Mixed-Valence Composite Nano Copper-Silica Gel As Efficient Fungicide/Bactericide For Crop Protection

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MATERIALS INNOVATION FOR SUSTAINABLE AGRICULTURE
MISA

Sustainable Nanotechnology Conference
Orlando, FL
November 10-12, 2016

NanoScience Technology Center

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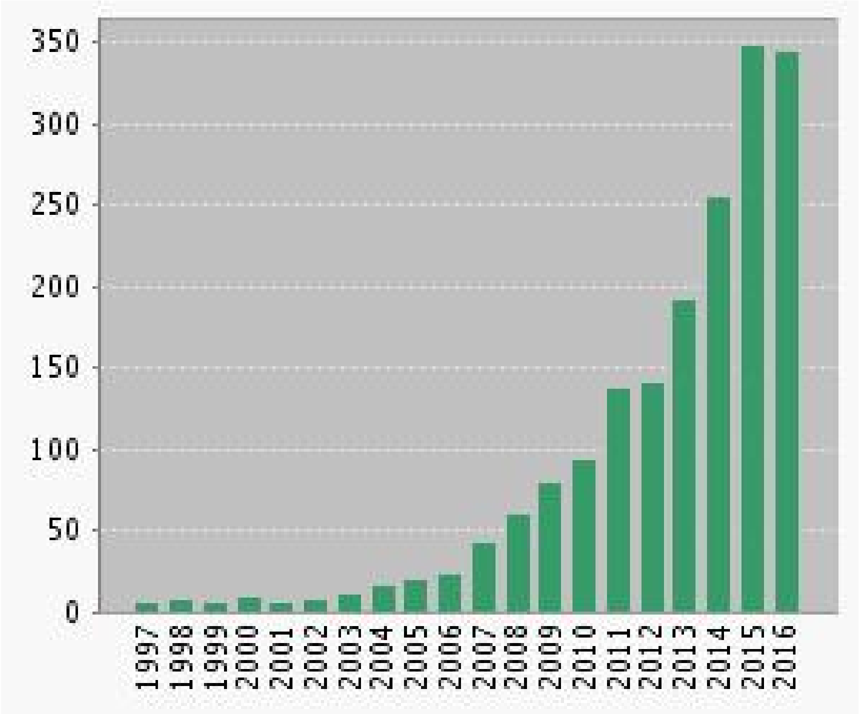
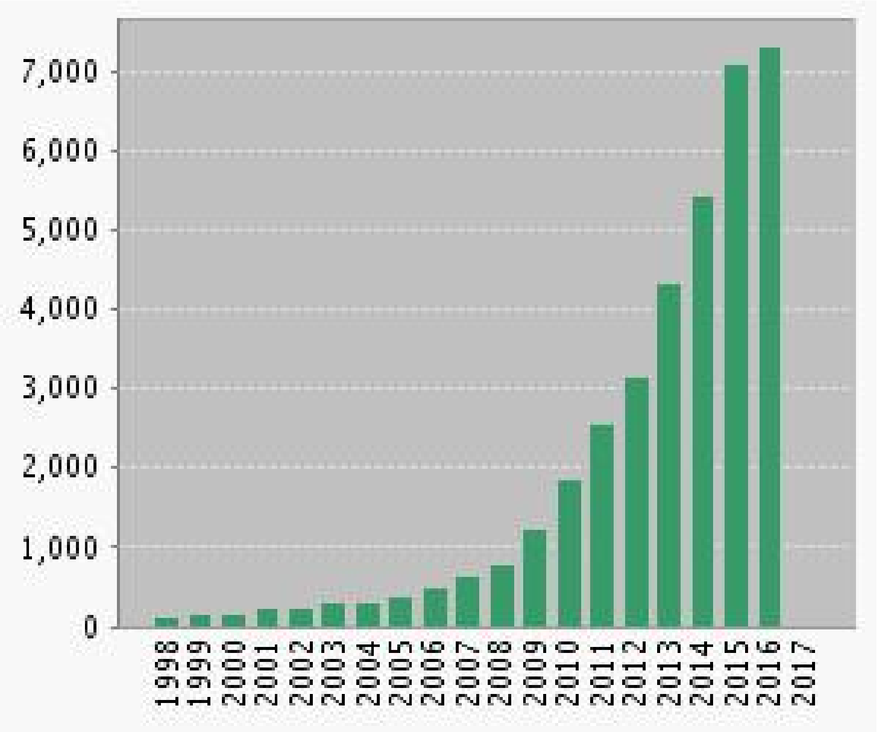
Nano* and Agri* Search

