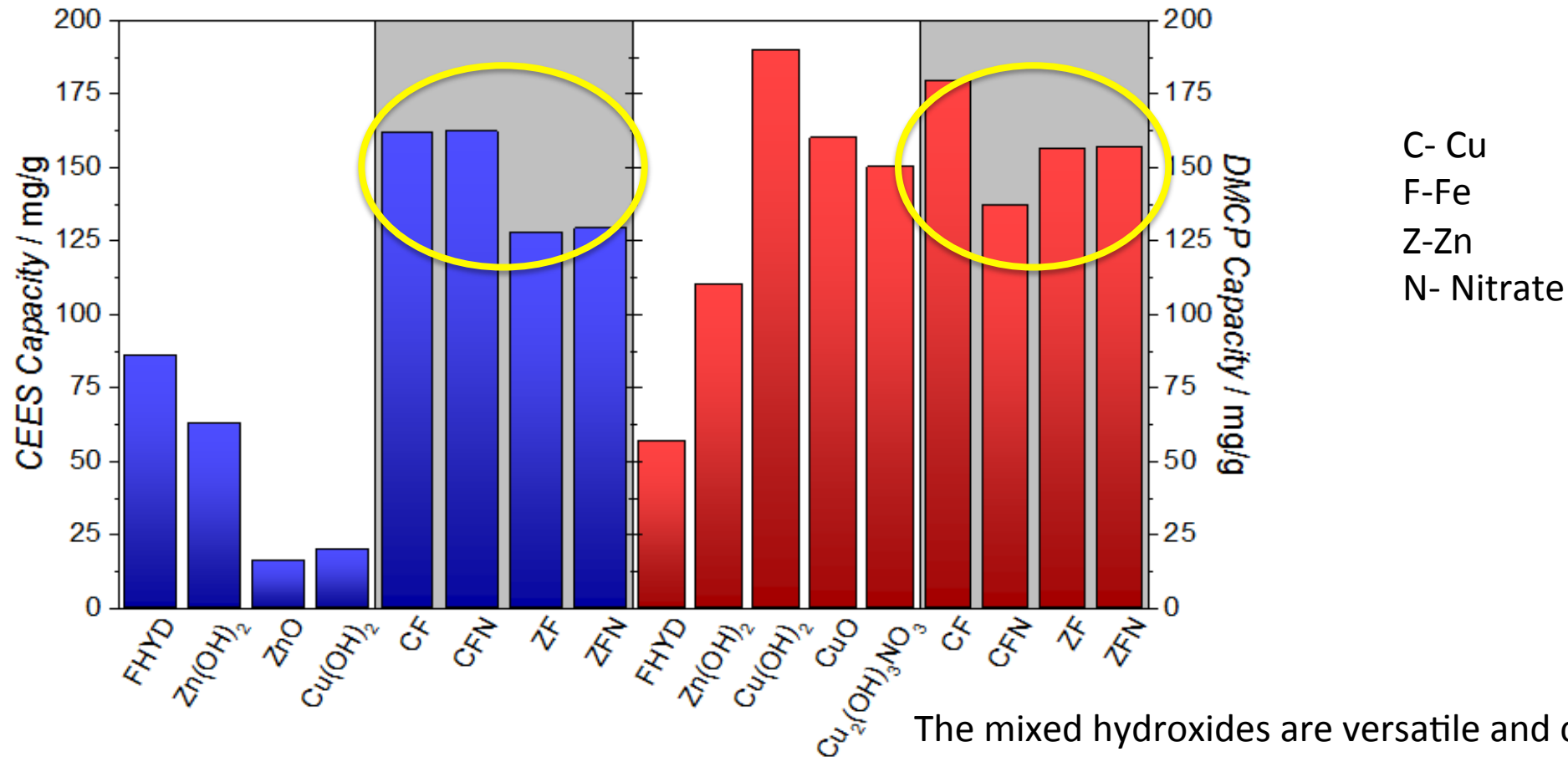
- The hydroxyl groups play a key role
- GO: increase the photocatalytic performance
- AgNPs: increased photo-reactivity/radical reaction (disulfides)

HYDROLYSIS and OXIDATION

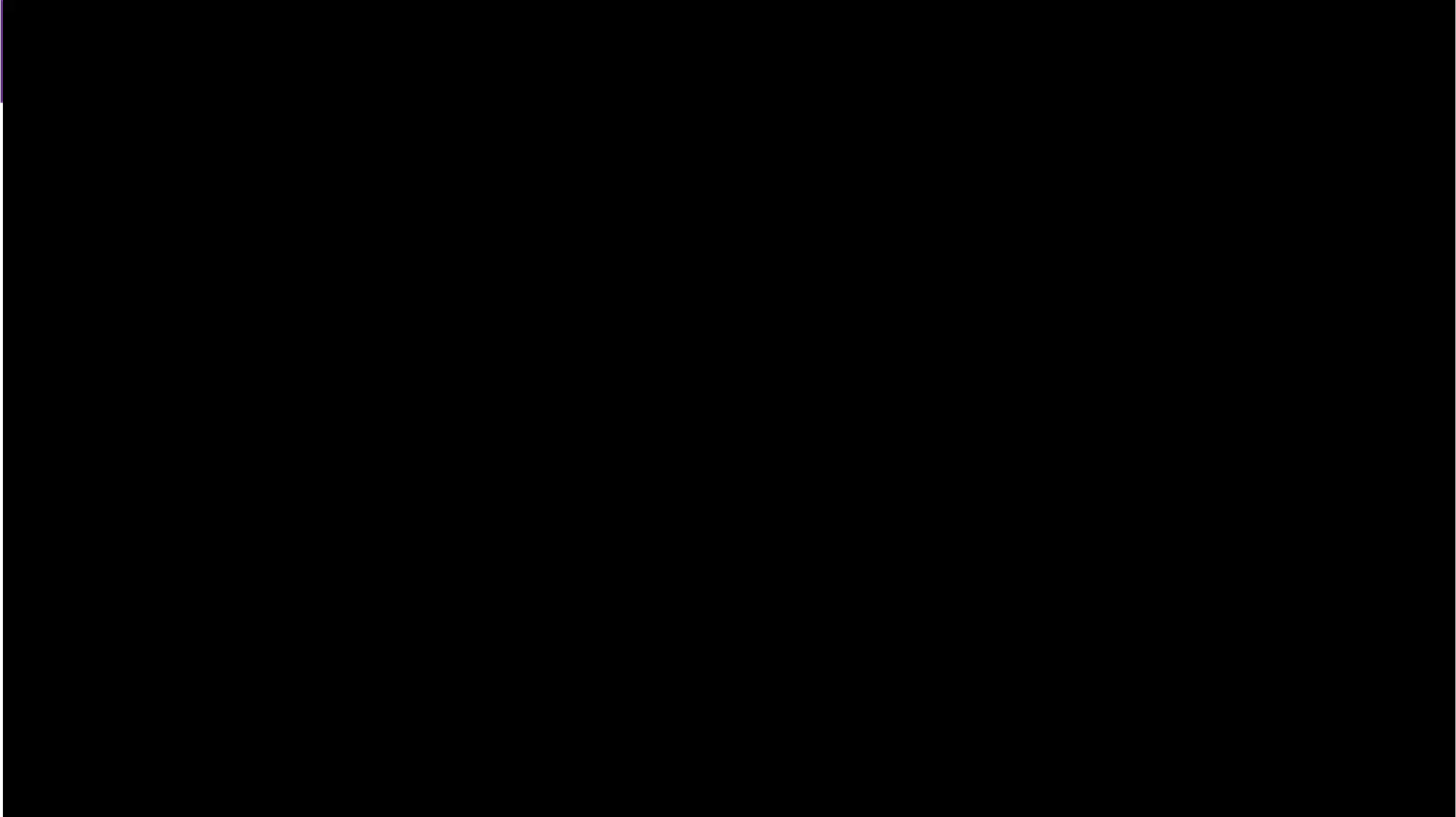
- GO considerably accelerates the DMCP decomposition
- Hydroxyl groups: direct interactions with DMCP
- Nitrate groups: NO_x formation



