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Sandia National Laboratories

Synthesis, Characterization, and Performance of Coated Copper Nanoparticles in High Humidity and H_2S Environments

Center 1800:
Material, Physical and Chemical Sciences

PRESENTED BY

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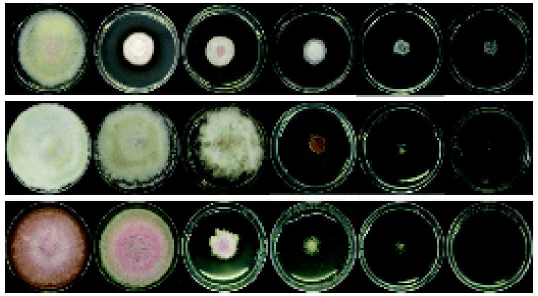
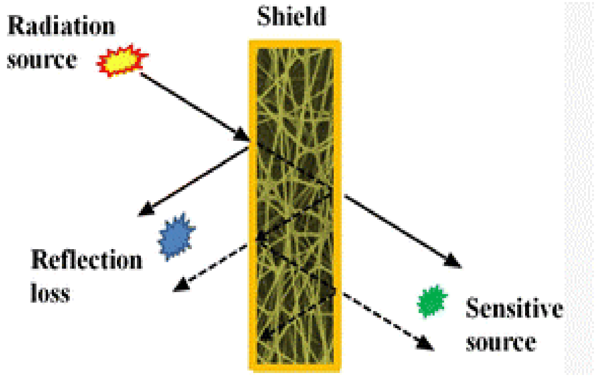
Metal Nanoparticles have Received Great Attention for use in Numerous Applications

- Coinage metal nanoparticles (NP = Au^o, Ag^o, and Cu^o) have been extensively researched for a wide range of application such as biosensors, optical, solar conversion, lubricants, catalysts, and additive manufacturing [1-2].
- They possess a diverse range of optical, electrical, thermal, antimicrobial, catalytic, magnetic properties that allow them to be deployed across multiple fields.
- In particular, the exceptional electrical properties silver (Ag) and gold (Au) nanoparticles (NPs) have made them the primary choice in electrical applications, but their high cost has led to the search for a more cost-effective alternative.

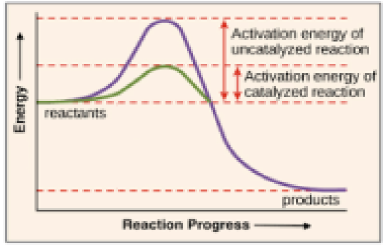
EMI Shielding Devices

Anti-microbial and Anti-fungal agents

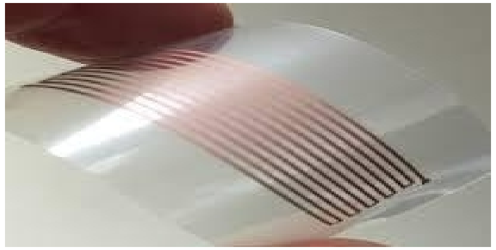




Catalysts



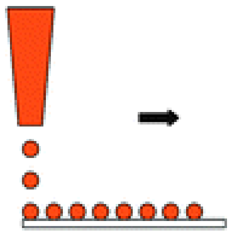
Printed Electronics

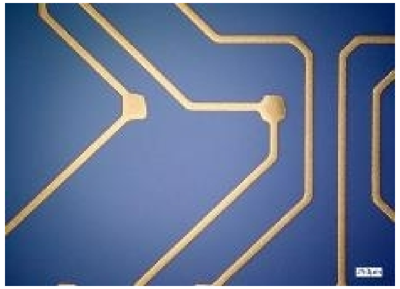


Copper is a Viable Alternative to Silver and Gold in Electronic Applications

Useful in Additive Manufacturing processes:

- Aerosol/ink-jet printing, roll-to-roll, etc.
- Electronic components: resistors, transistors, and capacitors



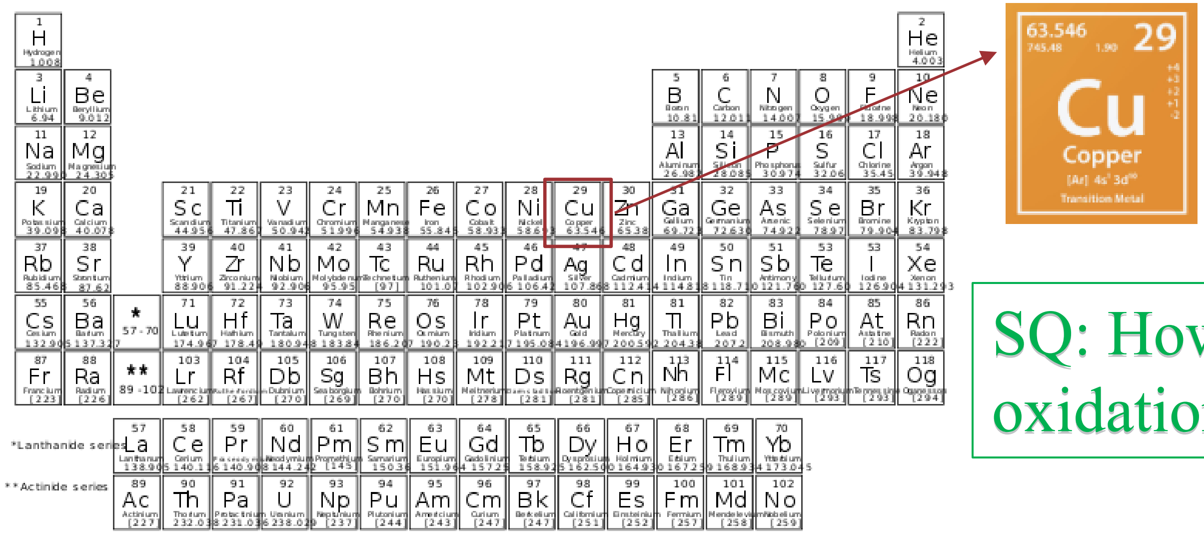


Advantages of Copper?

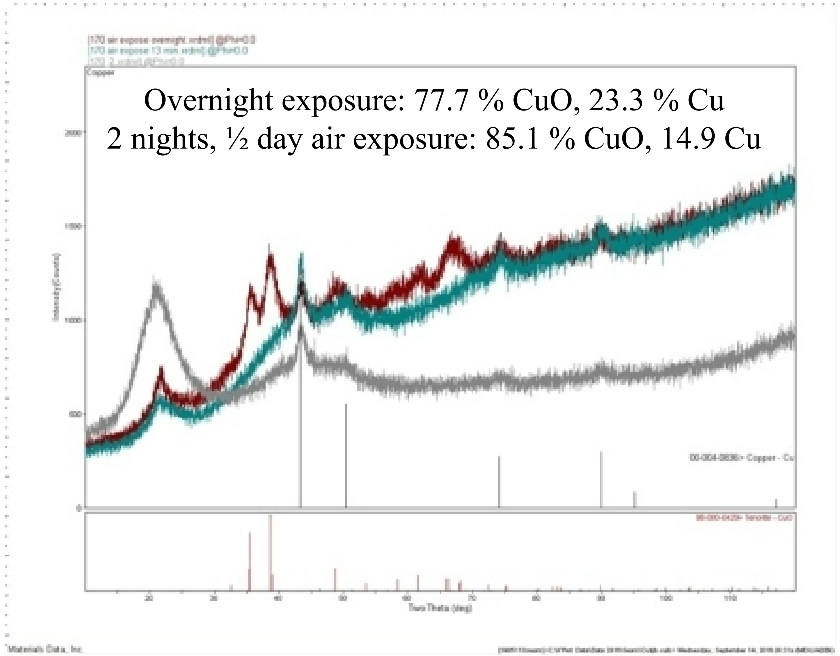
- Exceptional electrical and thermal conductor
- Cheaper option compared to other metals, such as gold and silver
- Cu = 0.18 USD <Ag = 23.48 USD <Au= 1962.55 USD per troy ounce
- Cu is 130x cheaper than Ag and 11,000x cheaper than Au!

Disadvantages of Copper?

- Intrinsic sensitivity to oxidation under atmospheric conditions
- Susceptible to corrosion



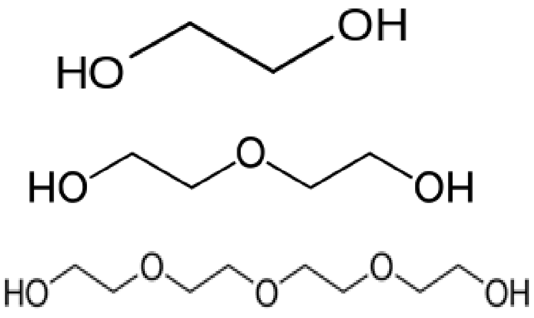
SQ: How can copper oxidation be mitigated?



CuO observed as early as overnight exposure to air

Surface Protection Through the Use of Green Surfactants

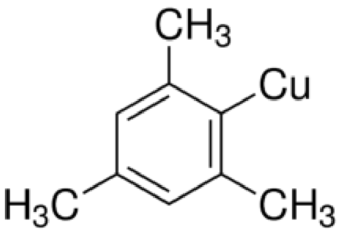
- Several attempts and concepts have been deployed to increase the oxidation resistance of Cu NPs by the addition of various compounds to serve as surfactants.
- Alkylamines (with various lengths), polyols, alkanethiols, allylamine, polyallylamine, and polyvinylpyrrolidone (PVP) have been used in previous research as surfactants for Cu NPs.
- Amine-based ligands such as oleylamine, hexadecylamine, benzotriazole, etc. have high affinity for Cu (111) surfaces and have been shown to provide exceptional oxidation resistance.
- Ligand–NP surface interaction can affect growth rates, morphology, and colloidal stability.
- Glycols preferable because of use as reducing agent, microwave activity, environmentally friendly.



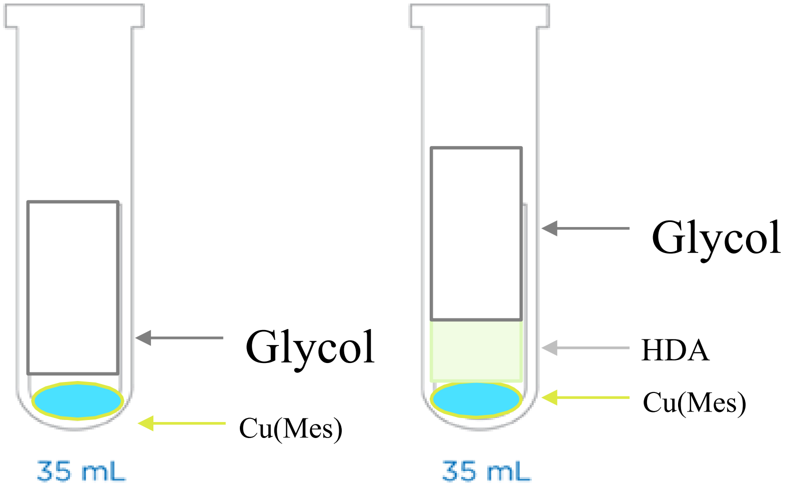
Polyols (solvent)

$CH_3(CH_2)_{14}CH_2NH_2$

Hexadecylamine (surfactant)



Copper (I) Mesityl (precursor)



SQ: How do glycols and amines affect the production and protection of Cu-NPs?