Published Items in Each Year

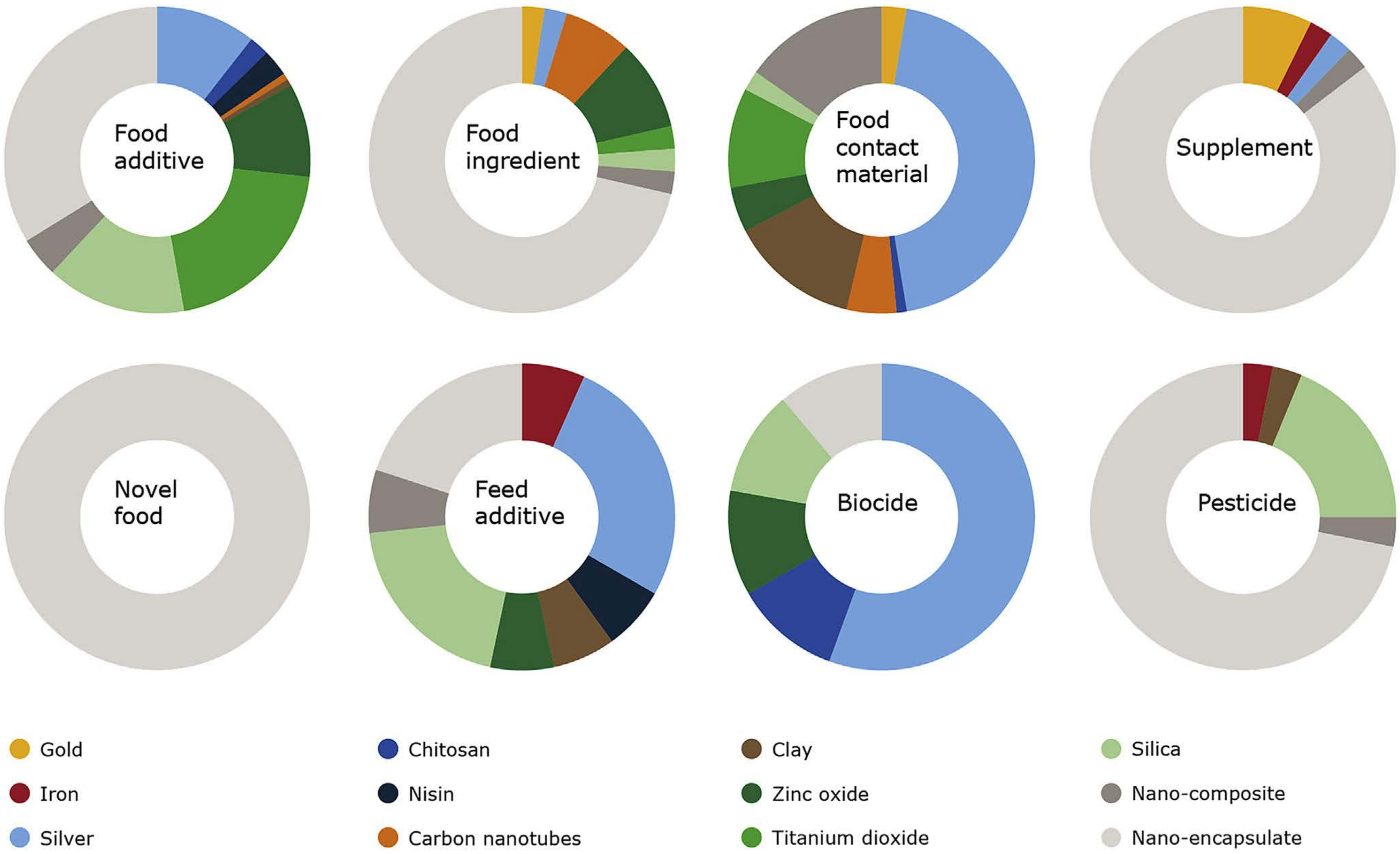


Citations in Each Year



ISI Web of Science Database (accessed on 11/11/2016); Total Publication: 1835

Nanomaterials in Agriculture



Trends in Food Science & Technology 54 (2016) 155-164

History of Cu biocide

Cu compound	Quantity (tones/year)	% of Market	Year introduced
Cu(II) oxychloride	71,000	51.1	1900
Cu(II) sulfate Cu(II) sulfate + lime (Bordeaux mixture) Cu(II) sulfate + soda ash (Burgundy mixture) Basic Cu(II) sulfate	48,000	34.6	**1761** 1873 1885 1930
Cu(I) oxide	6,000	4.3	1932
Cu(II) hydroxide	11,000	7.9	**1960**
Others: Cu(II) ammonia complex Cu(II) carbonate Cu(II) phosphate	3,000	2.1	- 1917 - -

Richardson, H.W., *Copper fungicides/bactericides*, in *Handbook of copper compounds and applications*, H.W. Richardson, Editor. 1997, Marcel Dekker, Inc.: New York, NY. p. 93-122

Limitations of Cu bactericides/fungicides

- Current Cu products are limited in several aspects

  - Cu bioavailability (Cu ions)

  - Rainfastness (maximum retention property)

  - Risk of development of bacterial resistance

  - Accumulation of Cu in soil (Environmental concerns)
- “Soluble Cu compound” versus “Insoluble Cu compounds”
- Soluble Cu compounds – maximum Cu bioavailability but minimum retention (quickly washes away with rain shower)
- Insoluble Cu compound – Limited Cu bioavailability and retention

Citrus canker – a bacterial disease

- Citrus canker is one of the most devastating diseases that has seriously affected citrus industry over thirty countries in Asia, the Pacific and Indian Ocean islands, South America, and the Southeastern USA. Canker has destroyed more than 16 million trees in Florida, adversely affecting Florida's 9B dollar citrus industry
- It is a bacterial disease caused by the Xanthomonas Axonopodis pv. Citri.
- The pathogen causes necrotic lesions on leaves, stems and fruit. Severe infections can cause defoliation, badly blemished fruit, premature fruit drop, twig dieback and general tree decline.
- The most serious consequence of citrus canker infestation is the impact on commerce resulting from restrictions to interstate and international transport and sale of fruit originating from infested areas, causing huge economic loss every year.

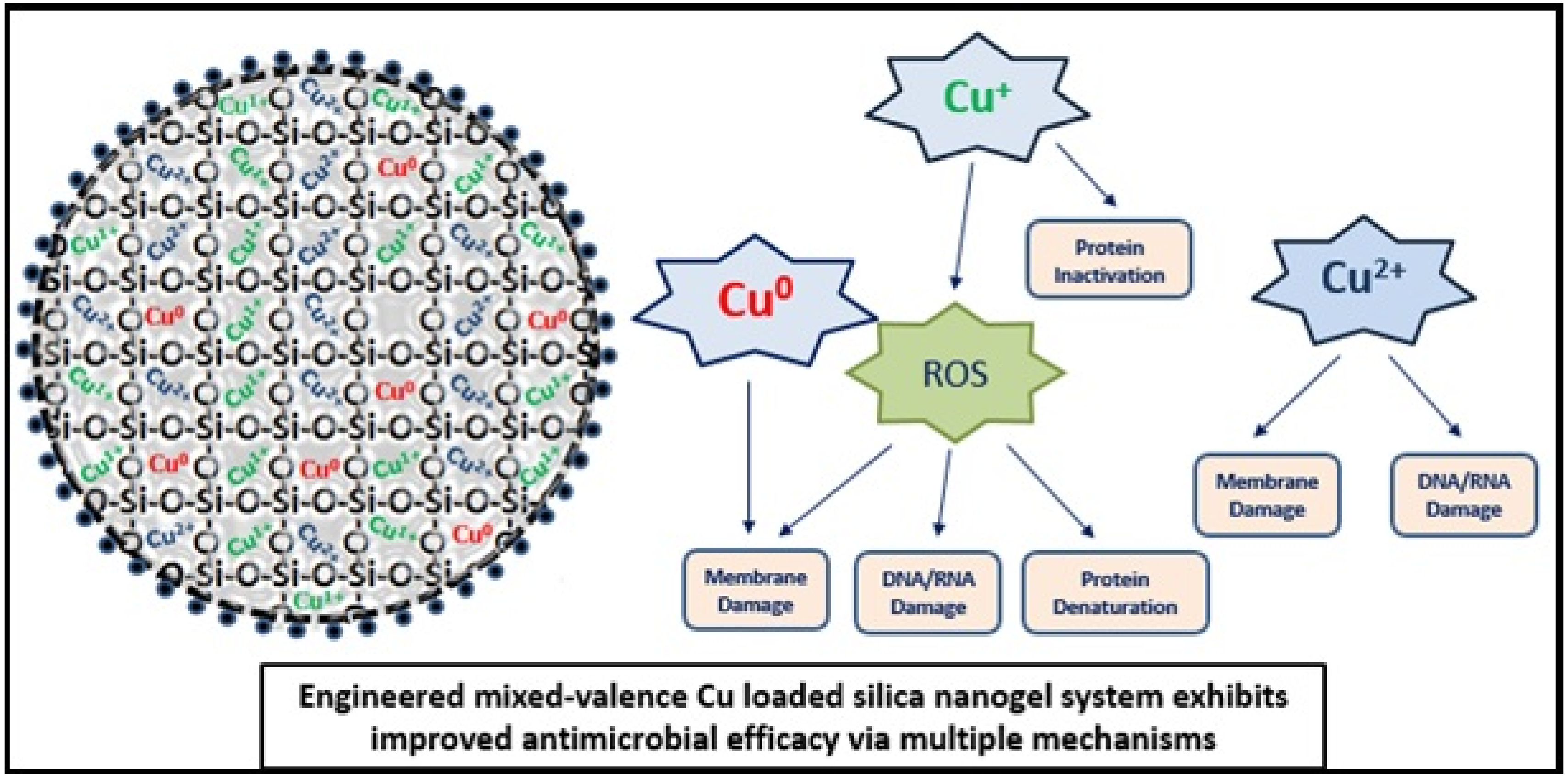
Courtesy: Tim S. Schubert et al. in Plant Disease, 2001, 85(4), 340-356.