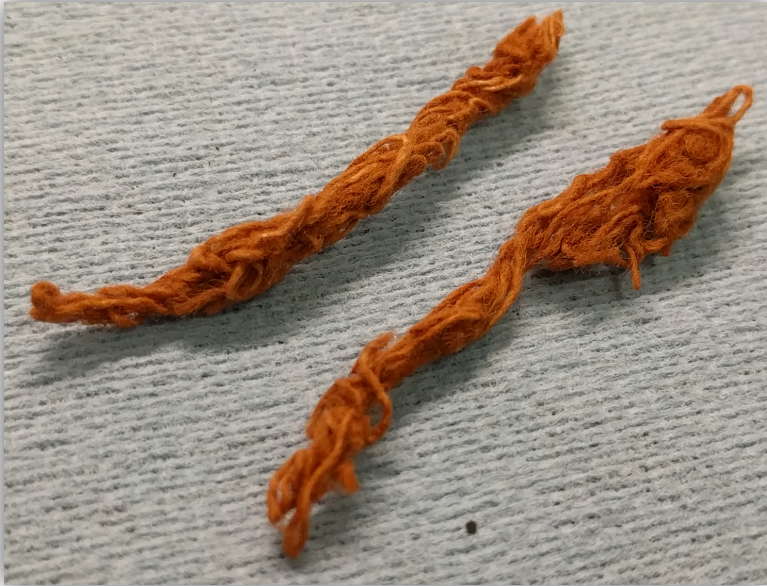
Major Findings: Mixed oxide performance



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



Ferrihydrite on cotton



Loose Fibers
7.1% Iron

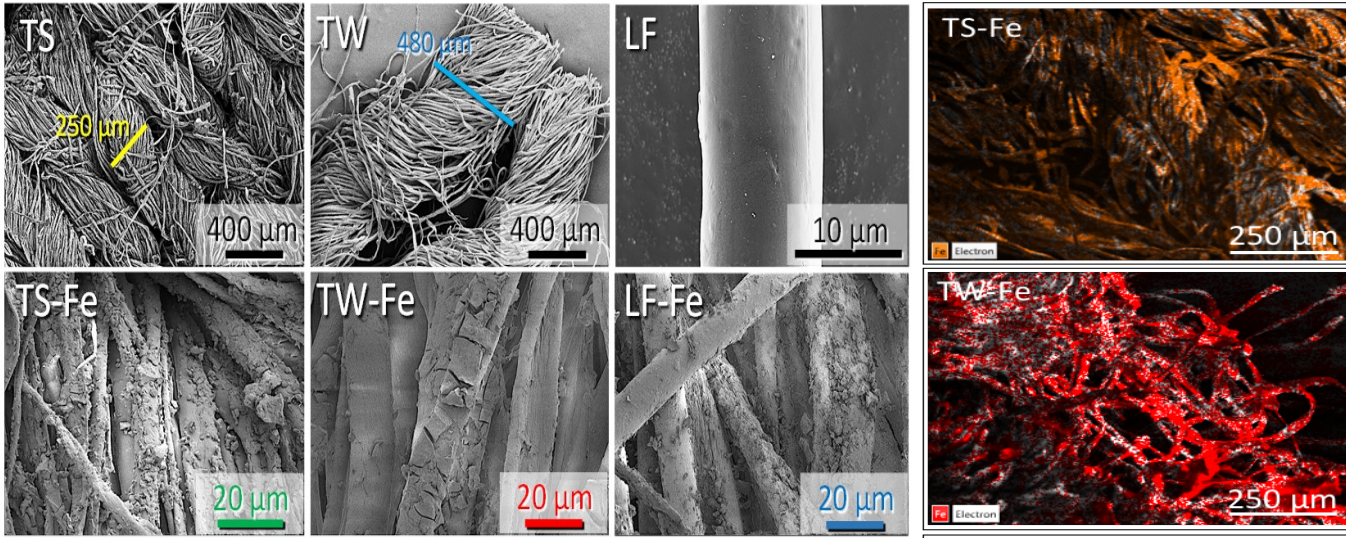
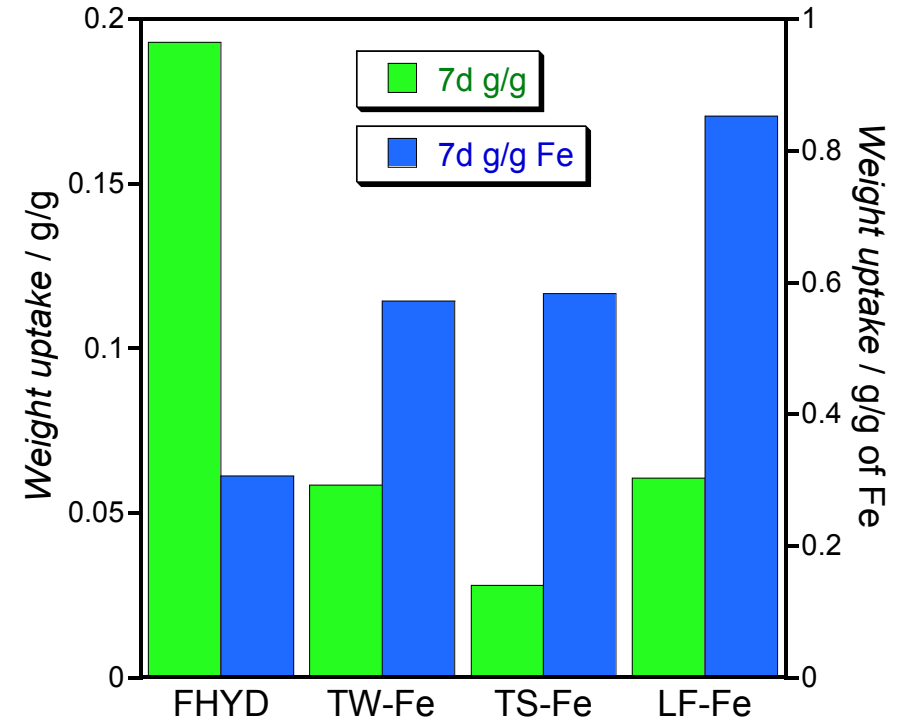
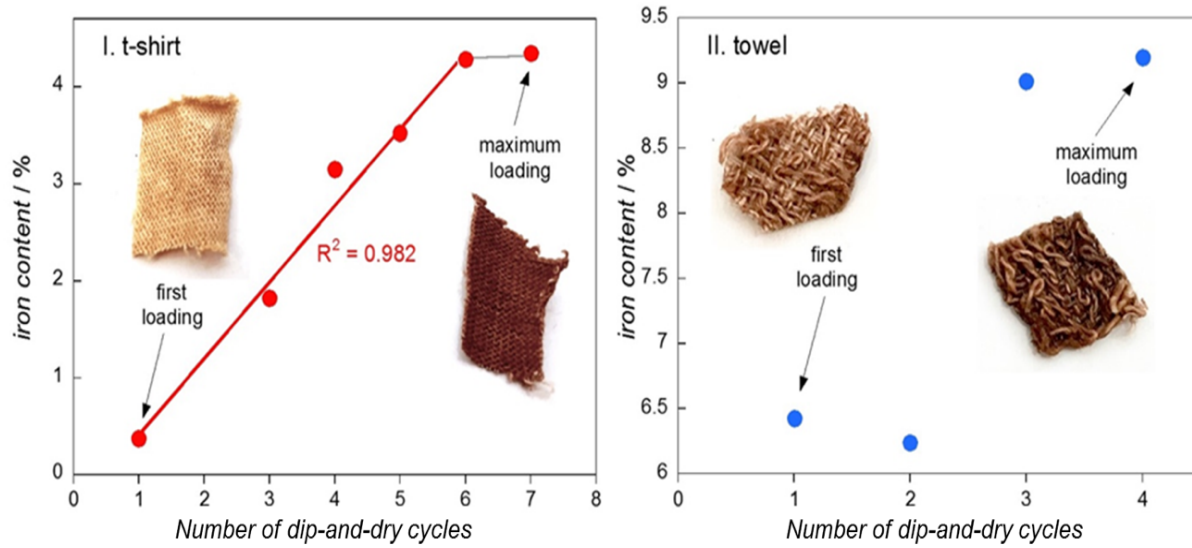