Experimental Flow Chart

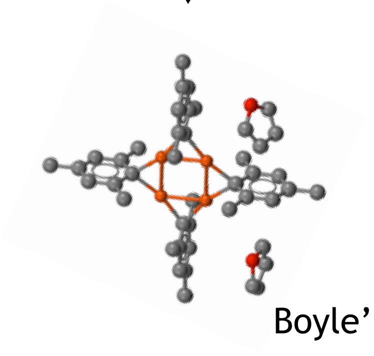
Precursor

Cu(Mes)

- Easily decomposable
- Environmentally friendly

CuCl + Mg(Mes)Br

THF



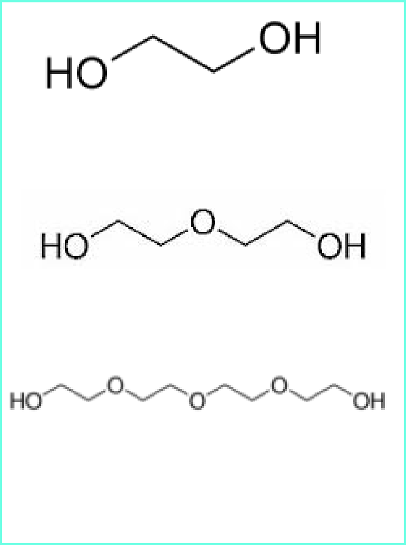
Boyle's Group

+

Solvent/ Surfactant

Polyols

- Inexpensive
- Microwave active
- Reducing agent

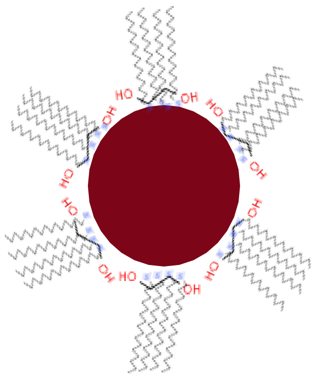


+

Surfactant

Provide NP Protection

- Oxidation resistance
- Agglomeration
- Ink performance
- Conductivity
- Reproducibility



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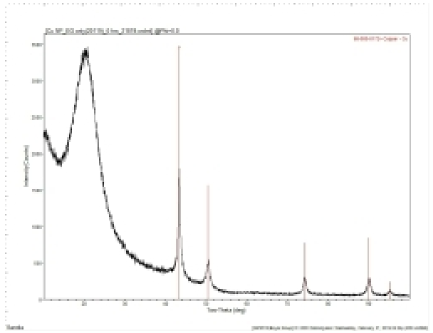
Environmental Testing

Characterization Techniques (inert vs air)

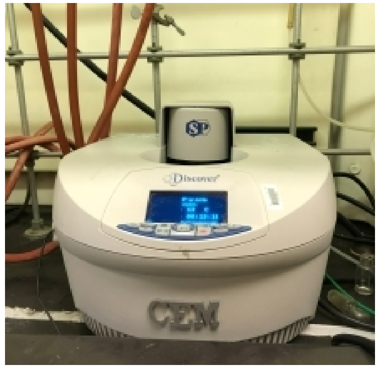
- PXRD
- TEM
- FTIR
- TGA
- FACT-testing (Cl_2, NO_x.etc)

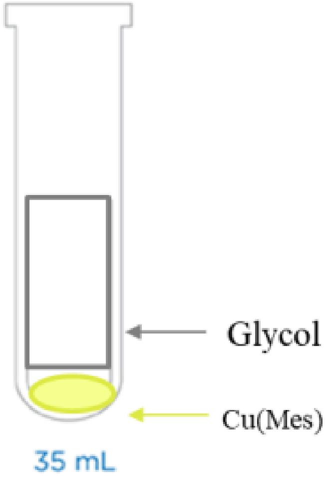


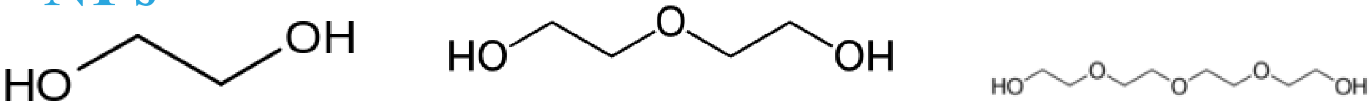
Printing (Future Work)

3D printing oxidation resistant nanoparticle

Understanding the Role of the Glycol Reactive Sites/Lengths on Cu-NPs







Ethylene glycol (EG)

Diethylene glycol (DEG)

Tetraethylene glycol (TEG)

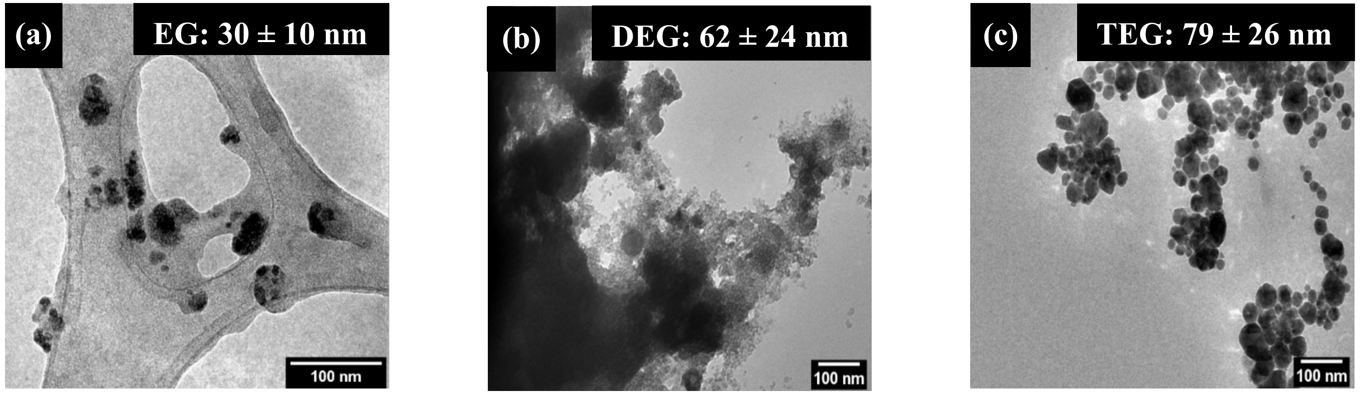
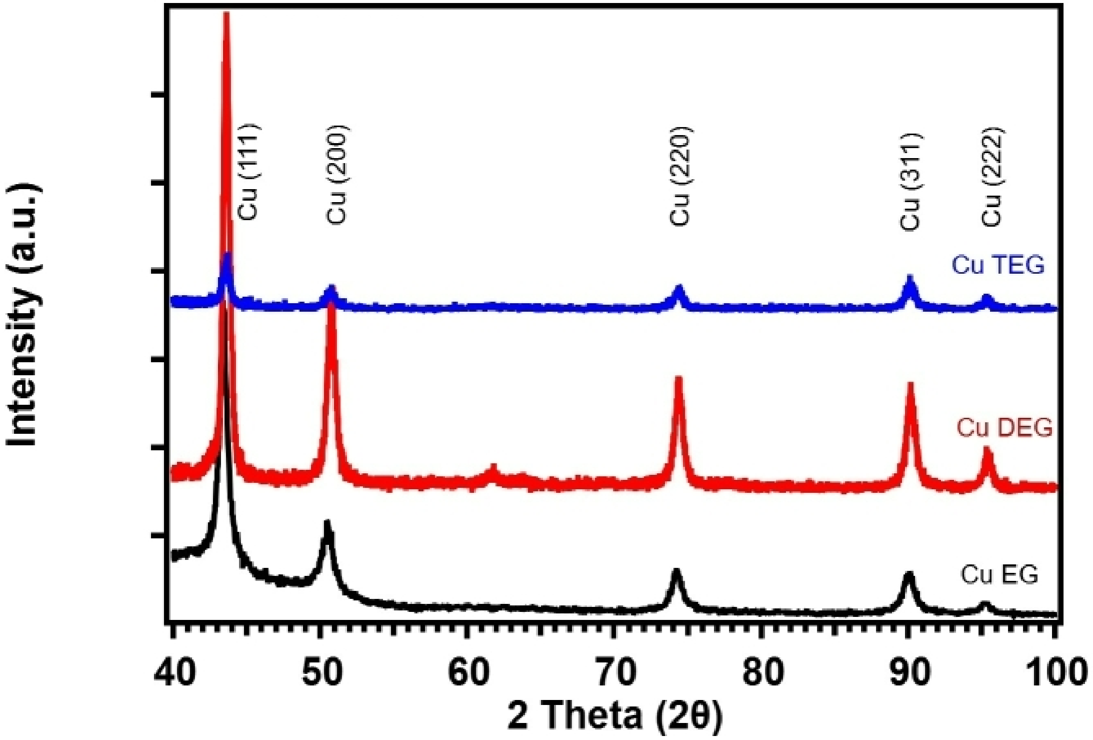
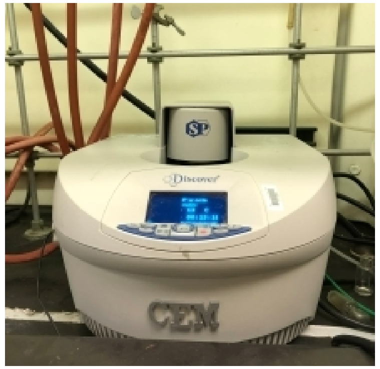


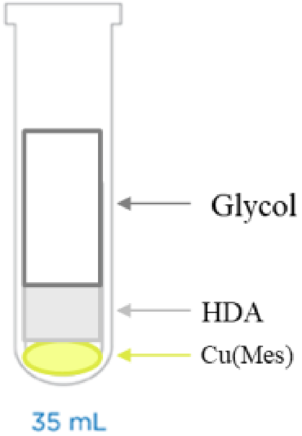
***Figure 1**. TEM images of Cu NPs synthesized with **(a)** EG, **(b)** DEG, and **(c)** TEG.*