Citrus Greening (Huanglongbing)

- Huanglongbing (HLB) is another deadly bacterial disease.
- It is caused by the phloem-limited bacterium 'Candidatus Liberibacter asiaticus' (Las) and vectored by the Asian citrus psyllid (ACP: Diaphorina citri)
- Since the 2005 discovery of HLB in Florida, HLB has spread rapidly throughout the state affecting approximately 90% of trees.
- Fruit drop has become a major issue. In the 2012-2013 season, HLB caused a record 20% fruit drop that increased to 30% in the 2013-2014 season.
- Once infected, tree will eventually die.

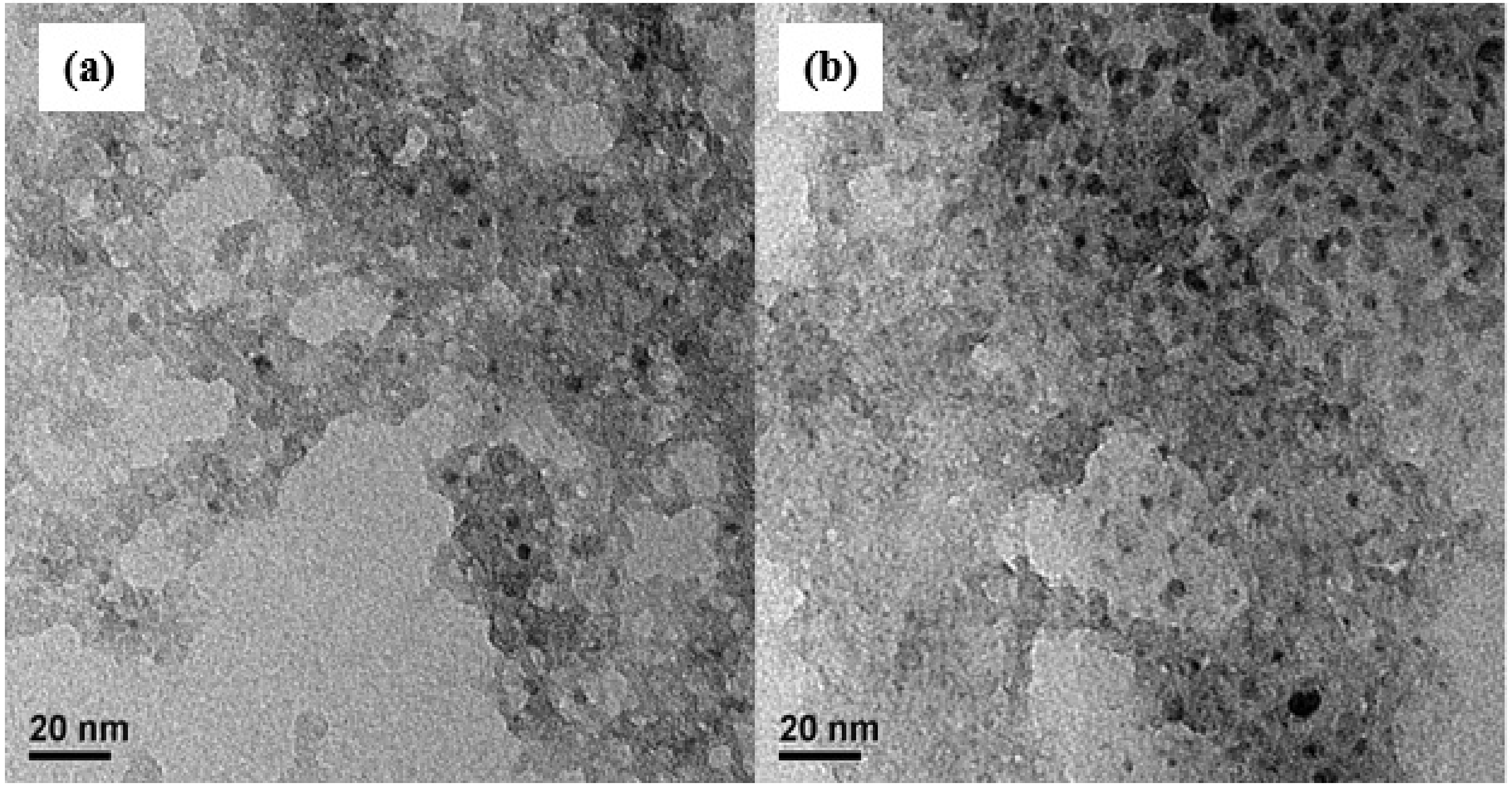
Photo by Courtesy Agricultural Research Service

Mixed-Valence Copper



Journal of Agricultural and Food Chemistry 2014, 62, 6043-6052.

HRTEM of CuSiNG and MV-CuSiNG

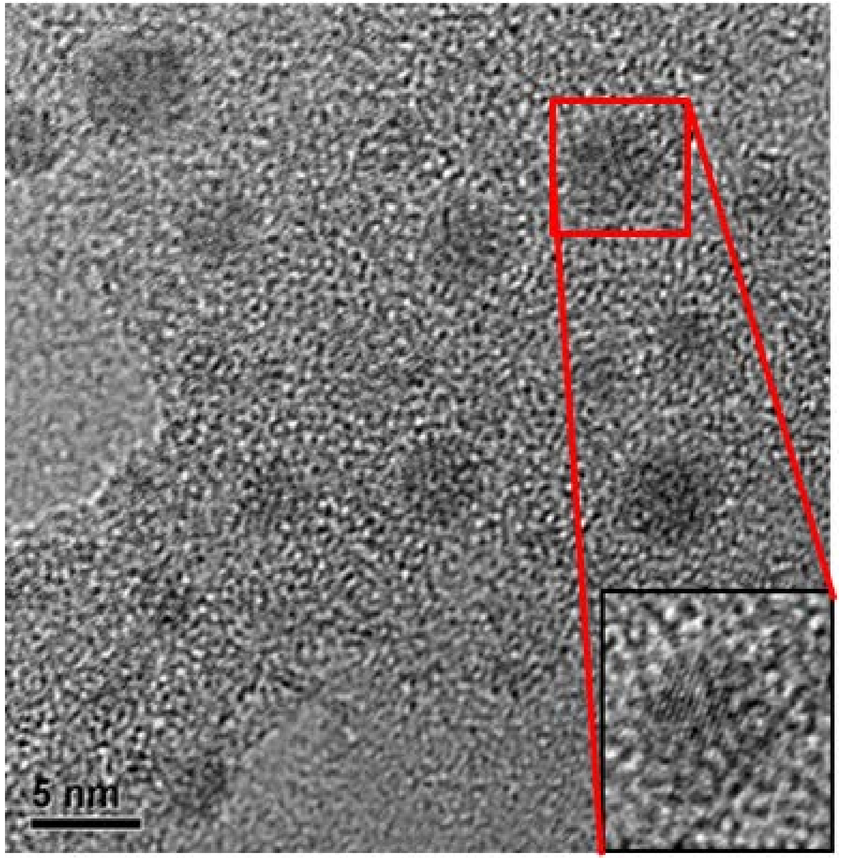


HRTEM image of (a) CuSiNG and (b) MV-CuSiNG at lower magnification with well distributed material with light and dark contrast.