Swatch from TW
10.2% Iron



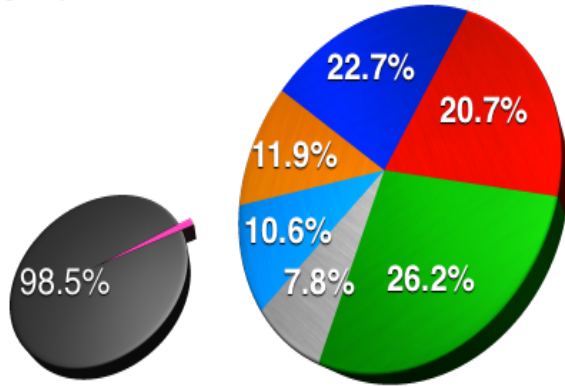
Swatch from TS
4.8 % Iron

Active Ferrihydrite phase on cotton: CEEES

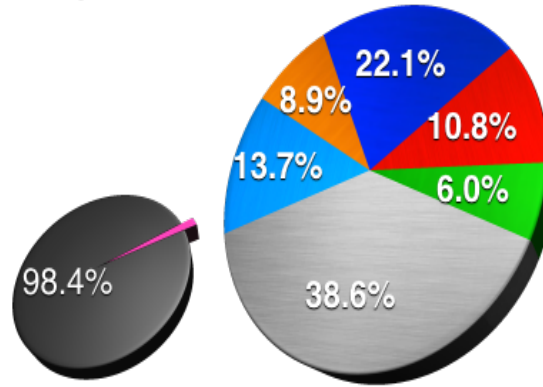


Active Ferrihydrite phase on cotton: extract analysis

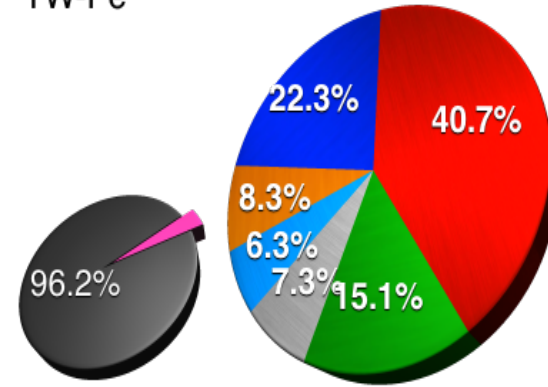
TS-Fe



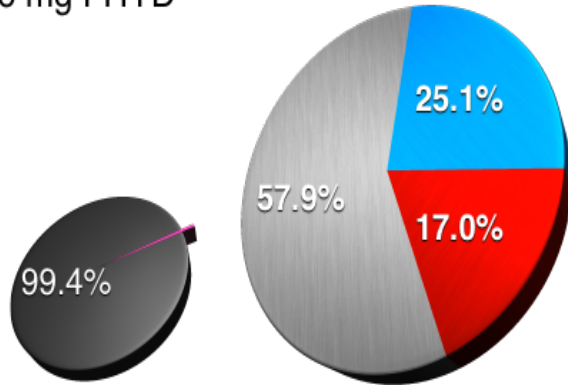
LF-Fe



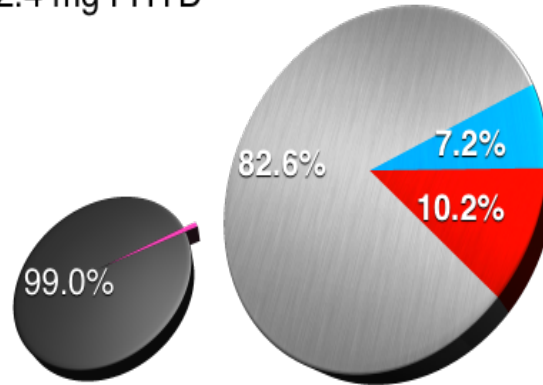
TW-Fe



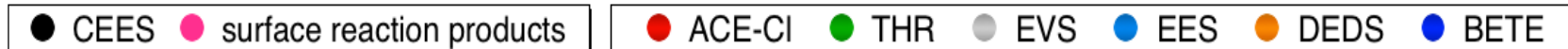
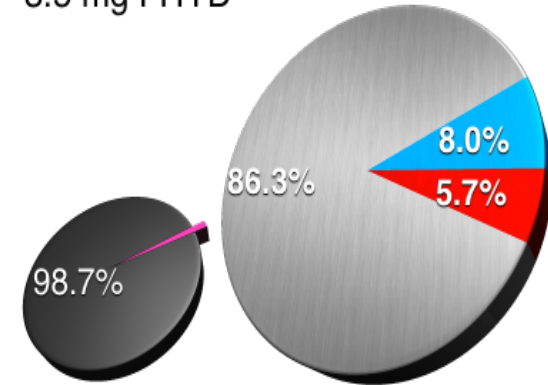
1.6 mg FHYD