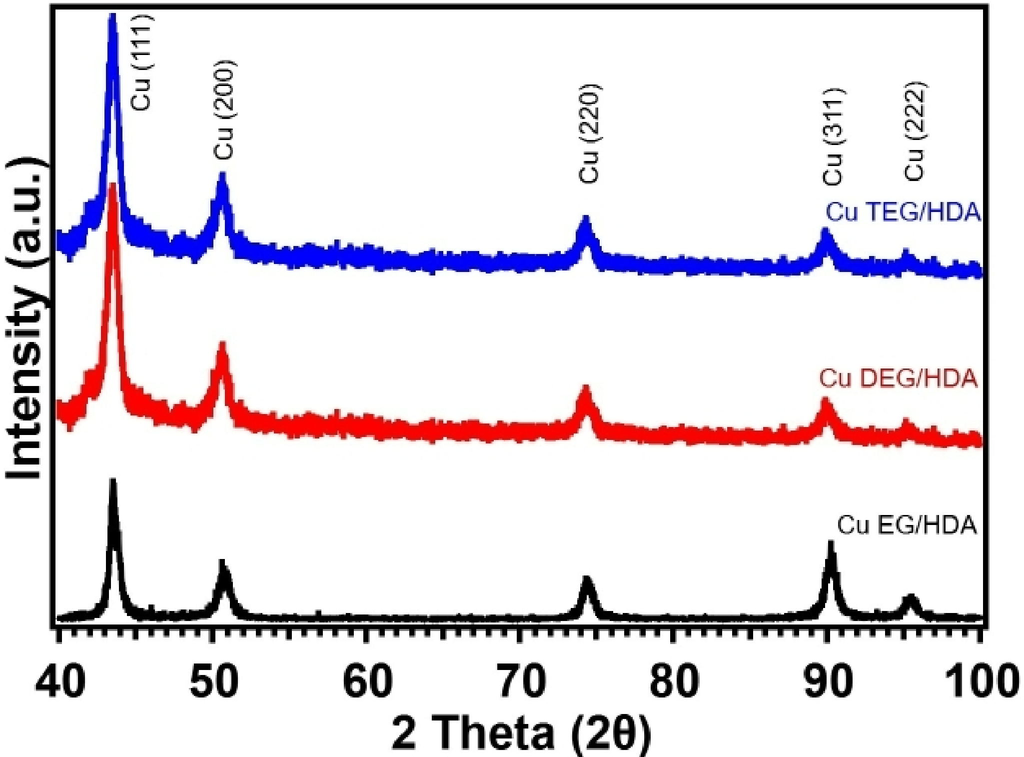


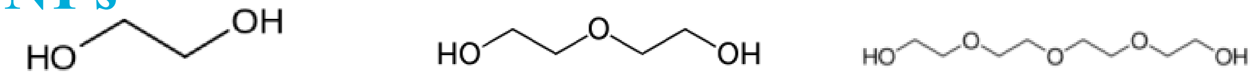
- Glycol-Cu-NPs exhibit irregular shapes and large size distributions NPs.
- As the glycol length increases, the particle size and deviation also increase.

Understanding the Role of the Glycol Reactive Sites/Lengths + HDA on Cu-NPs

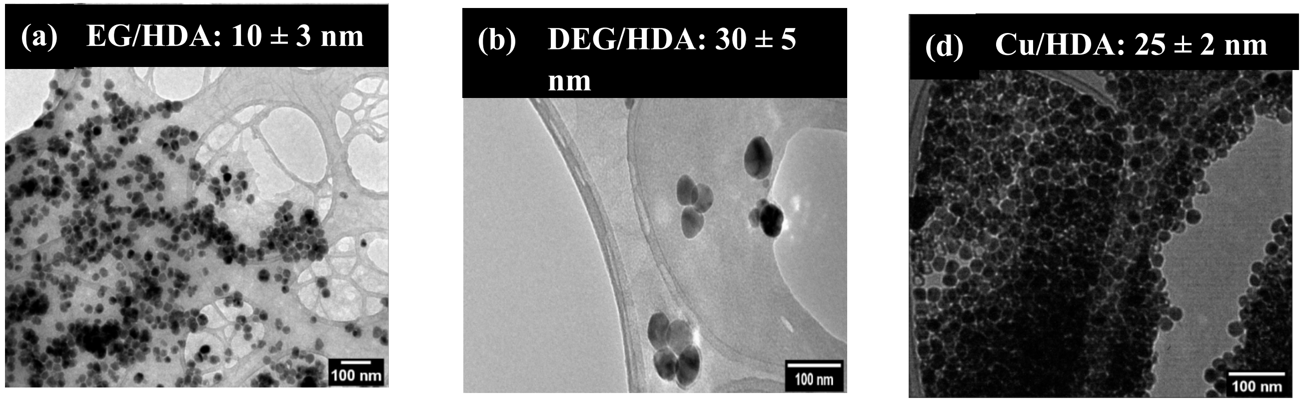


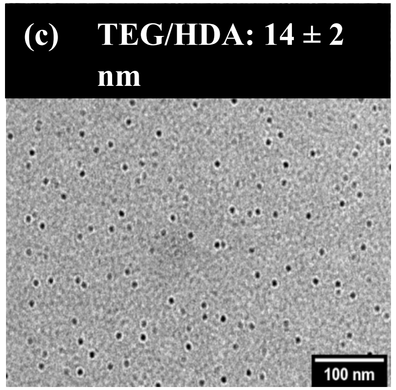






Ethylene glycol (EG) | Diethylene glycol (DEG) | Tetraethylene glycol (TEG)





$CH_3(CH_2)_{14}CH_2NH_2$
Hexadecylamine (HDA)

- ✓ Glycol/HDA-Cu-NPs yielded monodispersed and spherical particles with small size distribution.
- ✓ Amines bind to a specific facet of the Cu-NPs that enable the growth of spherical nanoparticles with or without glycol presence.
- ✓ NPs synthesized with only HDA present also yielded spherical Cu-NPs with small size.

Figure 2. *TEM images of Cu NPs synthesized with **(a)** EG/HDA, **(b)** DEG/HDA, **(c)** TEG/HDA, and **(d)** Cu/HDA*

FTIR & TGA of As Synthesized Cu NPs w/wo HDA

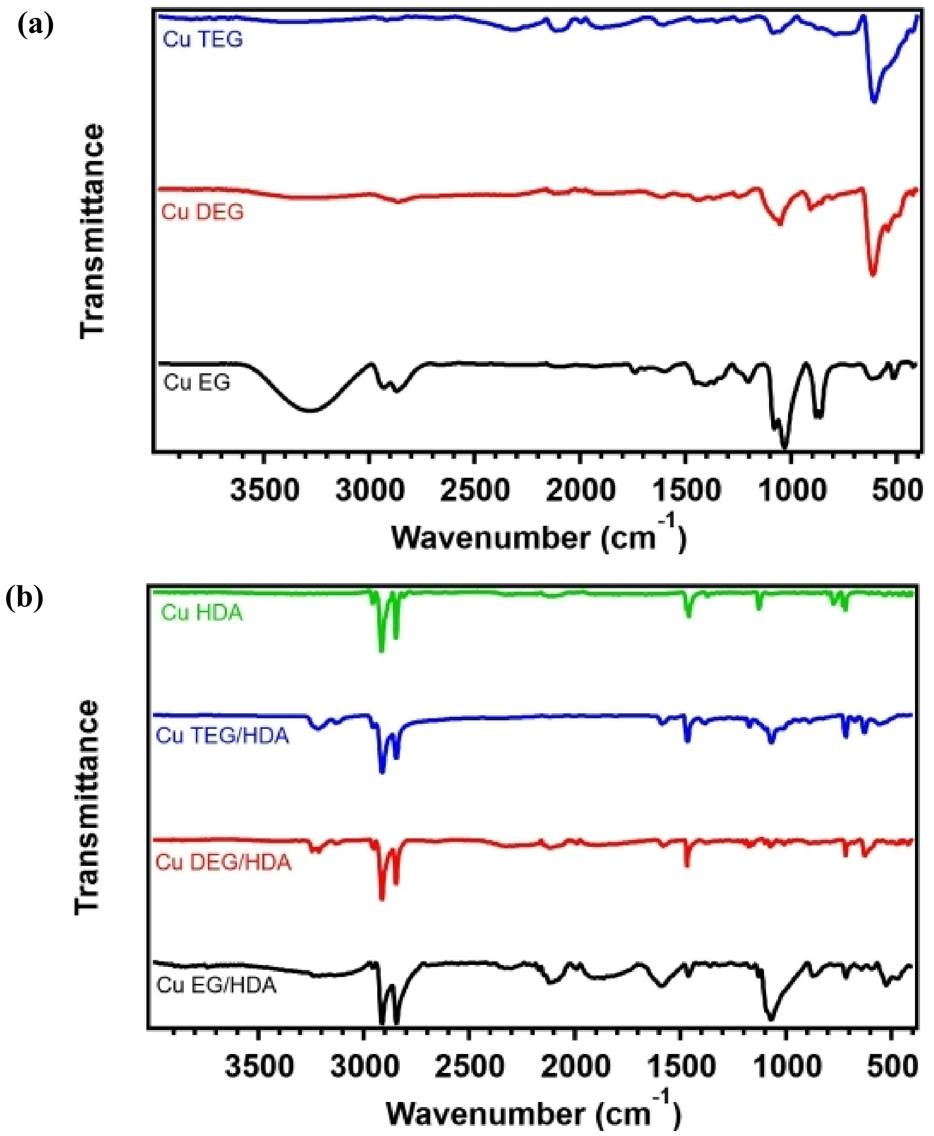
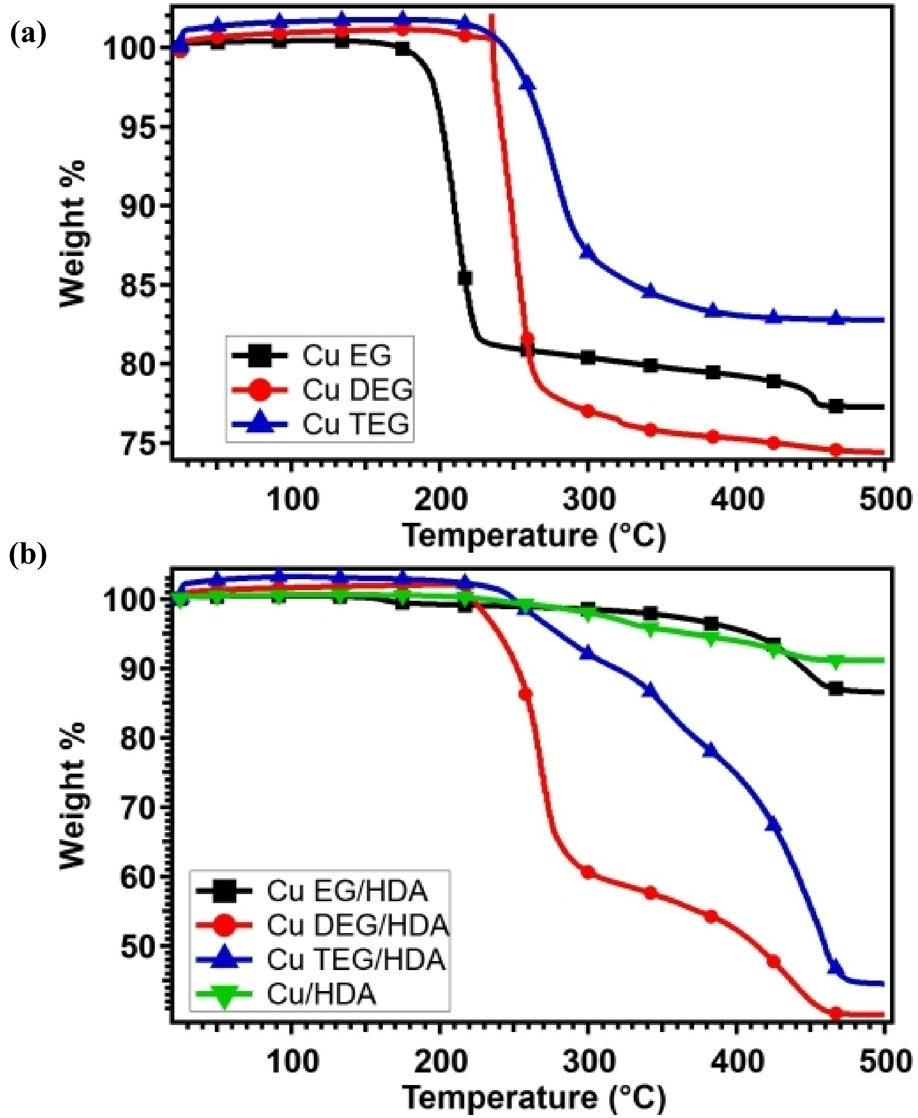