Journal of Agricultural and Food Chemistry 2014, 62, 6043-6052.

US patent # 8,632,811; US patent # 8,221,791

HRTEM of CuSiNG

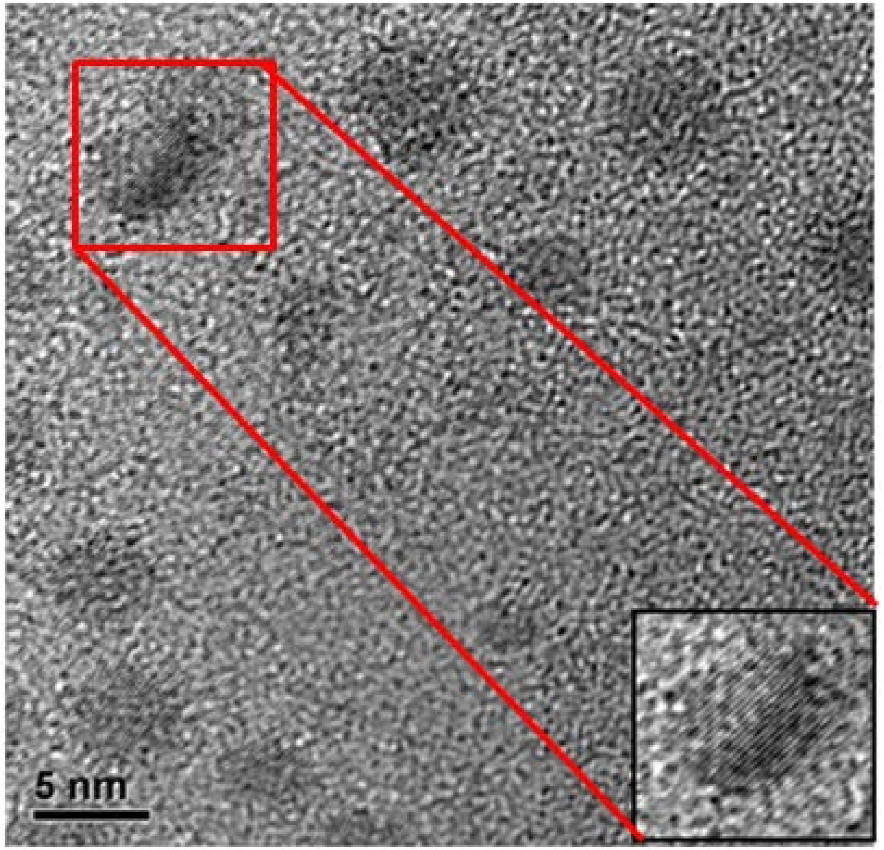


Compound	Lattice spacing (Å)
Copper (II) Oxide	2.32, 1.87
Copper (I) oxide	2.47, 3.02

Crystallite sizes: 4-8 nm.

Data, International Center for Diffraction. "Powder Diffraction File Search Manual." In Inorganic. PA.USA: JCPDS, 1984.

High magnification-HRTEM of MV-CuSiNG



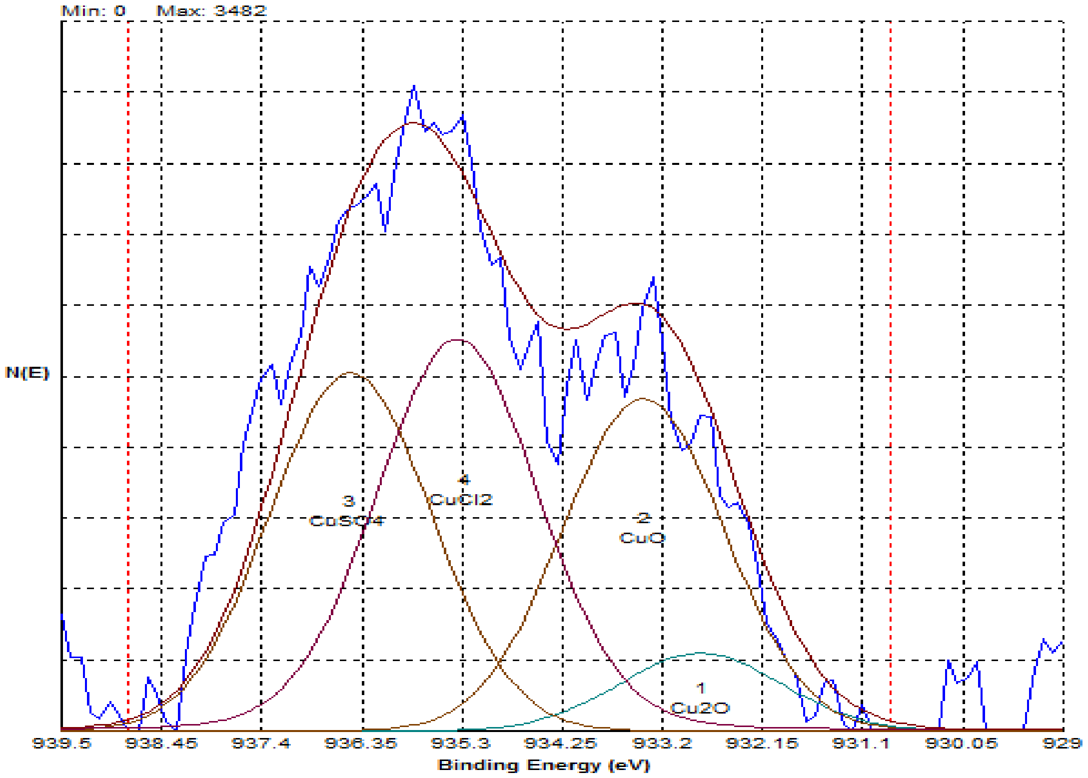
Compound	Lattice spacing (Å)
Copper (II) Oxide	2.32
Copper (I) oxide	3.02, 2.47
Cu	2.09

Crystallite sizes: 4-8 nm.

Data, International Center for Diffraction. "Powder Diffraction File Search Manual." In Inorganic. PA.USA: JCPDS, 1984.

X-Ray Photoelectron Spectroscopy (XPS)

High-resolution spectra of Cu in CuSiNG .