2.4 mg FHYD



3.5 mg FHYD



Active copper phase on cotton



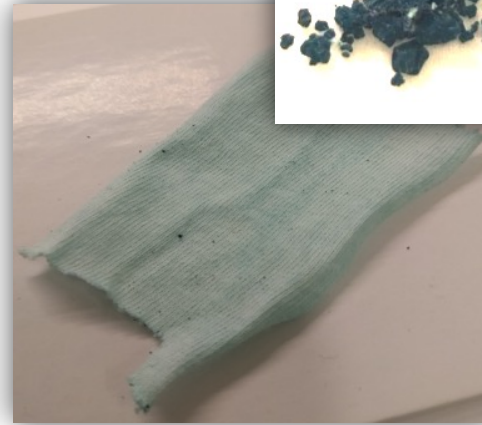
Swatch from Towel

Copper (hydr)oxide



Copper oxide

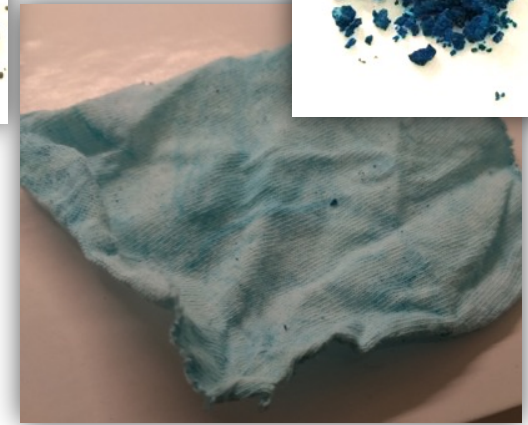
<2 % CuO



Swatch from T-shirt

Copper (hydr)oxide

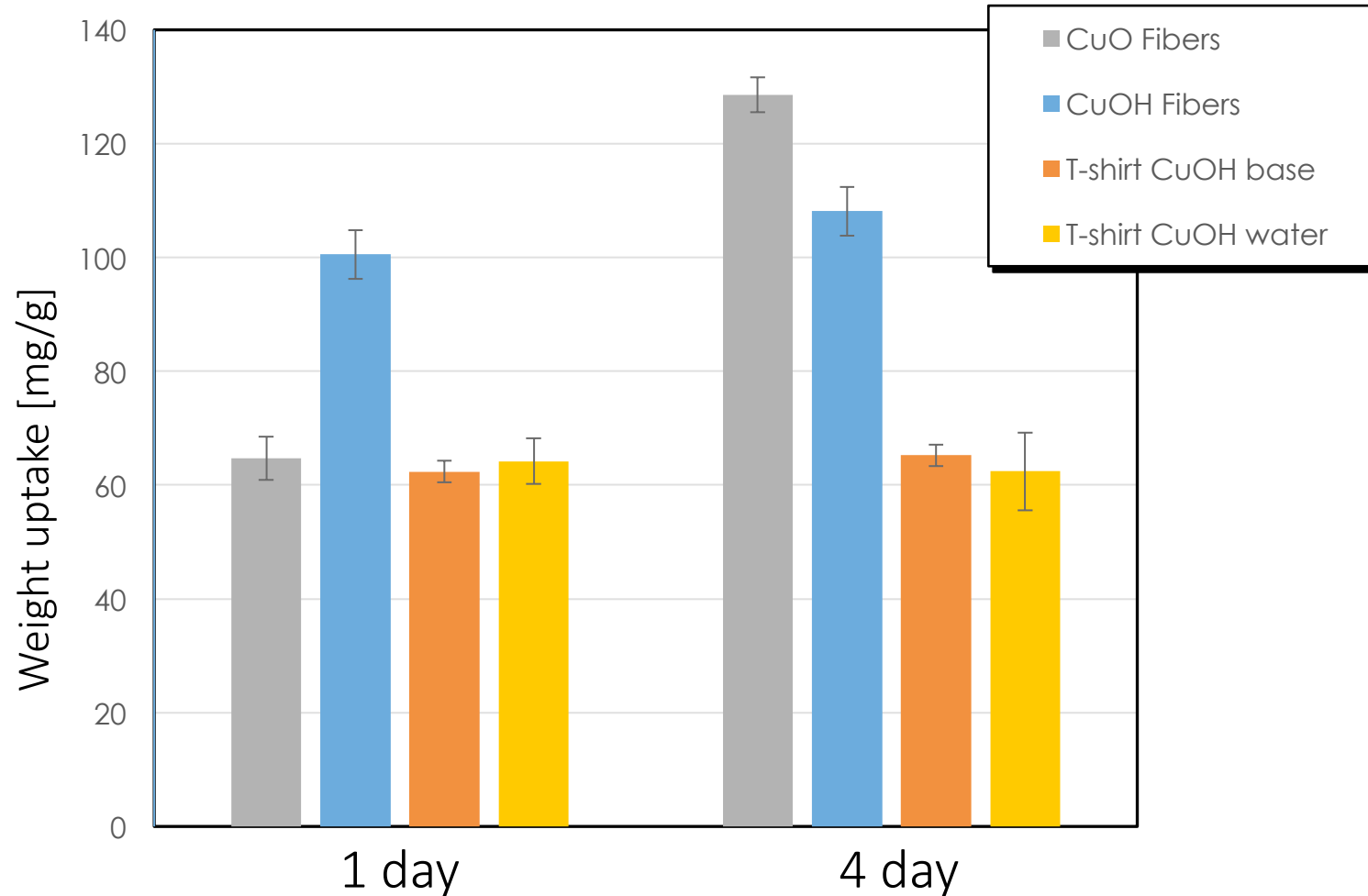
Washed with water



Washed with base

TA in air:
5 % CuO

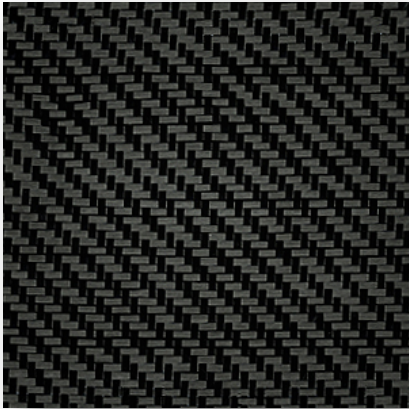
Active copper phase on cotton fibers-DMCP