***Figure 3. (a)** FTIR spectra of Cu NPs synthesized with EG, DEG, PG, and TEG. **(b)** FTIR spectra of Cu NPs synthesized with EG+HDA, DEG+HDA, PG+HDA, and with TEG+HDA.*

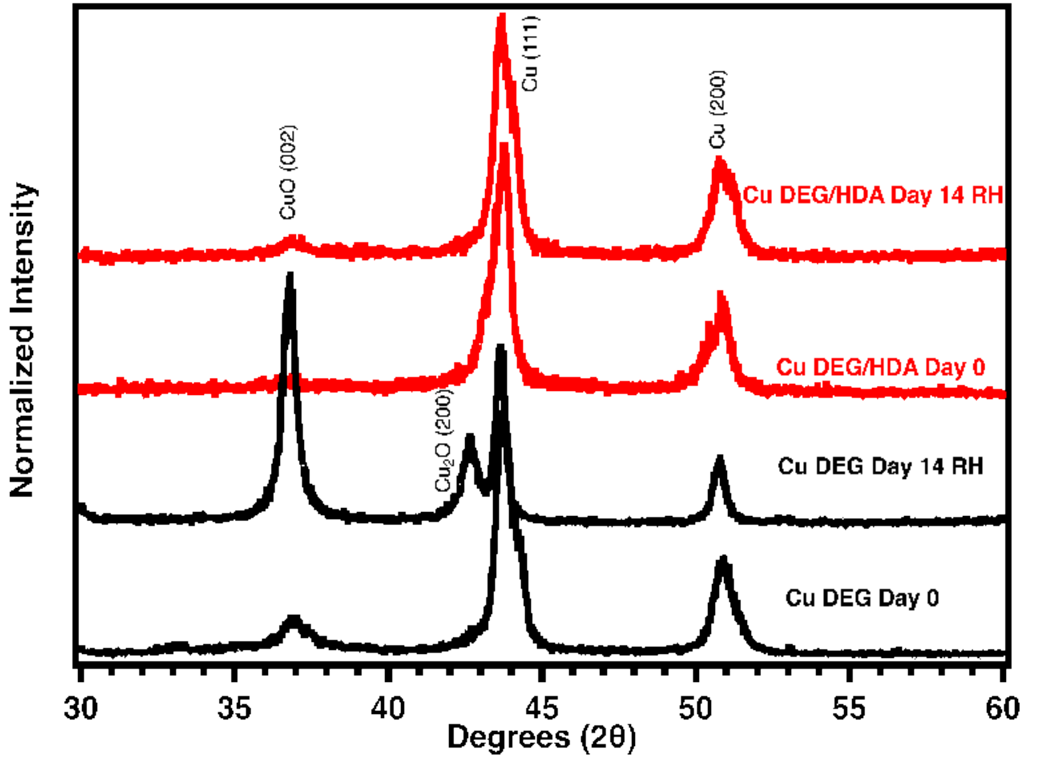


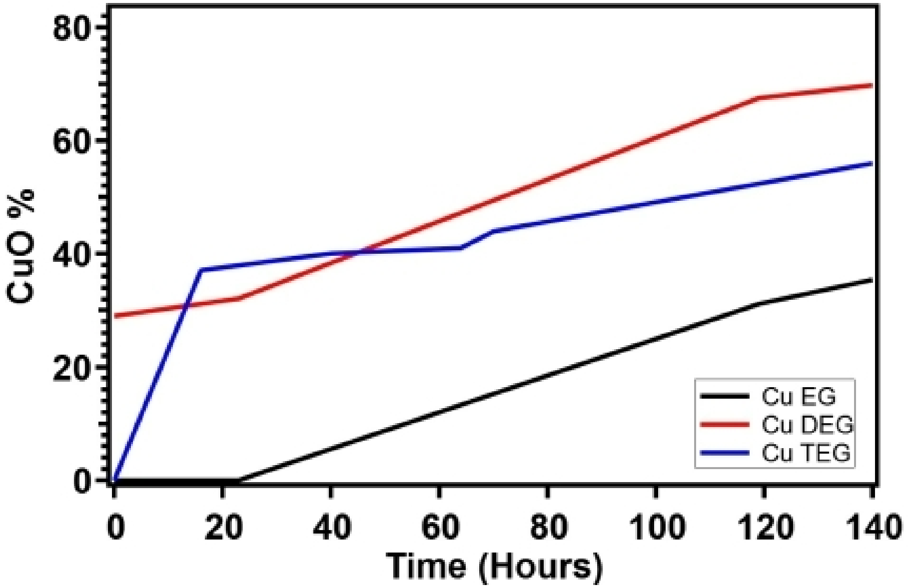
Sample	% Mass Loss
Cu EG	22.72
Cu DEG	25.59
Cu TEG	17.20

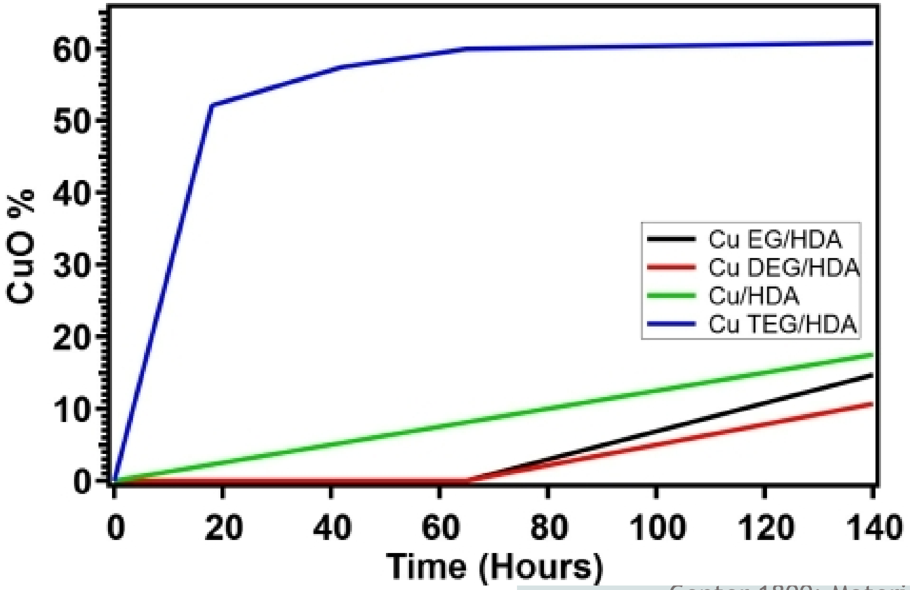
Sample	% Mass Loss
Cu EG/HDA	0.5/12.9
Cu DEG/HDA	36.64/23.26
Cu TEG/HDA	18.46/36.94
Cu/HDA	8.86

***Figure 4**. TGA spectra of Cu-NPs synthesized with only glycol (a) and Cu-NPs synthesized with glycol and HDA (b).*

Cu-NP in 100% RH Environment for 14 Days







GES System for Environmental Testing

- ✓ PXRD indicates that the combination of the glycol and HDA, gives the Cu-NPs much higher resistance to oxidation in high humidity.
- Glycols have exceptional coating performance of Cu-NPs, but their miscibility in water could lead to poor oxidation protection.
- HDA on the other hand is extremely hydrophobic which can prove beneficial in preventing water from reaching the Cu-NP surface.

Periodic DFT for Cu (111) surface, DEG, HDA, and H_2O Interactions

- DEG has a consistent binding energy (BE) with the Cu (111) surface at both concentrations.
- For the HDA, the BE is stronger at higher concentrations (-1.27 eV) and weaker at lower concentrations.
- In solutions where both HDA and DEG molecules are present, initial binding will be between the Cu(111) surface and the HDA up to ~0.1 #/nm^2, and then subsequent DEG binding.
- This supports the results from TEM, FTIR, and oxidation studies indicating that for Glycol/HDA-Cu-NPs, binding of HDA first, followed by subsequent binding of the glycol occurs.

Table 1: *Binding energy (eV) between the surfactant (HDA or DEG) and the Cu(111) surface*

Surfactant	Concentration (#/nm^2)	Binding Energy (eV) Surfactant to Cu (111)
DEG	0.1	-0.727
	0.2	-0.715
HDA	0.1	-1.273
	0.2	-0.534

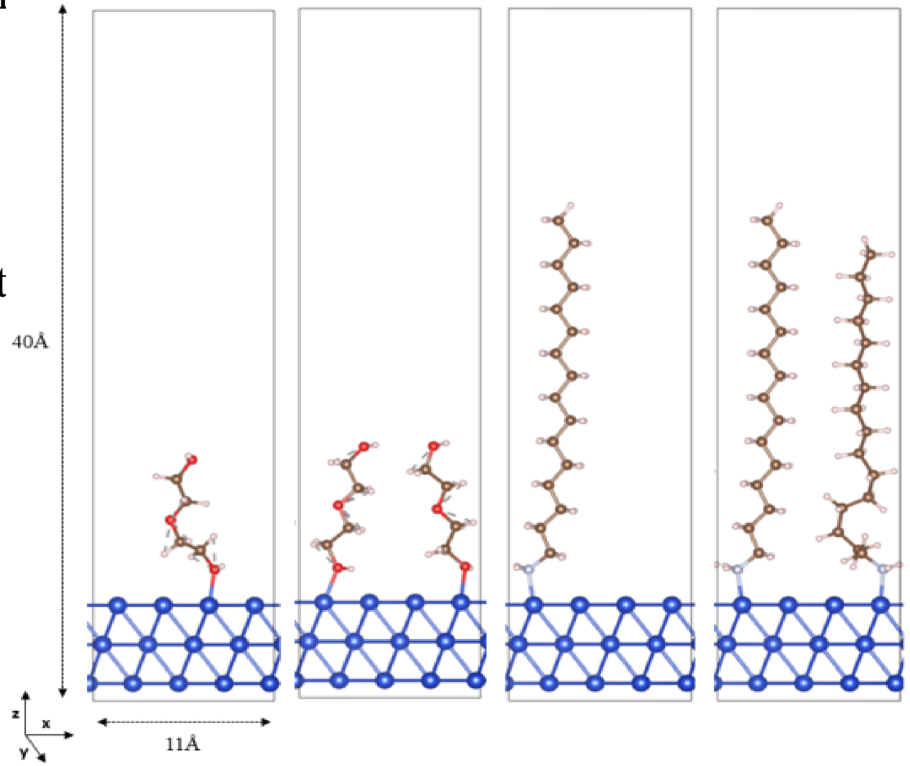


Figure 5*. DFT structural models for (111) Cu surface with either one or two DEG and HDA molecules. Colors: copper (royal blue), carbon (grey), oxygen (red), hydrogen (white), nitrogen (light blue).*

Periodic DFT Explains Synergistic Surfactant Oxidation Performance of Cu-NPs

- With any surfactant present, a clear increase in BE is observed when the H_2O molecules need to pass through the surfactant to access the surface, an effect which was more clear on the Cu(111) surfaces with higher surfactant concentration.
- For example for the Cu(111) surface with 0.2 HDA/nm^2 there was a increase in binding energy by ~0.2 eV, when the water molecule passes the surfactant molecule (~15 Å from the surface).
- ✓ While this only represents an initial investigation into the HDA/DEG terminated Cu(111) surface, it does demonstrate that there is some interaction between the HDA/DEG that is protective of bare Cu surfaces in the presence of water.
- ✓ Overall, the water molecules bound more strongly to the bare Cu(111) surface than to the surface with the surfactant present, with energy penalties between 0.03-0.36 eV.