Cu Compounds identified
$CuSO_4$
$CuCl_2$
CuO
Cu_2O

Strohmeier B.R., Leyden D.E., Field R.S., Hercules D.M. J. Catal. 94, 514 (1985), Yoshida T., Yamasaki K., Sawada S. Bull. Chem. Soc. Jpn. 51, 1561 (1978)
Robert T., Bartel M., Offergeld G. Surf. Sci. 33, 123 (1972); Ghijsen J., Tjeng L.H., van Elp J., Eskes H., Westerink J., Sawatzky G.A. et al Phys. Rev. B 38, 11322 (1988)

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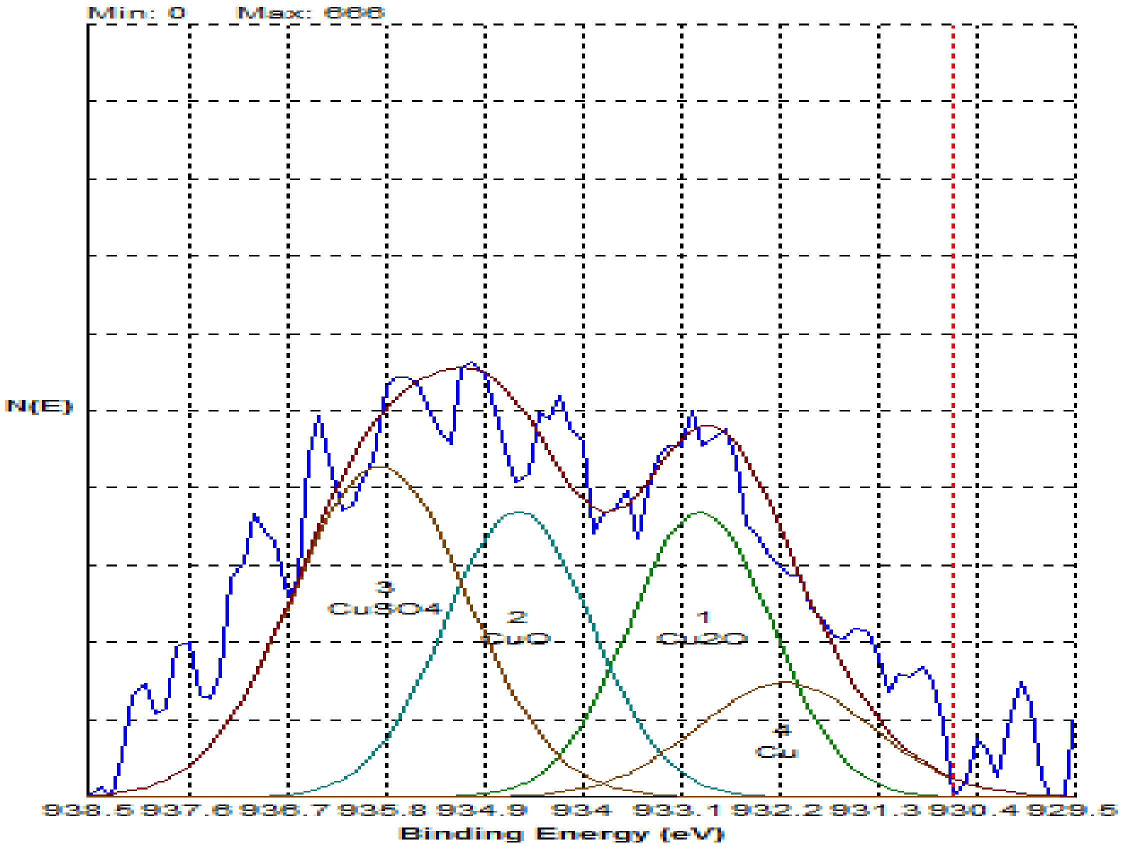