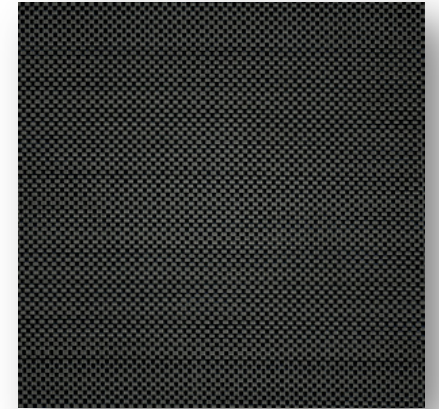
Copper content < 2 %

Active copper phase on carbon fibers

Types of Carbon

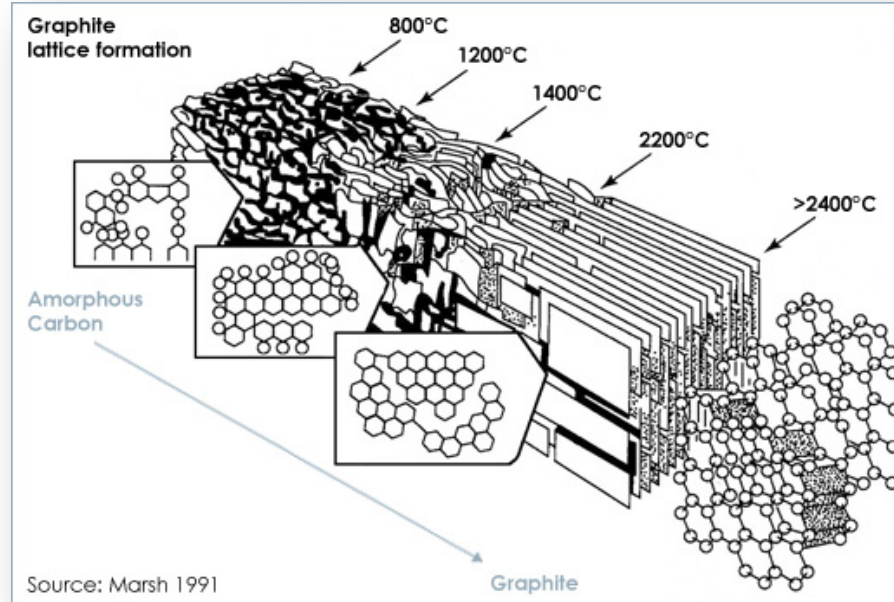


Graphite fiber swatch



Carbon swatch

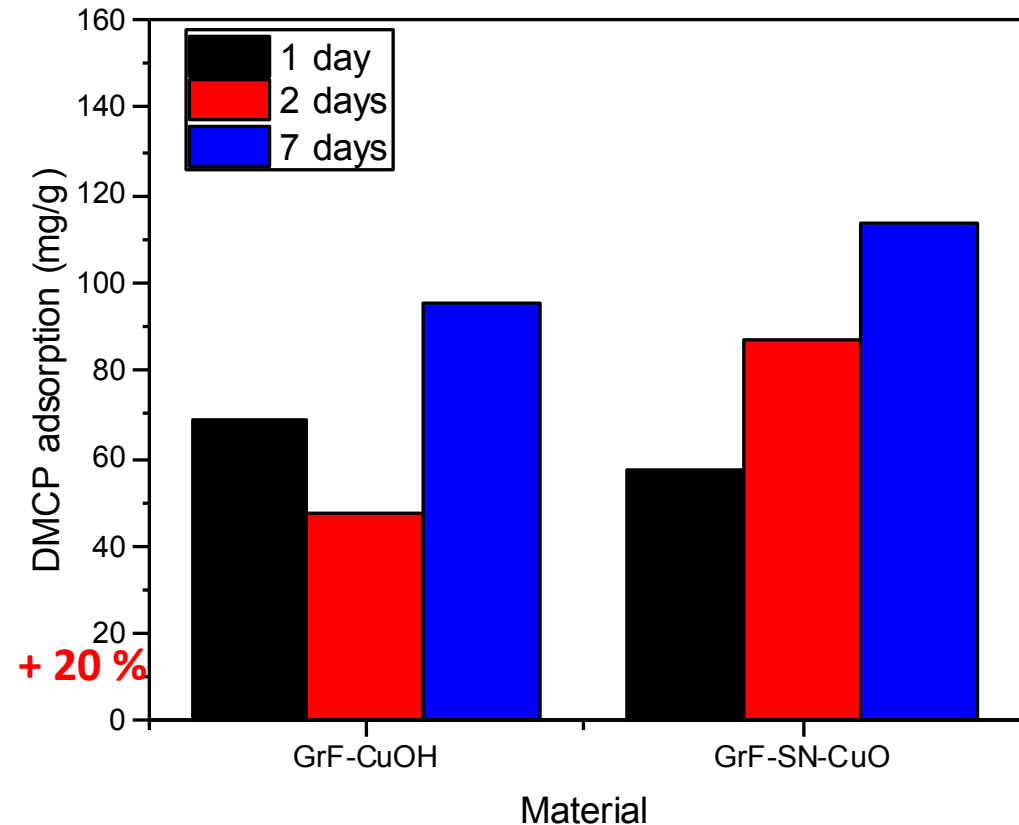
Fibers
from swatch



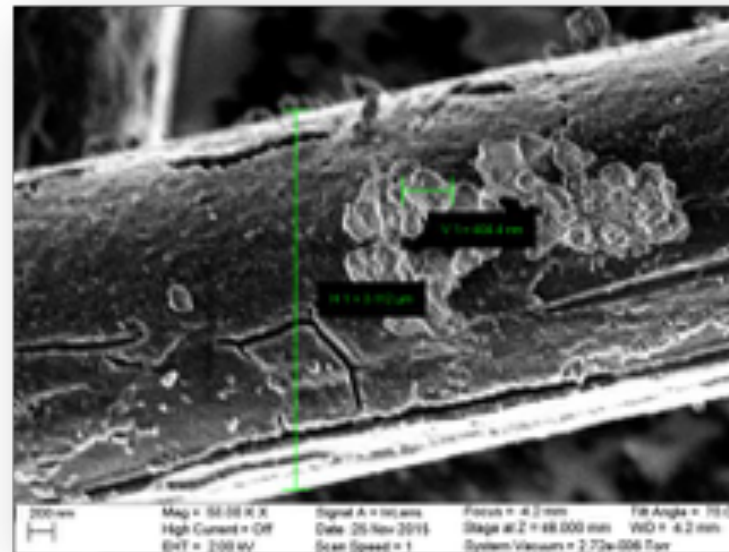
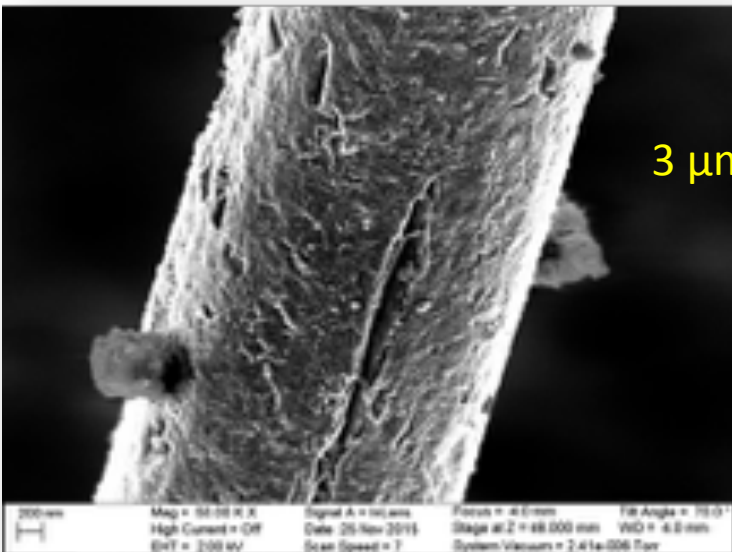
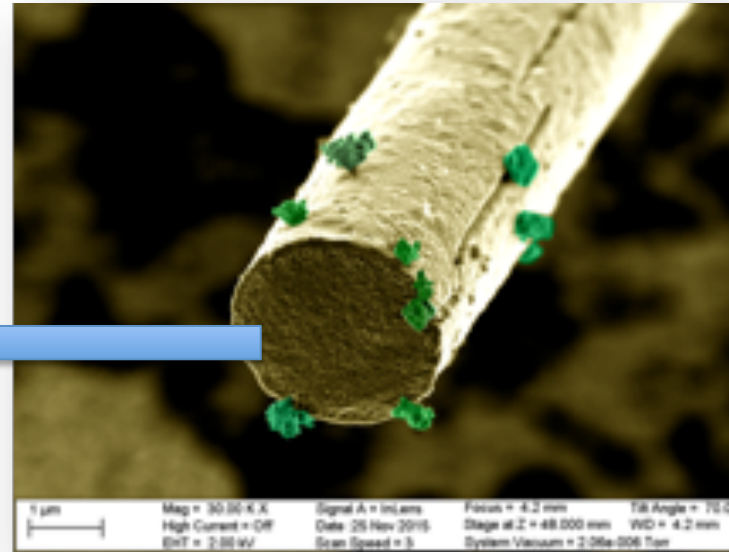
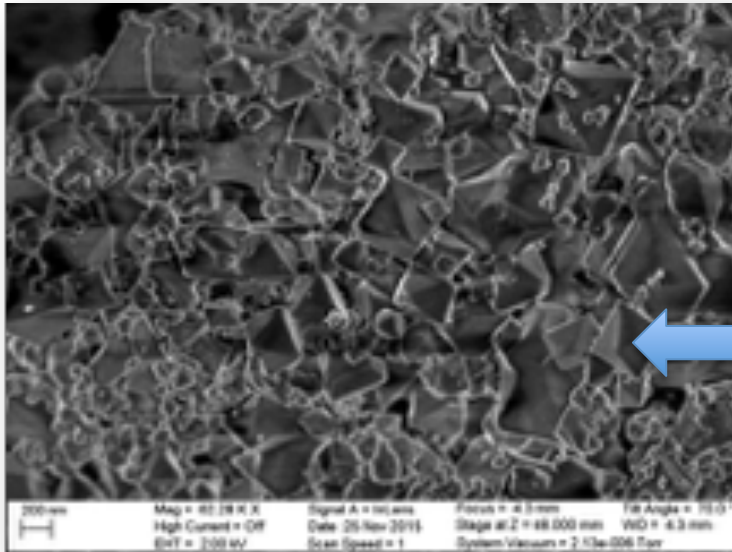
Active copper phase on graphitic carbon fibers