Table 2: *Binding energy (eV) between the surfactant (HDA/DEG) and the Cu(111) surface and in the presence of water.*

Surfactant	Concentration (#/nm^2)	H_2O to Cu (111)+Surfactant
DEG	0.1	-1.25
	0.2	-1.51
HDA	0.1	-1.30
	0.2	-1.06

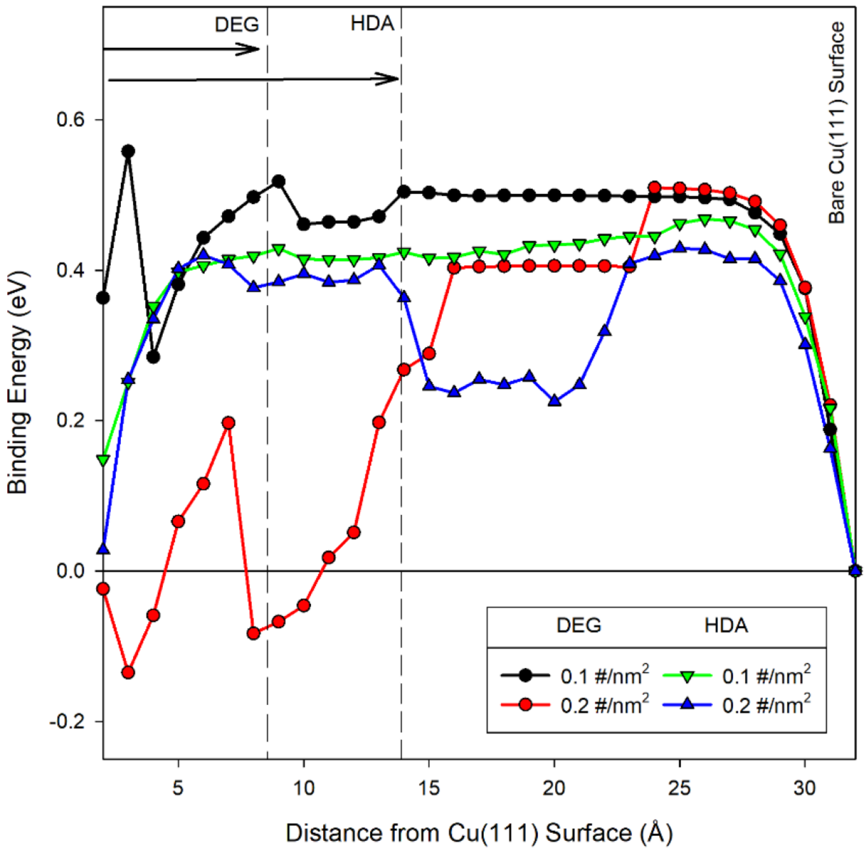
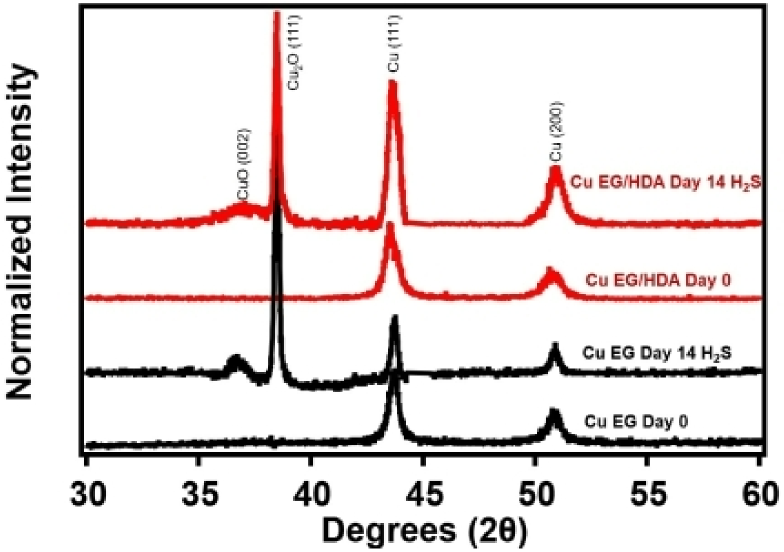
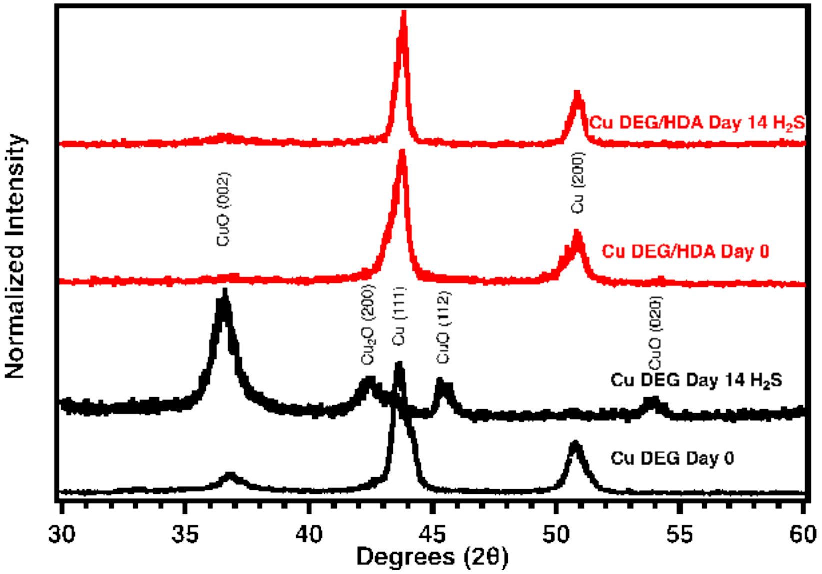


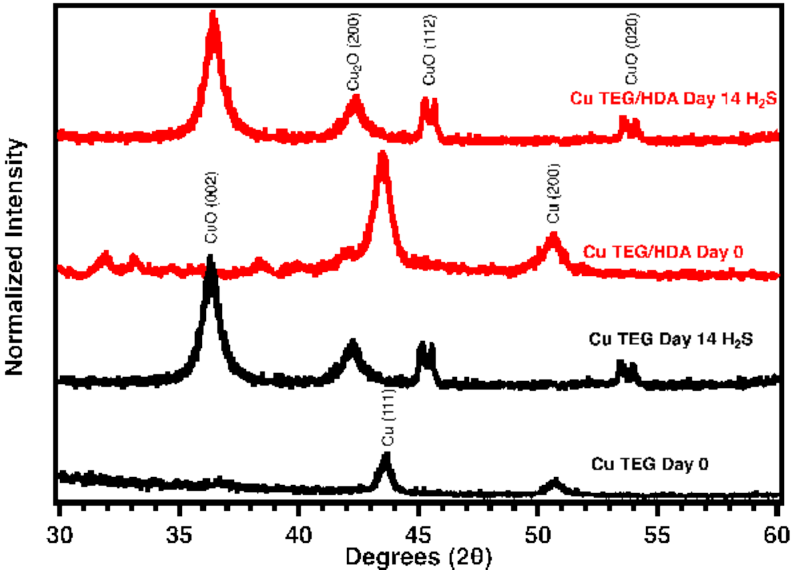
***Figure 6**. Binding energy (eV) of water with a Cu(111) with either 0.1 #/nm^2 or 0.2 #/nm^2 surfactant molecules bound to the surface.*

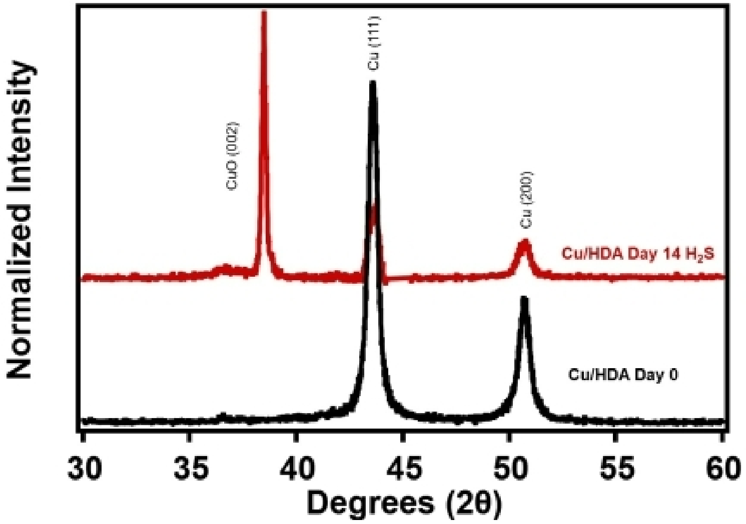
Cu-NP in 10 ppm H_2S/50% RH Environment for 14 Days