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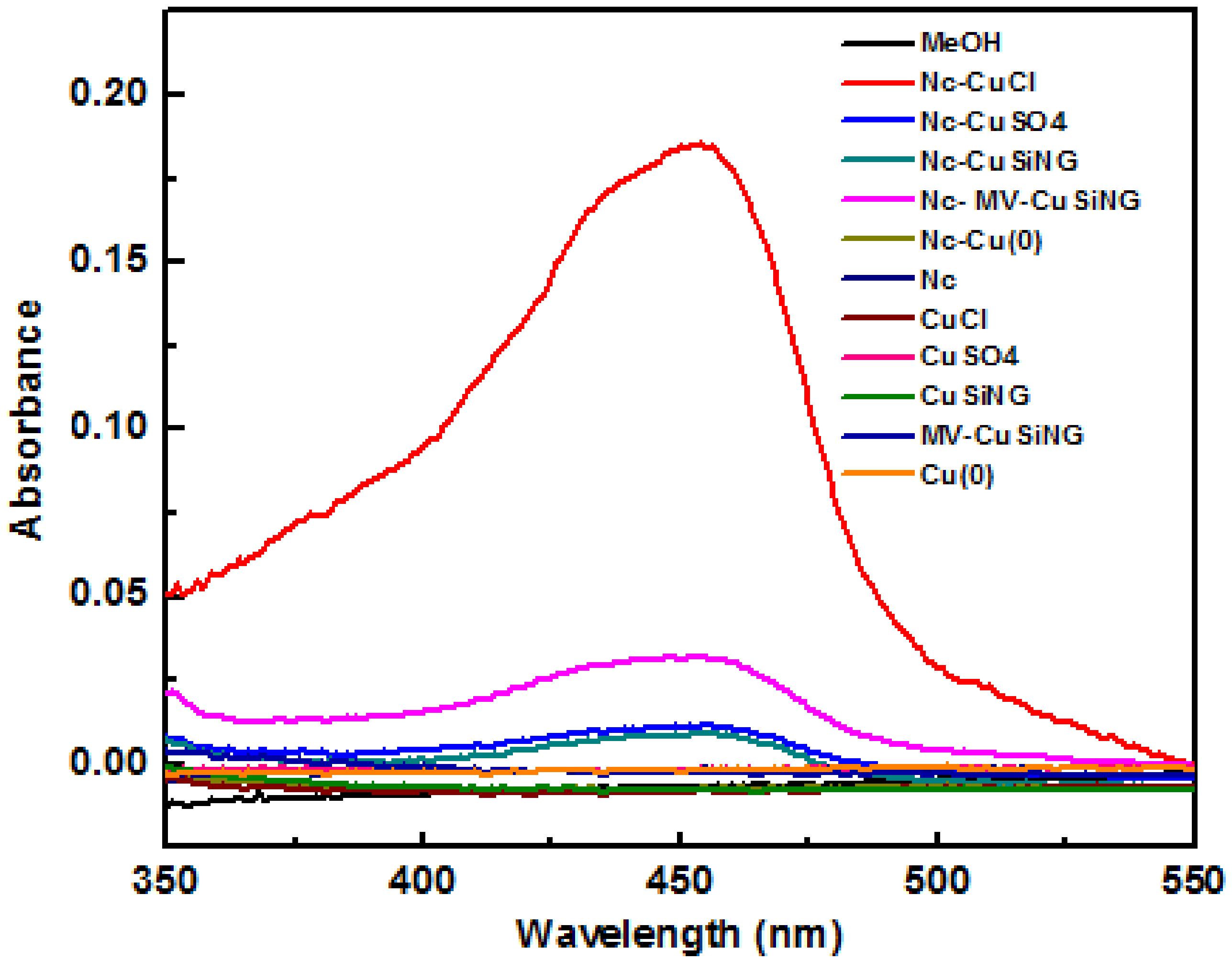
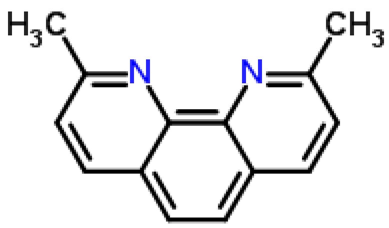
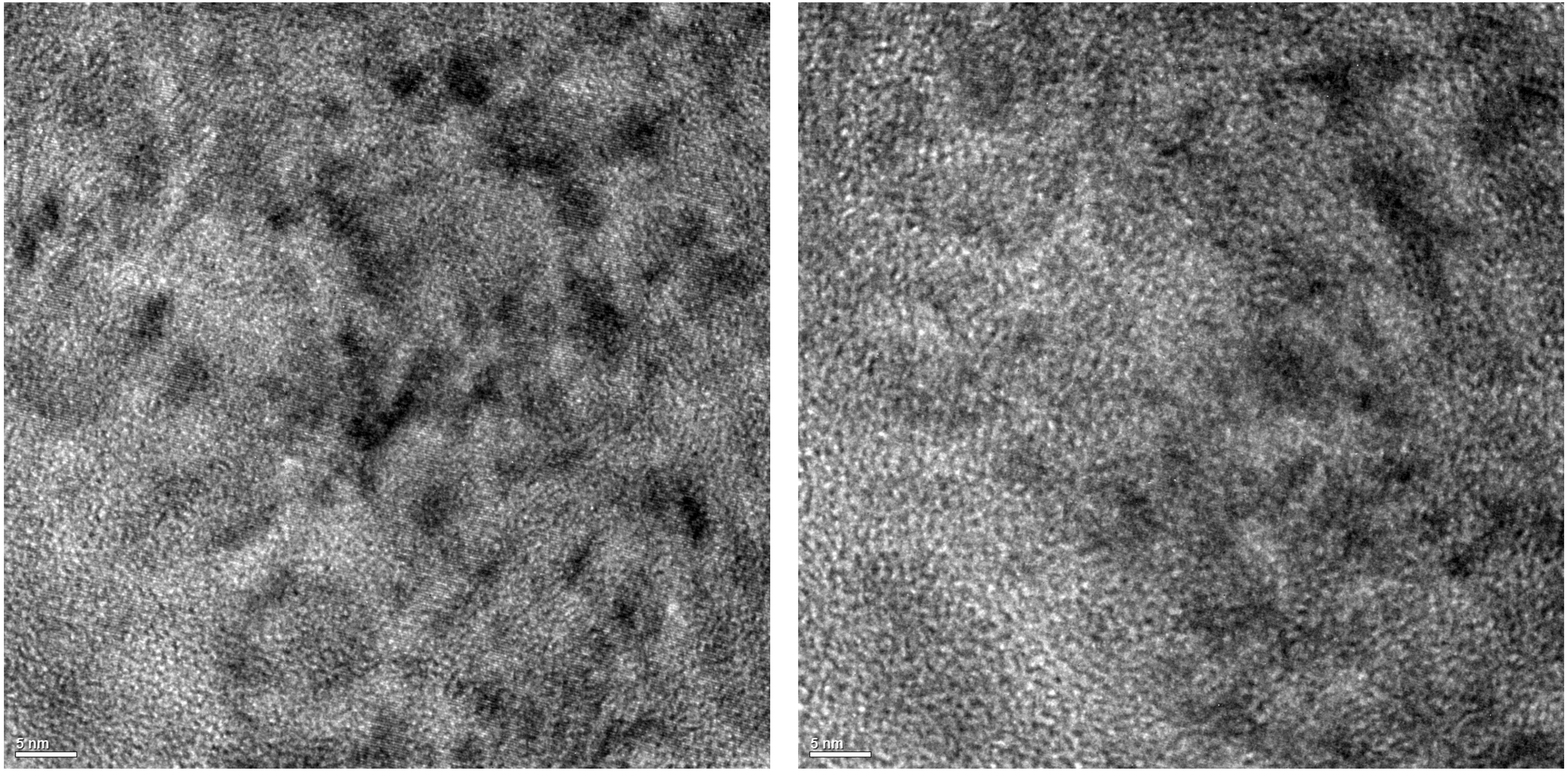
UV-Vis spectra of CuSiNG -Neocuproine (Nc)





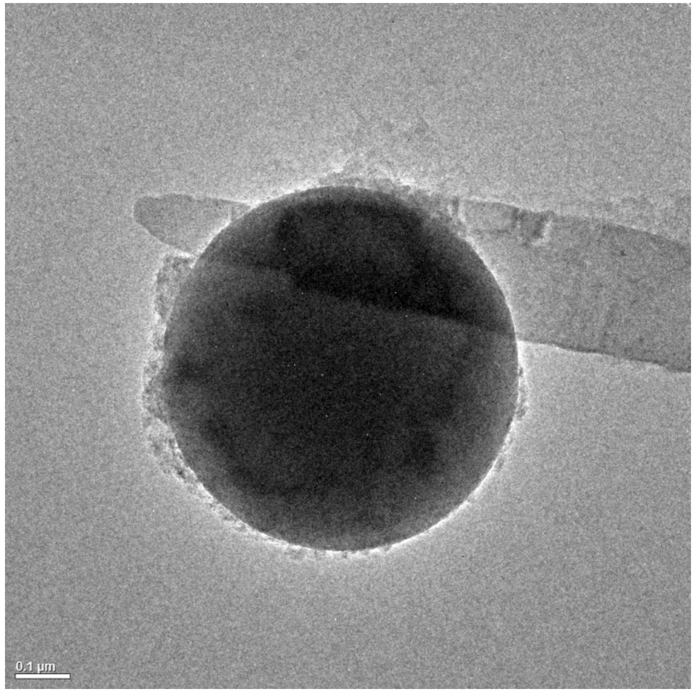
(Nc)

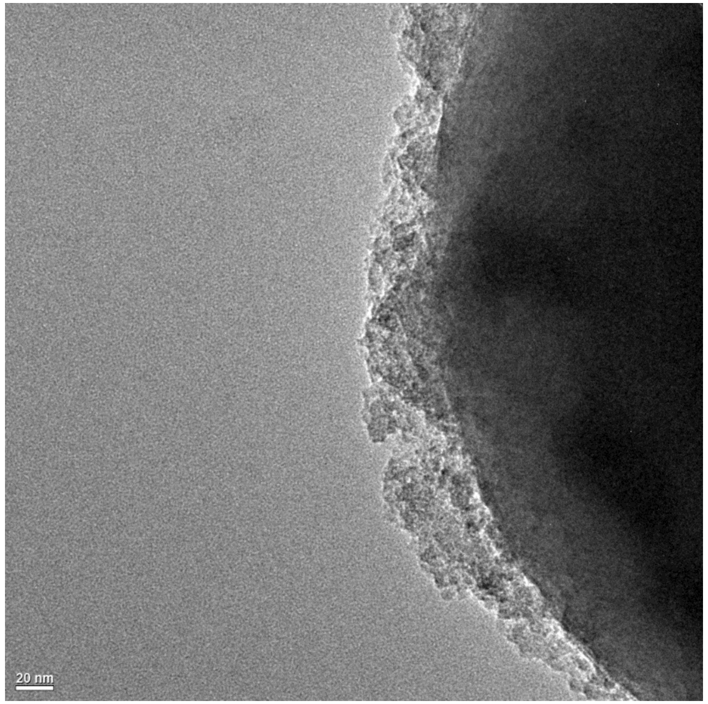
TEM of Mixed-Valence Copper-silica composite material (agri-grade chemicals)