< 3 % CuO

Material	DMCP adsorption mg/g	
	1 day	1 week
GrF+CuOH	69.1	95.2
GrF-NS+CuO	57.1	113.6

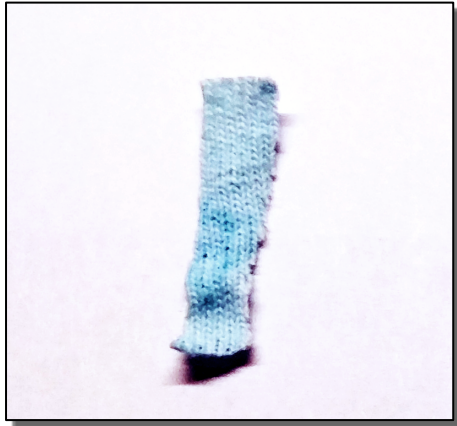


Active copper phase on carbon fibers-Cu-BTC

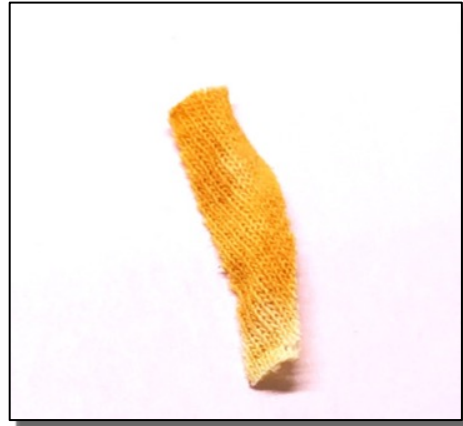


Sensing capability

Swatch from T-shirt, $\text{Cu}(\text{OH})_2$, base washed

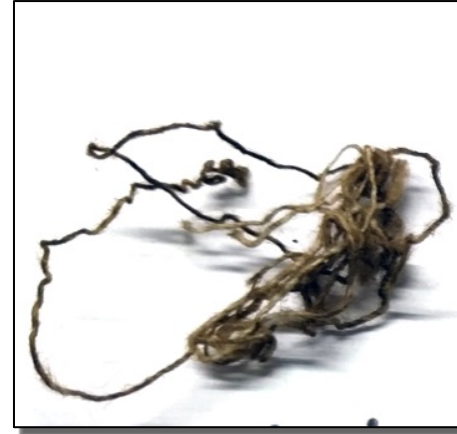


initial



24 hours

Swatch from Towel, CuO



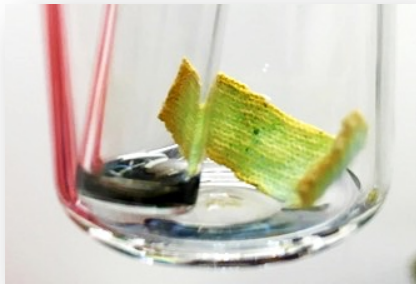
initial



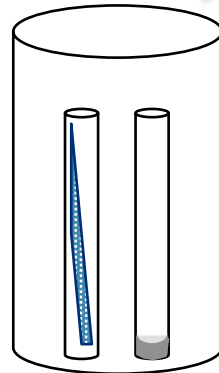
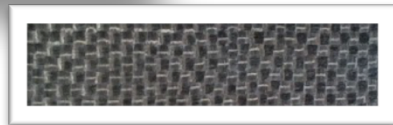
24 hours



3 hours



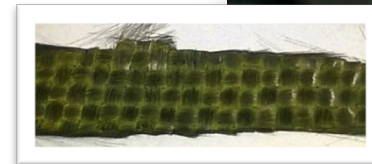
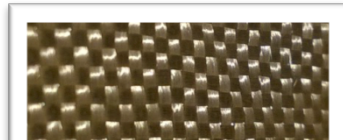
CF-SN+CuON



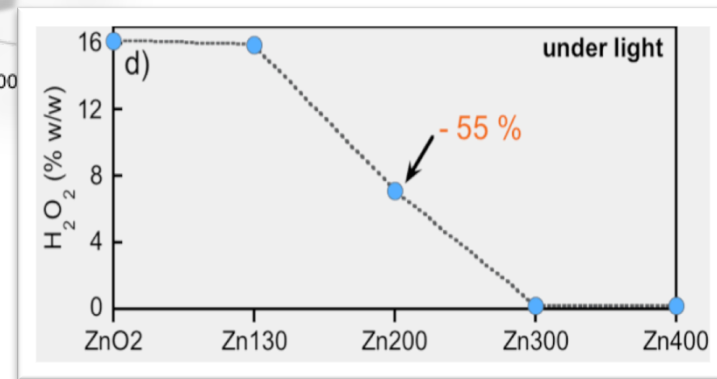
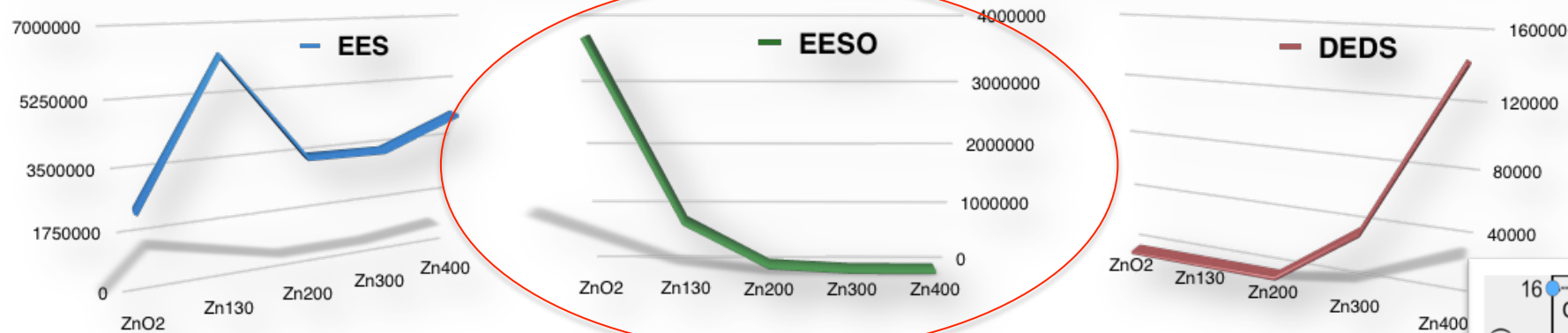
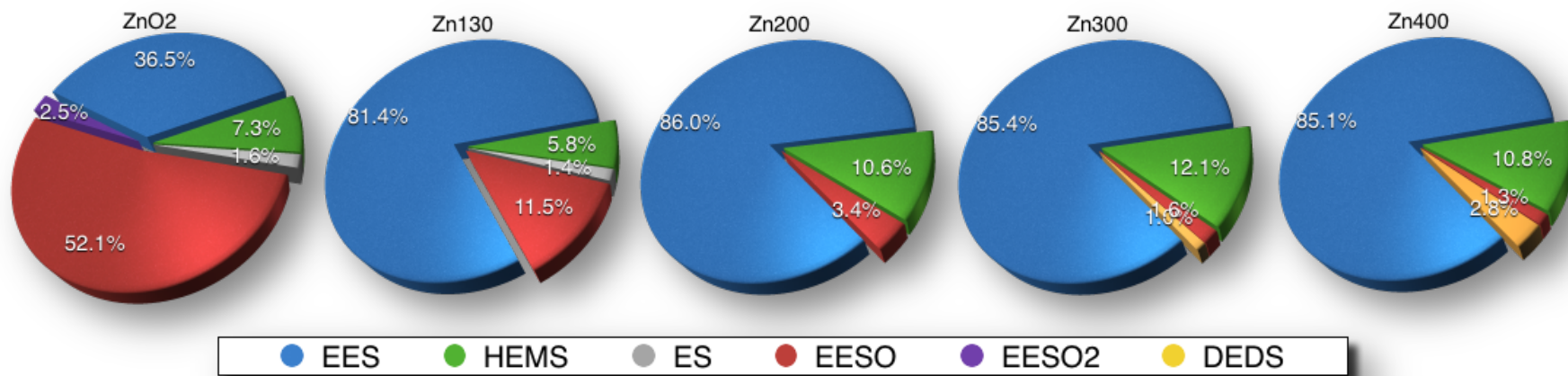
3 hours