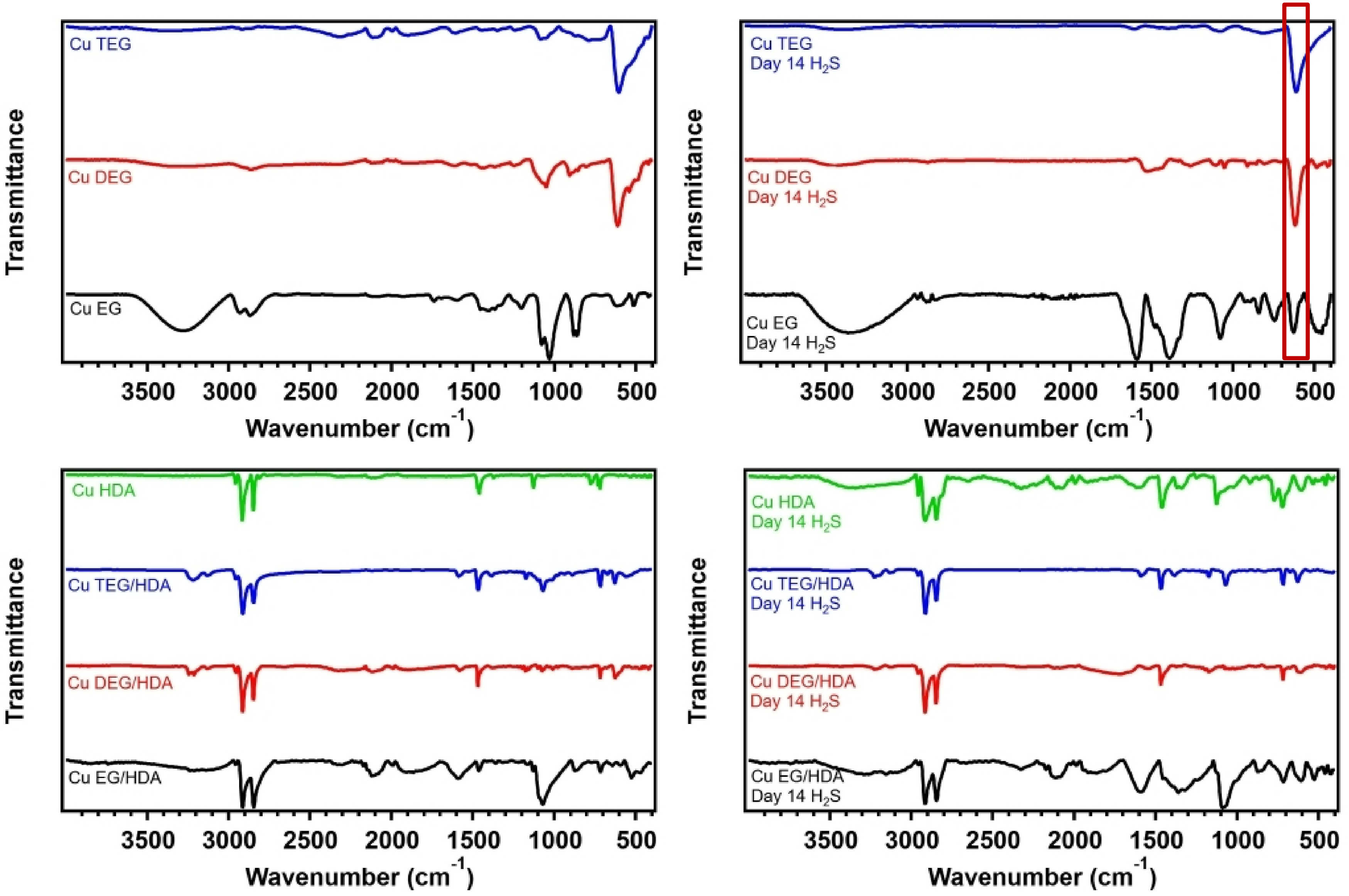
GES System for Environmental Testing





Sample	Cu %
Cu DEG	20
Cu DEG/HDA	77.6
Cu TEG	25.1
Cu TEG/HDA	46.6
Cu/HDA	33

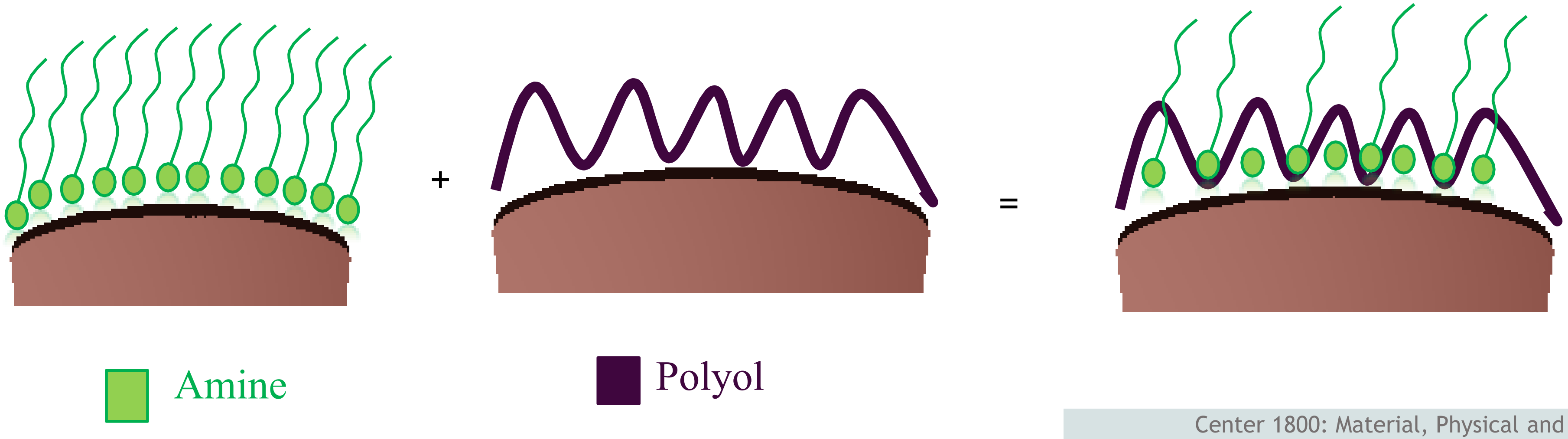
FTIR of Cu-NPs after H_2S Exposure



- Glycol-Cu-NPs show strong peaks near 600 cm^{-1}, which are associated with Cu-O bonding (denoted by red box).
- Their increase in intensity over time supports oxidation of the Cu NP surface.
- This peak behavior isn't seen in polyol/HDA particles.

Conclusion

- ✓A novel Cu-NP synthesis recipe via a microwave-assisted polyol method at was developed.
- ✓This recipe was also modified to synthesize oxidation-resistant Cu nanoparticles via the addition of HDA during the synthesis procedure.
- ✓FTIR & TGA show the surface chemistry of the Cu-NPs indicating both species being present.
- ✓The synergistic effects between the coating performance of the polyol and the hydrophobic properties of HDA leads to exceptional overall oxidation resistance in harsh environments.
- ✓While O_2 adsorption on (111) oriented fcc Cu surface is thermodynamically favorable, amines have been shown to have an exceptional affinity to the same (111) surfaces.
- ✓Overall, cost effective, oxidation-resistant copper nanoparticles were able to be quickly synthesized and efficiently.



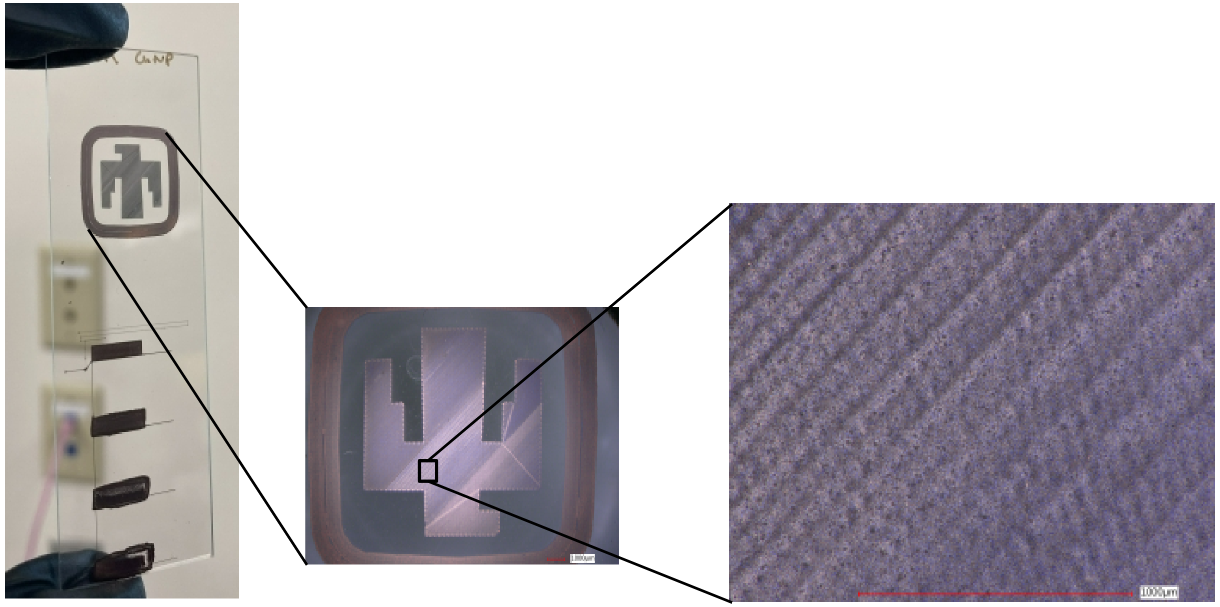
Future Work

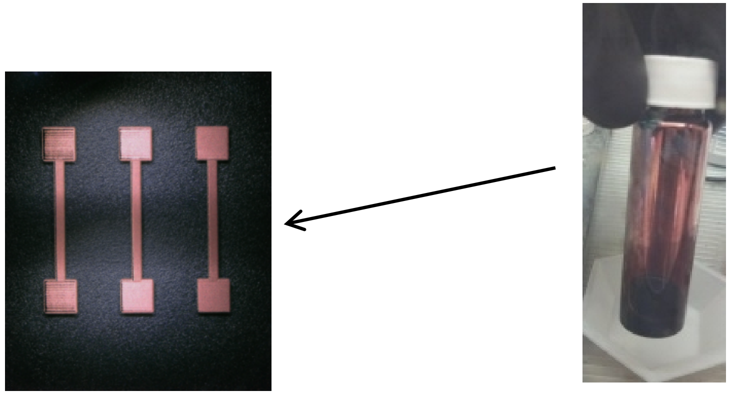
Goal:

- Printable and conductive ink with homogenous distribution
- Easily dispersed in solution
- Able to be sintered

Current Status:

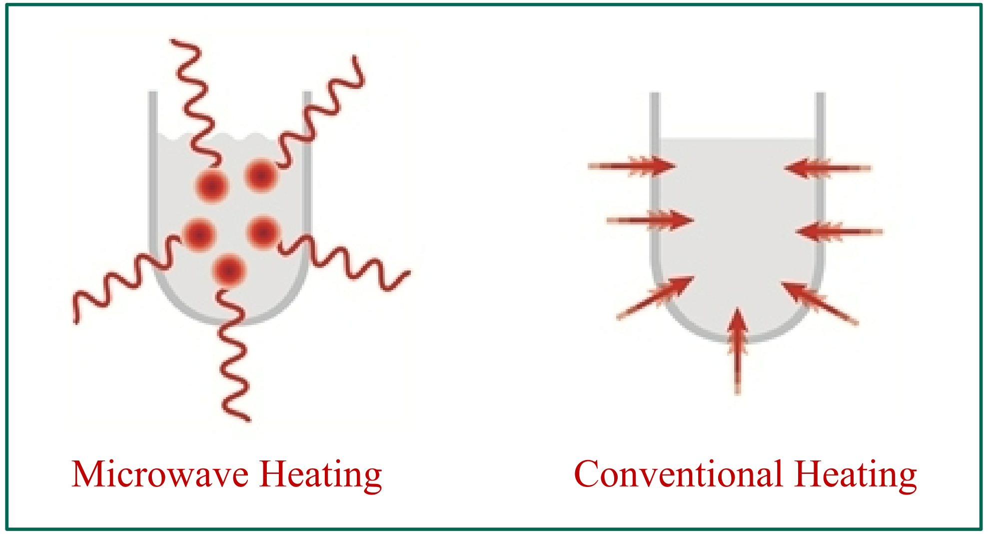
- Able to aerosoljet print Cu NP inks
- Currently optimizing ink performance to be comparable to bulk Cu
- Best performing ink is 54x bulk Cu





QUESTIONS?