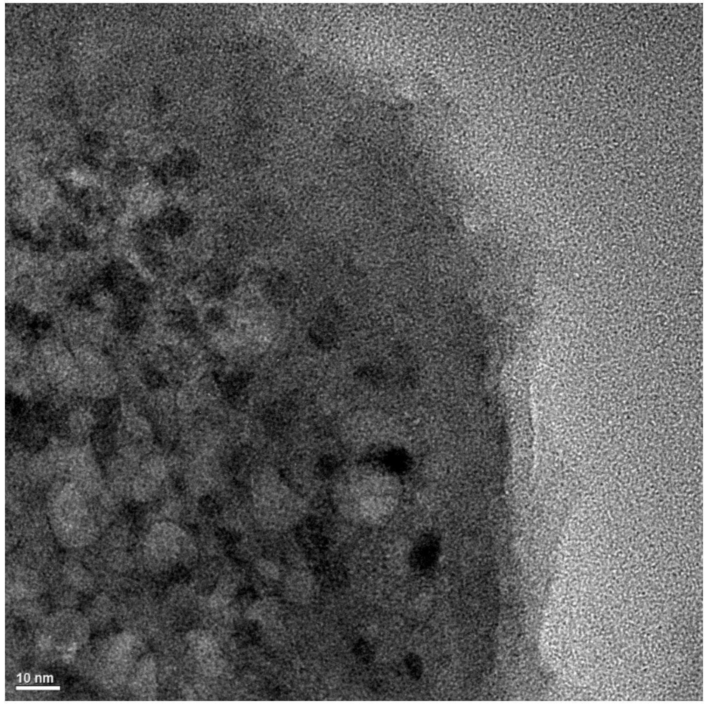


HRTEM image of MV-CuSiNG with scattered dark contrast confirming presence of electron-rich material

TEM of CS-CuSiNPs







HRTEM (low mag) image of CS-CuSiNPs with scattered dark contrast confirming presence of electron-rich material

J Biomed Nanotechnol 2012, 8(4), 558-566

Phytotoxicity of Vinca sp (Annual ornamental)

Material Tested	Metallic Cu (µg/mL)	Time (hr)		
		24	48	72
Untreated	-	-	-	-
$CuSO_4$	500	+	+	++
$CuSO_4$	900	+	++	+++
Kocide 3000	500	-	-	-
Kocide 3000	900	-	-	-
Cu-CS	500	-	-	-
Cu-CS	900	-	-	-
Cu-MV	500	-	-	-
Cu-MV	900	-	+	+

Results indicate a strong potential for Cu-CS and Cu-MV to used for crop protection

Antimicrobial Studies
Minimum Inhibitory Concentration (MIC)

Materials	MIC (µg/mL)				
	X. alfalfae (ATCC 49120)	*Pseudomonas syringae (ATCC 19310)*	*Clavibacter michiganensis (ATCC 10202)*	*X. perforans (GEV 485)*	*X. perforans (91-118)*
CS-CuSiNPs	**125-250**	**125-250**	**125**	**250**	**125**
MV-CuSiNG	**125-250**	**62.5-125**	**62.5-125**	**125-250**	**62.5**
Kocide 3000	**250-500**	**250**	**125-250**	**500**	**125**
$CuSO_4$	**250-500**	**250**	**125-250**	**250-500**	**62-125**

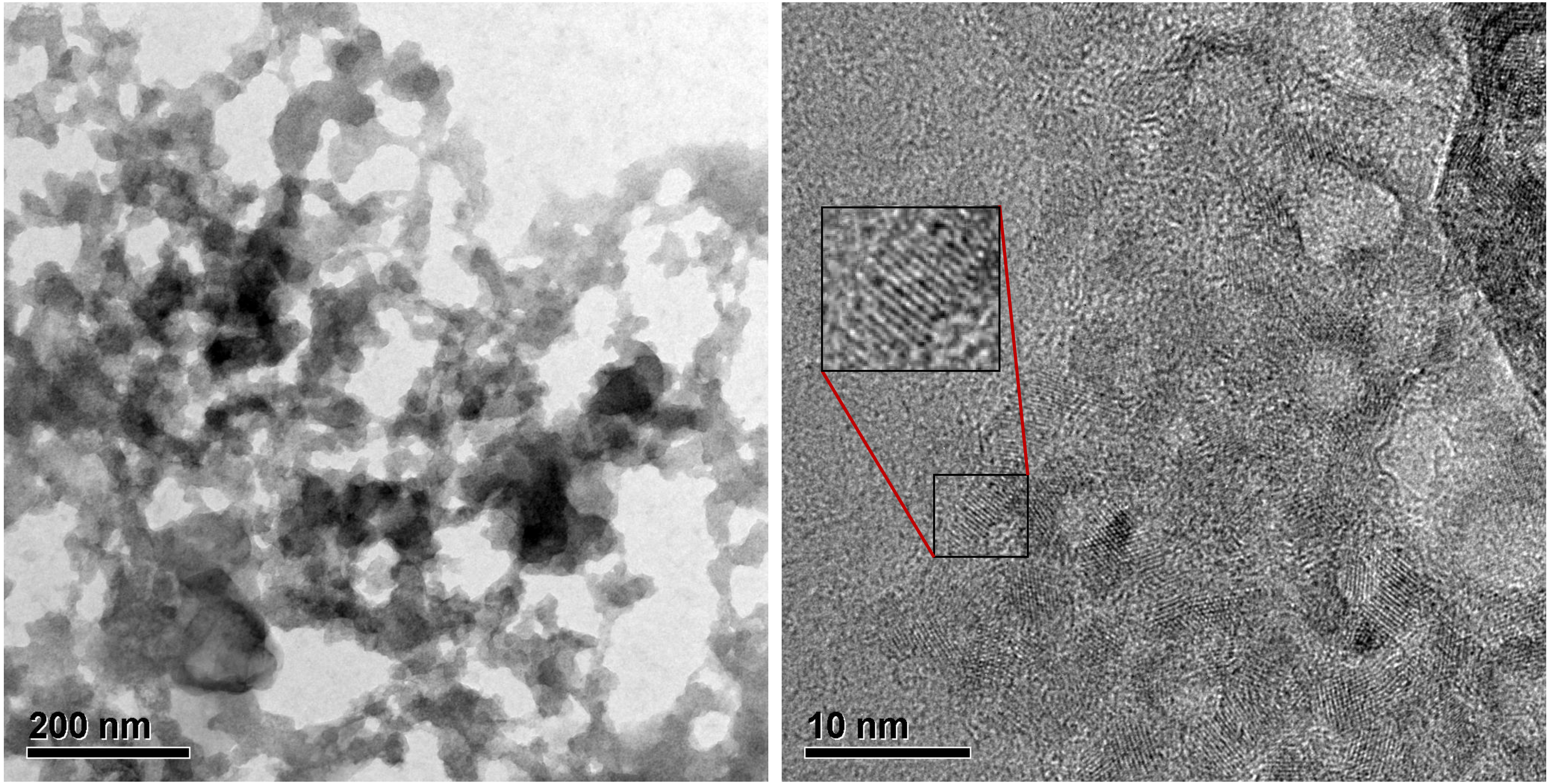
***In-vitro* antimicrobial studies indicate strong potential of experimental nano-Cu materials over traditional commercial Cu.**