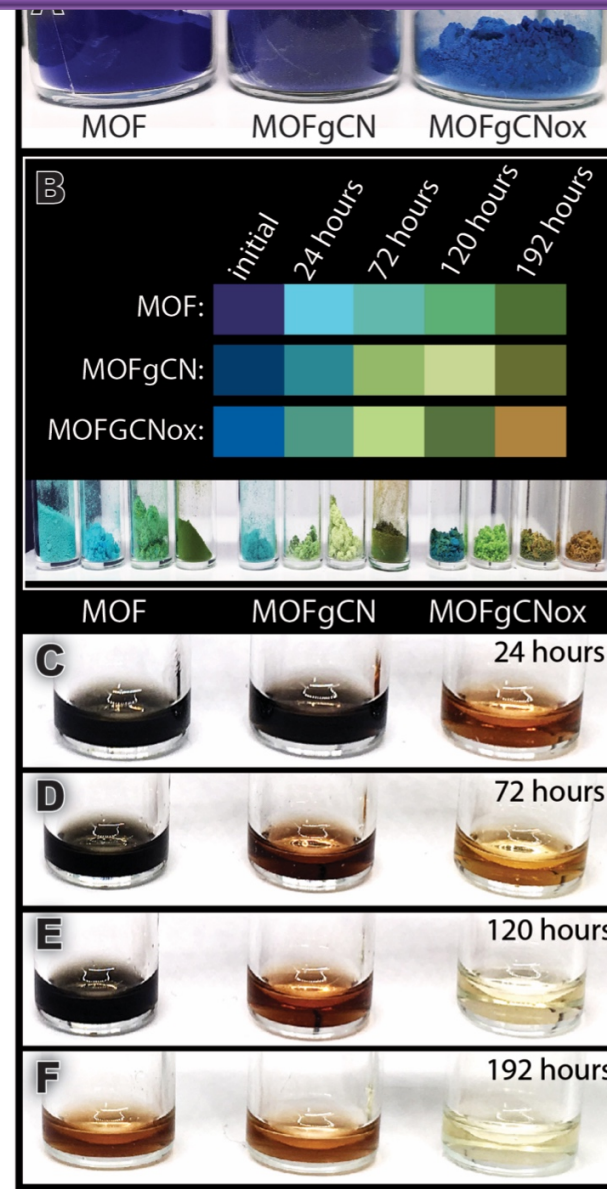
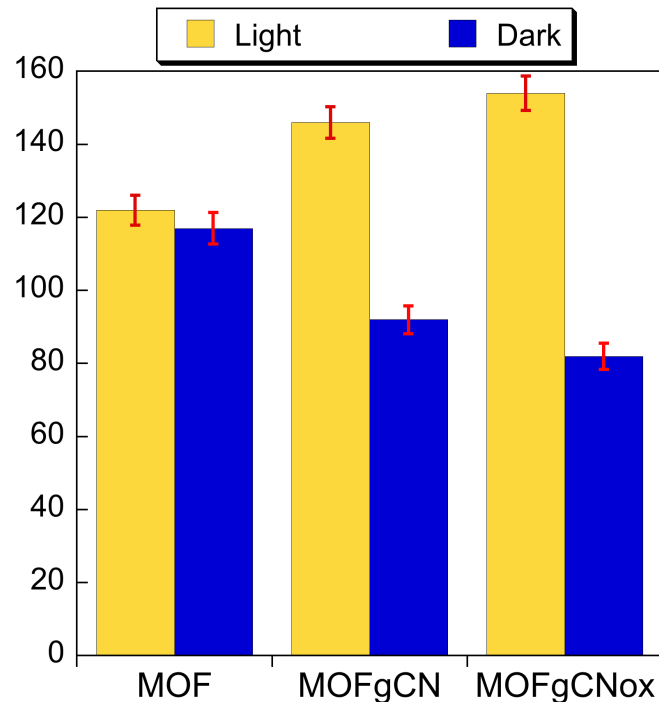
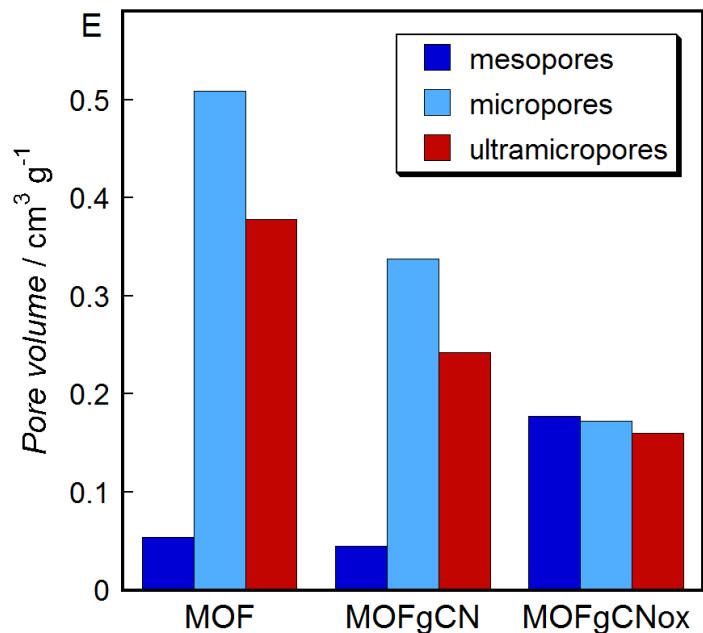
CF-SN+CuO