Microwave Synthetic Route for Cu NP Production

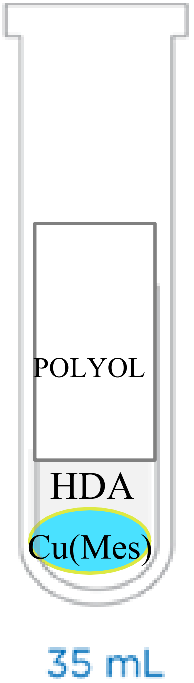


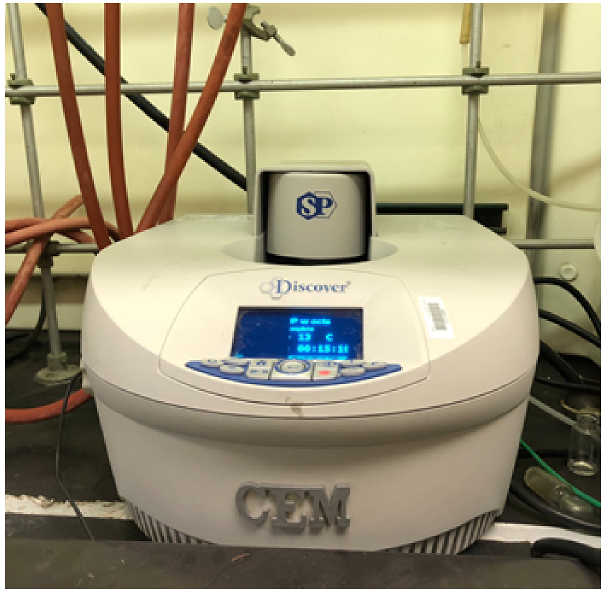
Benefits of microwave heating:

- Direct interaction with materials
- Increased reaction rate
- Milder reaction conditions
- Greater chemical yield
- Rapid synthesis
- Uniform heating

Procedure:

1. Add 1 g of Cu(Mes) to vial
2. Add 3 g of hexadecylamine to vial, opt.
3. Add 20 mL of polyol solvent
4. Select “Cu NP” program on CEM Discover microwave





FTIR of Pure Glycols

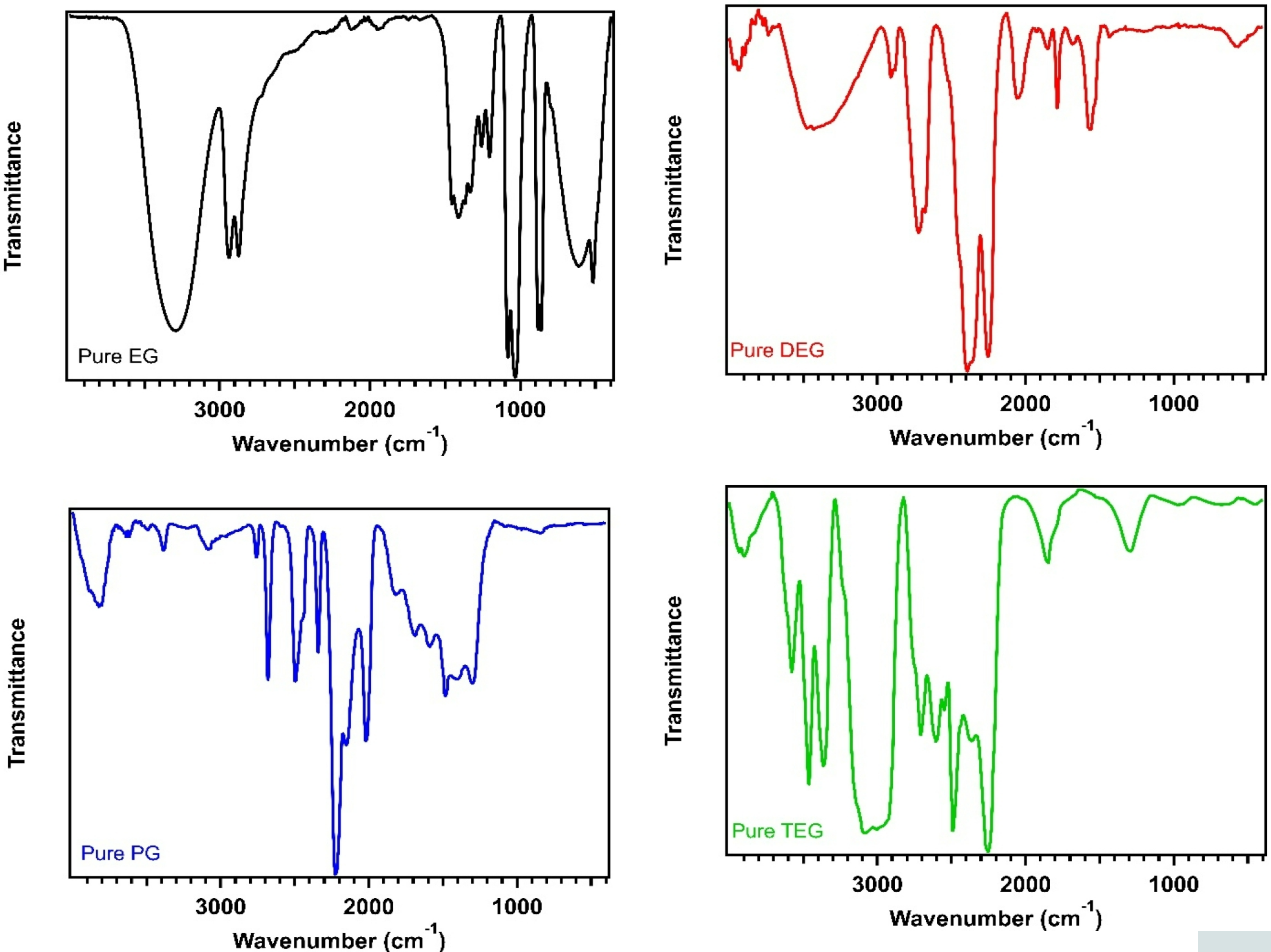
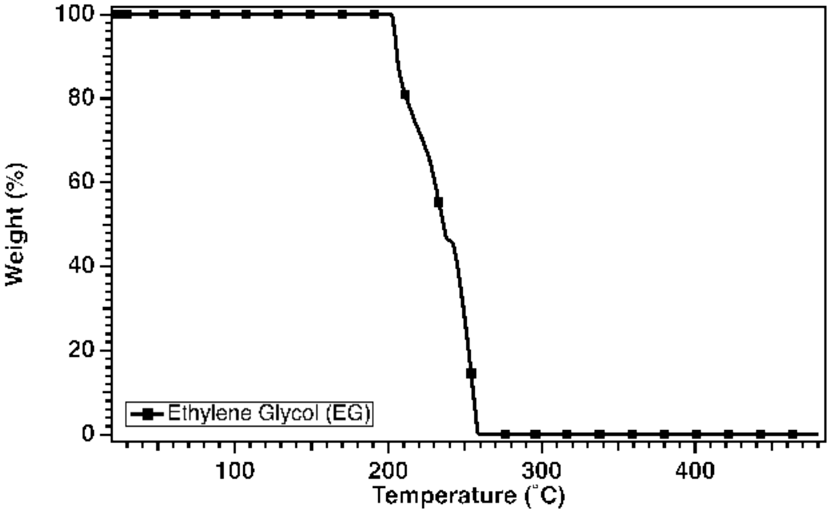
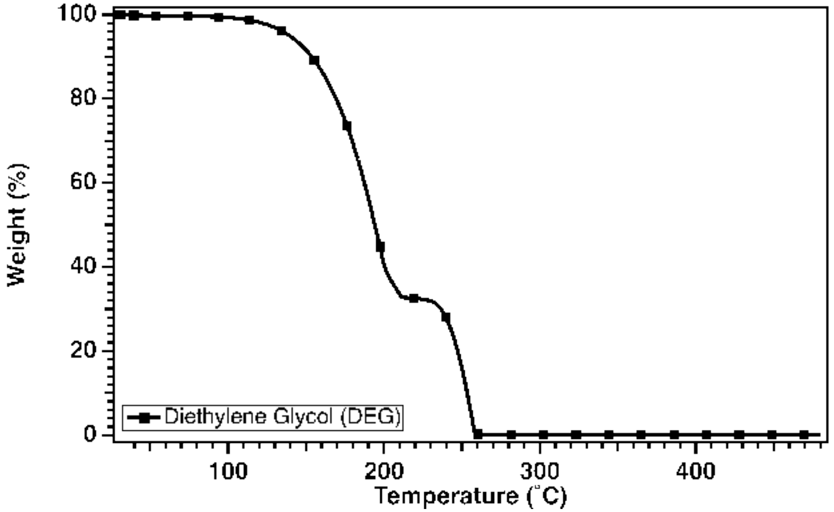
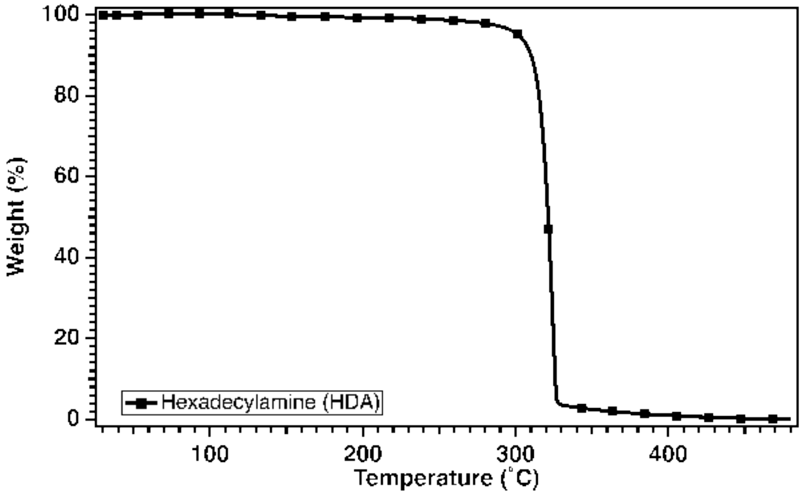


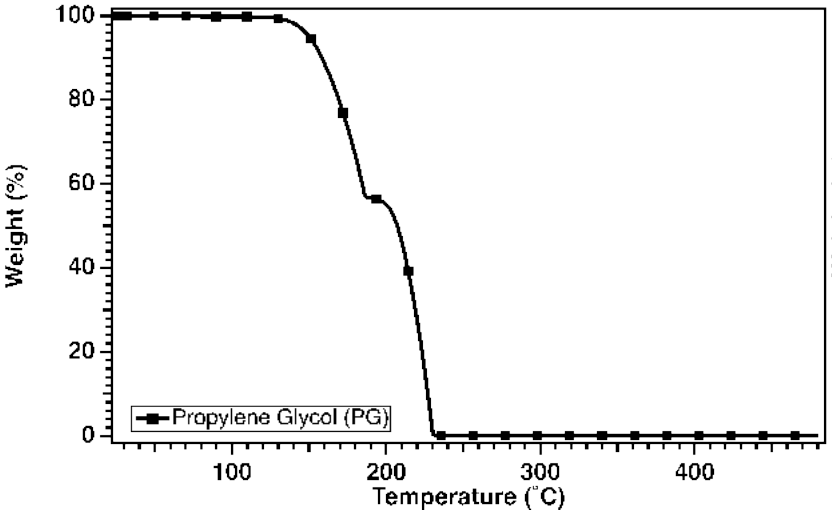
Figure A2. *FTIR spectra of pure ethylene glycol (EG), pure diethylene glycol (DEG), pure propylene glycol (PG), and pure tetraethylene glycol (TEG).*