2014 and 2015 Citrus Canker field trial

Field Trials for Copper formulations on incidence of citrus canker on fruit of 6- and 7-yr-old ‘Ray Ruby’ grapefruit trees in October 2014 and 2015 at Vero Beach, FL					
Trial year Treatment – Rate	Metallic Copper (kg/ha)	Metallic Zinc (kg/ha)	Incidence of old lesions (%)	Incidence of young lesions (%)	Total incidence (%)
2014					
Untreated check (UTC)	--	--	45 a [z]	18 a [z]	63 a [z]
Cu oxide – 1.12	1.12	--	17 b	4.4 b	21 b
Cu oxide/Zn oxide – 0.56	0.56	0.56	16 b	8.8 b	25 b
MV1-CuSiNG	0.20	-	16.4 b	4.4 b	20.8 bcd
CS-CuSiNPs	0.20	-	11.6 bc	4.0b	15.6 cde
2015					
Untreated check (UTC)			23 a	37 a	60 a
Cu oxide – 1.12	1.12	--	10 bc	20 b	29 b
Cu oxide/Zn oxide – 0.56	0.56	0.56	8.2 bcd	13 cd	21 cd
CS-CuSiNPs	0.20	-	11 cde	14 bc	25 cd

[z] Treatments within each trial year followed by unlike letters are significantly different at $\alpha = 0.05$ according to Student-Newman-Keuls multiple range test.

ZnO based antimicrobial Qdots (ZinkicideTM)



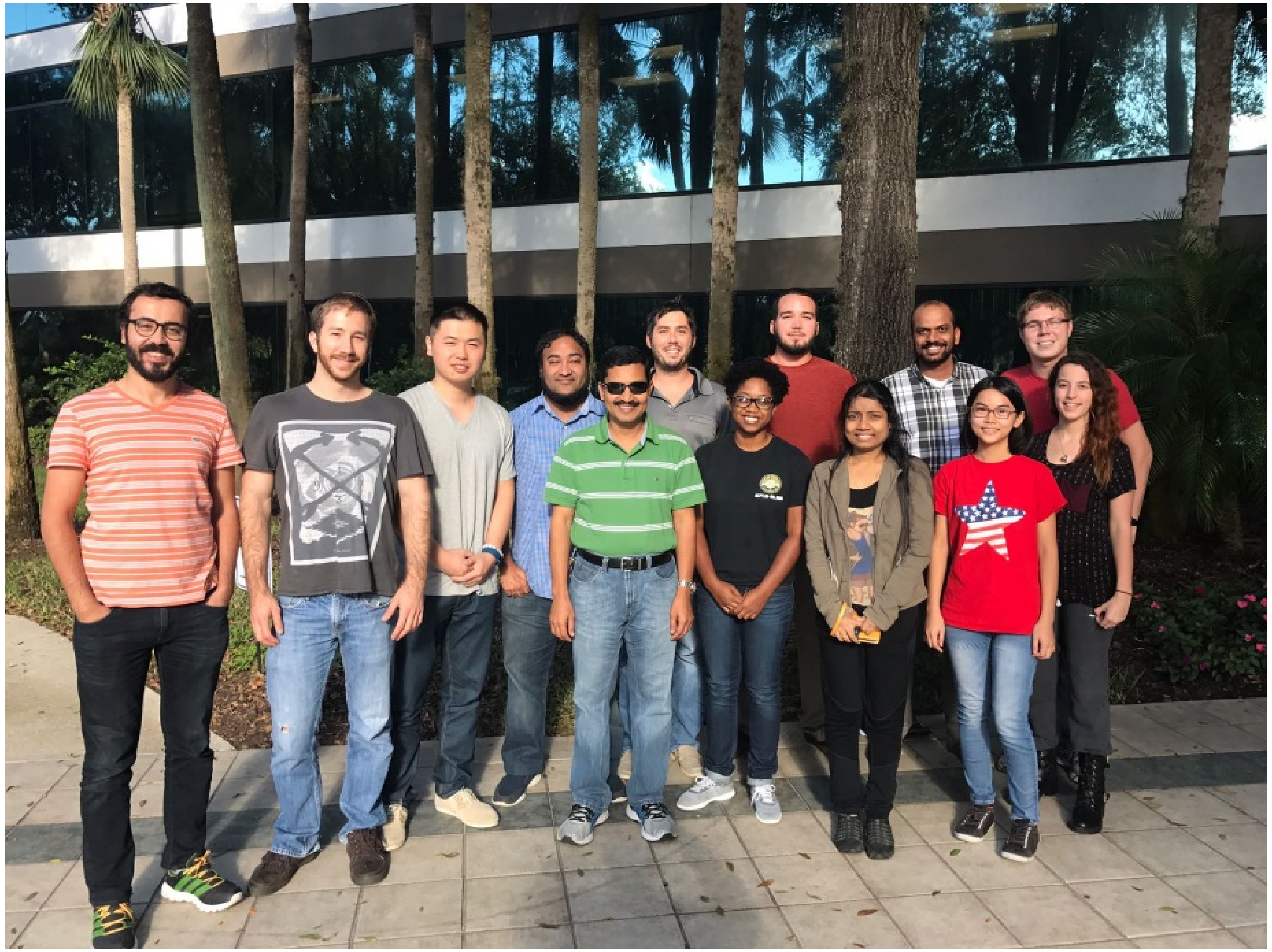
US patent # 9,215,877
Plant Disease, 2016, 100(12): 2442-2447

2014 Grapefruit canker field trial

Treatment	Metallic Cu or Zn (lb/ac)	Incidence old lesions (%)	Incidence young lesions (%)	Total incidence (%)
1) Nordox 75WG	1.0	16.8 b	4.4 b	21.2 bcd
2) Nordox 30/30 WG 1.5 lb	0.50	15.8 b	8.8 b	24.6 b
3) Zinkicide™ SG6	0.5 (Zn)	4.6 cd	2.4 b	7.0 ef
4) Untreated check (UTC)	-	45.0 a	17.8 a	62.8 a

[z] Treatments followed by unlike letters are significantly different at $P \leq 0.05$ according to Student-Newman-Keuls multiple range test.

Acknowledgements



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USDA NIFA

CRDF Citrus Research and Development Foundation, Inc.