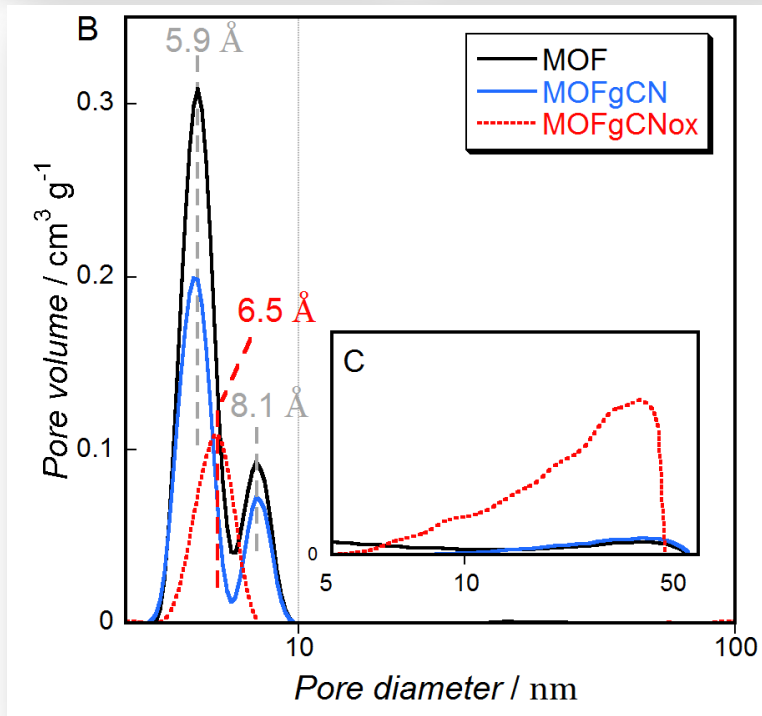
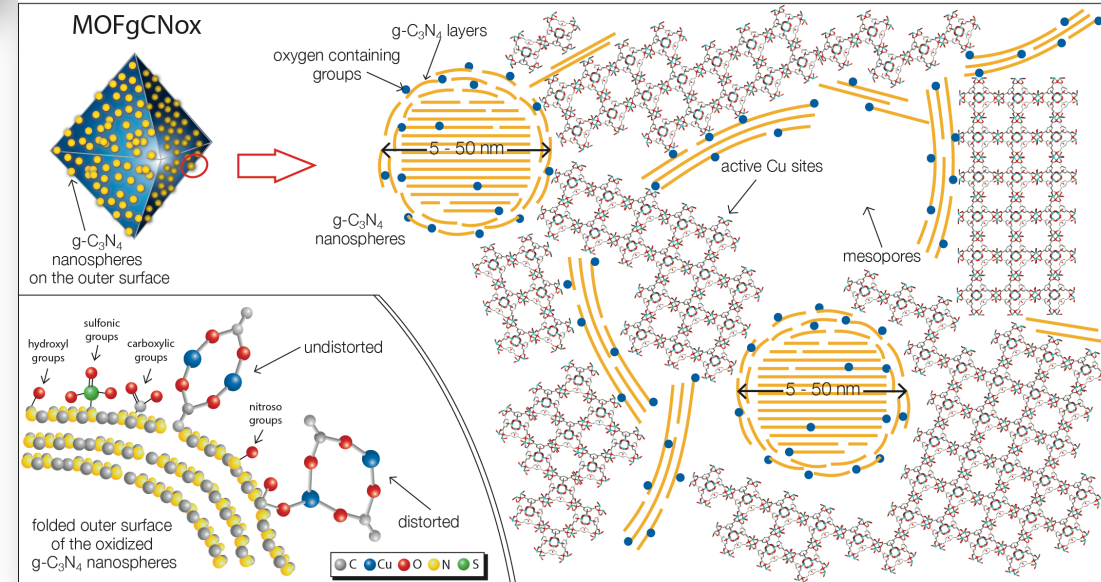
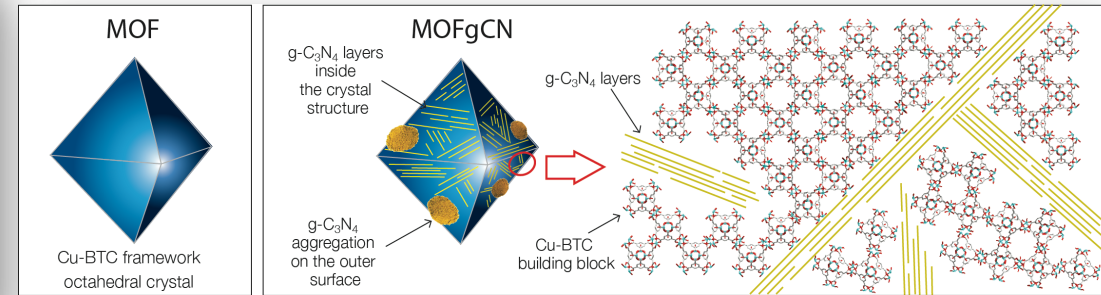
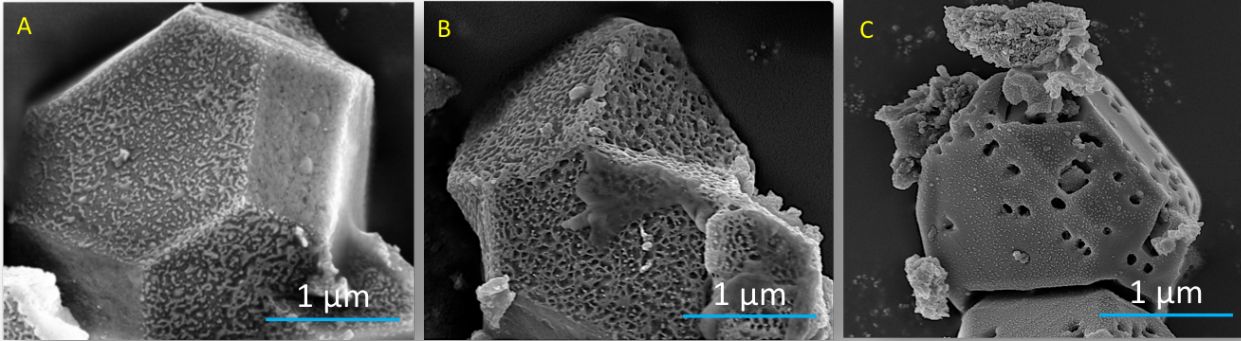
ZnO₂ activity: EES conversion- Extracts analysis



Cu-BTC/g-C₃N₄ composites: Activity- DMCP



Cu-BTC/g-C₃N₄ composites: Porosity

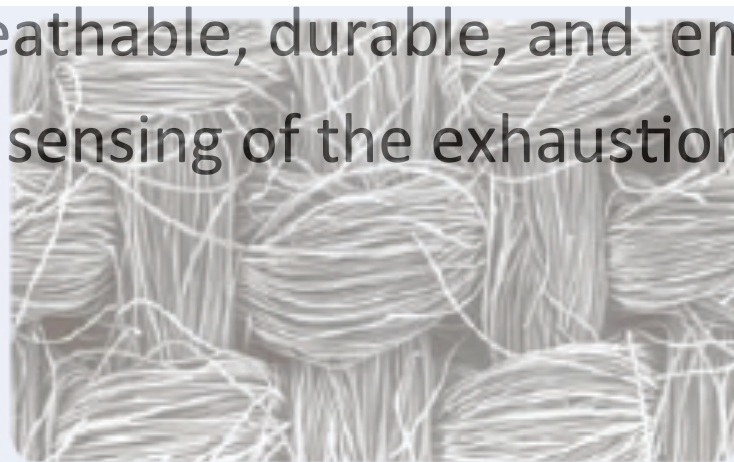


Key Findings

- ❑ 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 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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