TGA of Pure Glycols and HDA









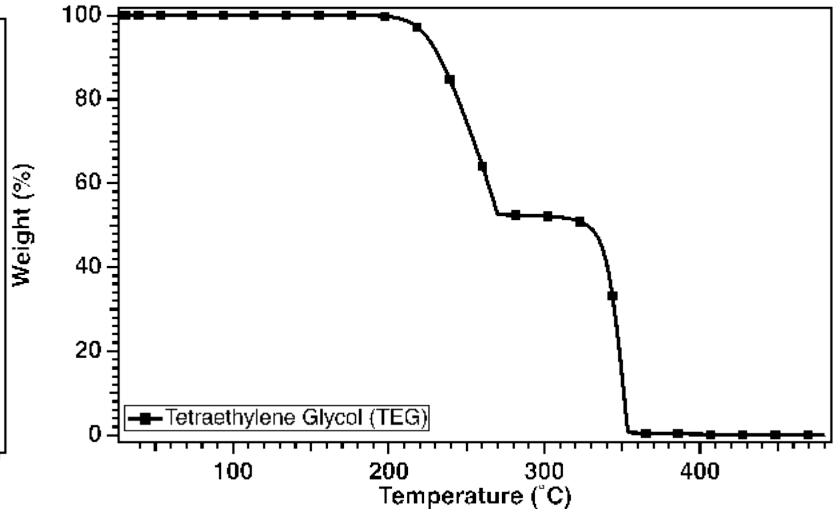
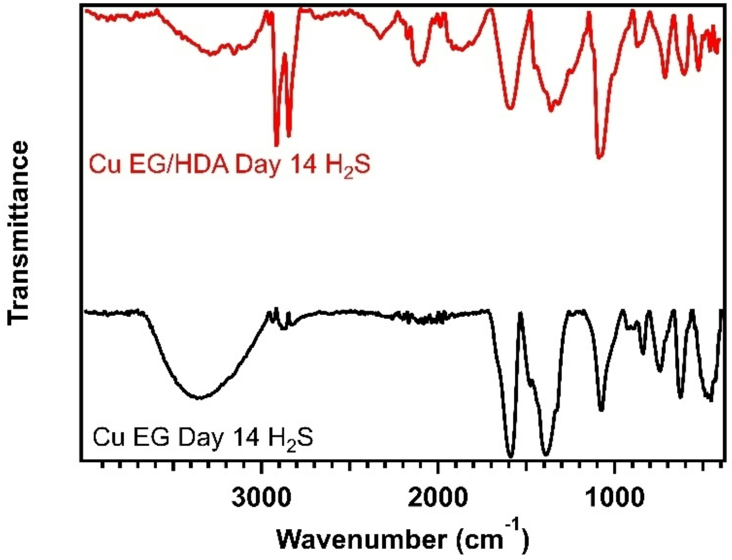
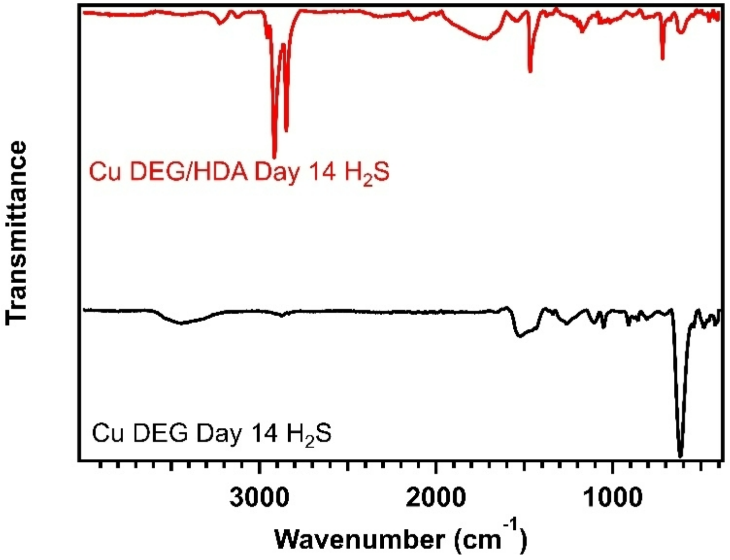
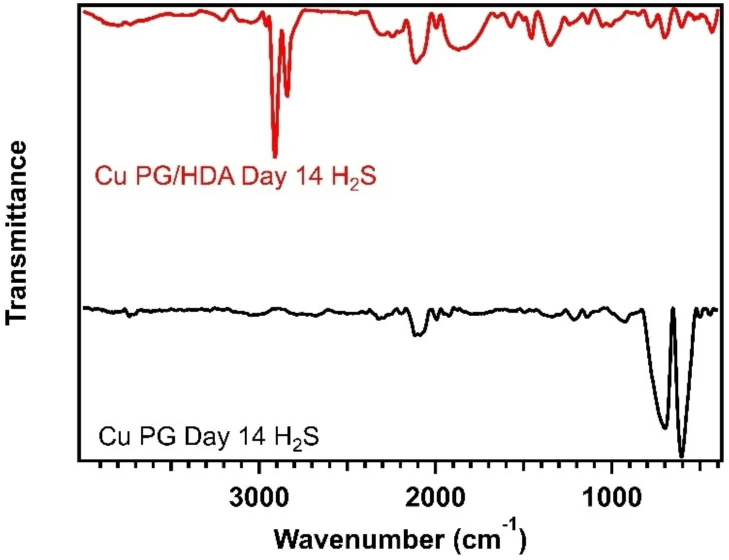


Figure A3. *TGA of ethylene glycol, diethylene glycol, propylene glycol, tetraethylene glycol, and hexadecylamine.*

FTIR of Glycol vs. Glycol/HAD After 14 Days in H_2S







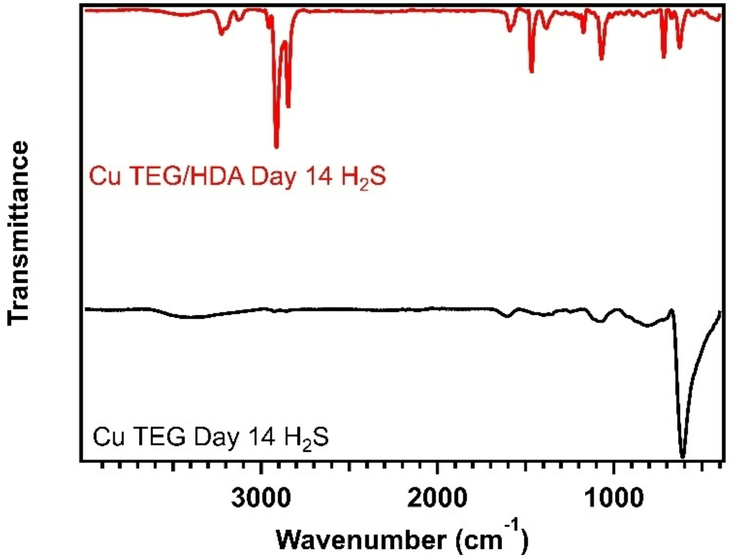


Figure A4. *FTIR comparison of polyol vs polyol/HDA after 14 days in 10 ppm H_2S/50% relative humidity environment*

FTIR of Pure EG & Pure HDA Before & After H_2S Exposure

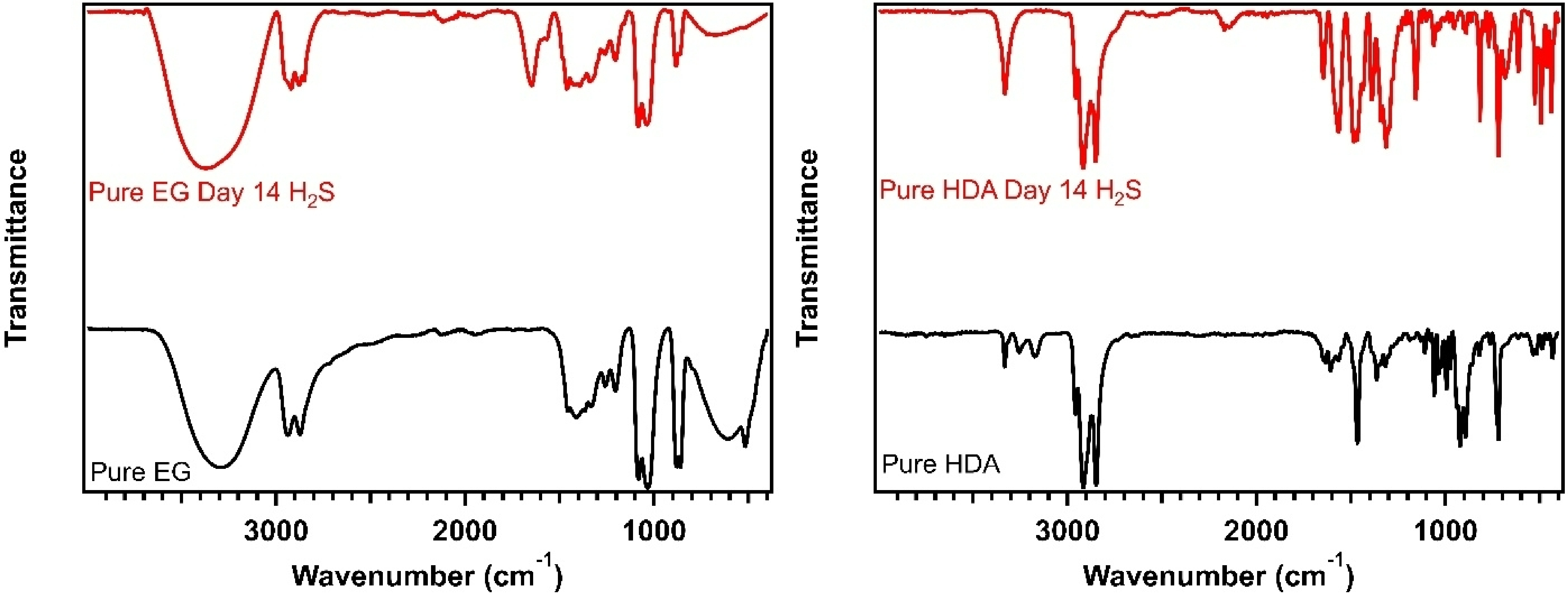


***Figure A5.** FTIR spectra of **(a)** pure ethylene glycol and **(b)** pure hexadecylamine before and after exposure to 10 ppm H_2S/50% RH.*