Surface-mechanical and electrical property evaluation of nano-cone structured Cu–ZrO_2 composite coating

By

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Introduction

SURFACE MODIFICATION OF COPPER (BY Cu-ZrO_2 COMPOSITE COATING)

Applications

Copper: wires, cables
Integrated Circuits
Printed circuit boards
Electrical busbars
Circuit inter connectors
Heat sinks
Heat exchangers, etc.

Properties

Higher electrical conductivity
Higher Thermal Conductivity
Corrosion resistance at ambient temperature
Excellent workability
Abundantly available
Reproducible
Cheaper
Poor mechanical properties
Poor oxidation resistance

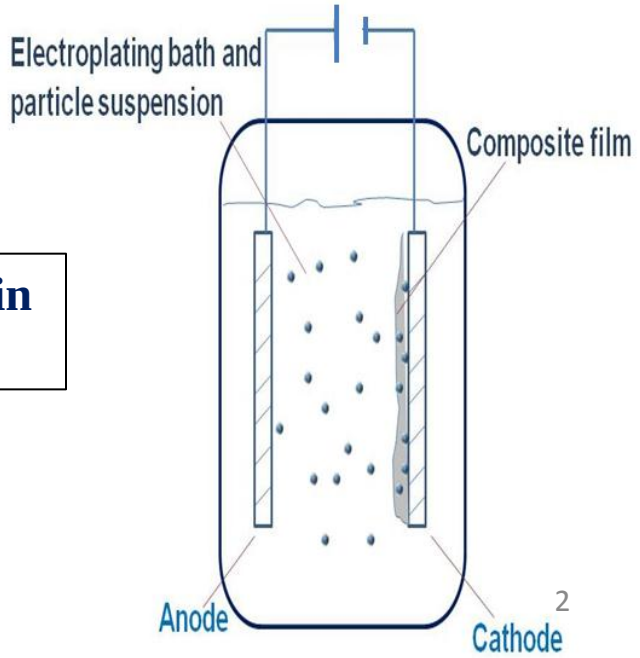
Without much deterioration of electrical conductivity

Improvement in **Hardness, Wear**

Advantages (Electrodeposition)

- Low cost and industrial applicability
- Simple operation
- High production rates
- Versatility
- Capability to handle complex geometry
- Precise control, near room temperature operation
- Reduction of waste

Possible application in Electrical contacts



Experimental

Copper Sulfate Solution

Second phase particles (ZrO_2)

Suspension for Electro-codeposition (ECD)

Prepared Cu Substrate

ECD Process (pulsed)

Characterizations

Bath composition and deposition parameters:

Item	Details
Electrolyte	Copper Sulfate ($CuSO_4.5H_2O$): 200 g/l, Sulfuric acid (H_2SO_4): 50 g/l
pH	~2.17
Current density	8 A/dm^2
Temperature	Room temperature
Plating time	20 minutes
Dispersion Surfactant	ZrO_2: 10 g/l Cetyl trimethylammonium bromide (CTAB): 0.1, 0.5 and 1 g/l
Deposition mode	Pulsed electrodeposition [pulse frequency: 5 kHz and duty cycle (pulse on time):30%]

Phase Analysis (XRD)

Composition & Microstructure (EDS, SEM, FESEM)

Mechanical (Hardness, Wear)

Electrical conductivity

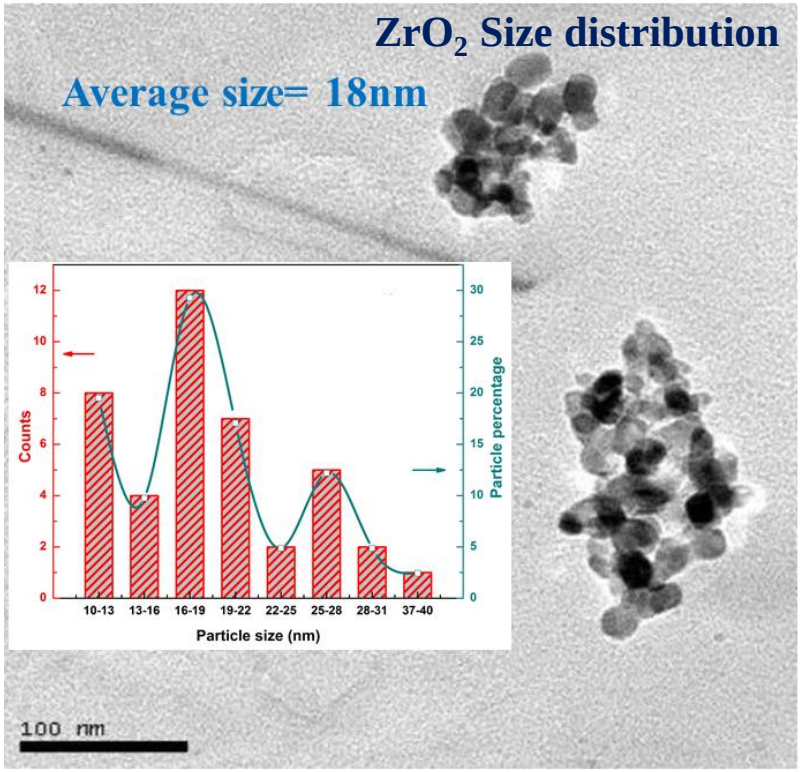
Powder characterizations

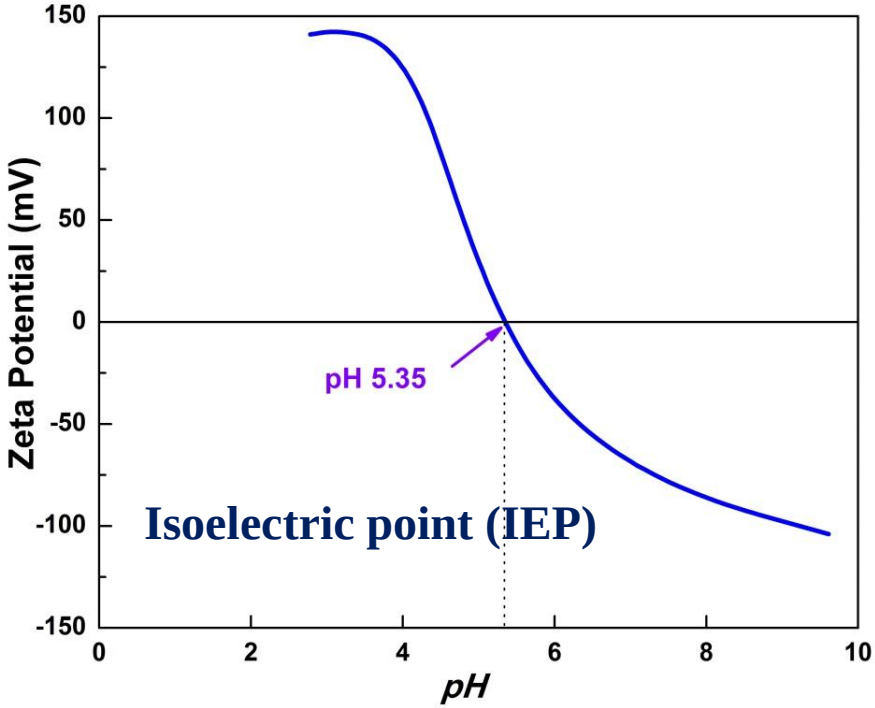
IEP = 5.35 pH

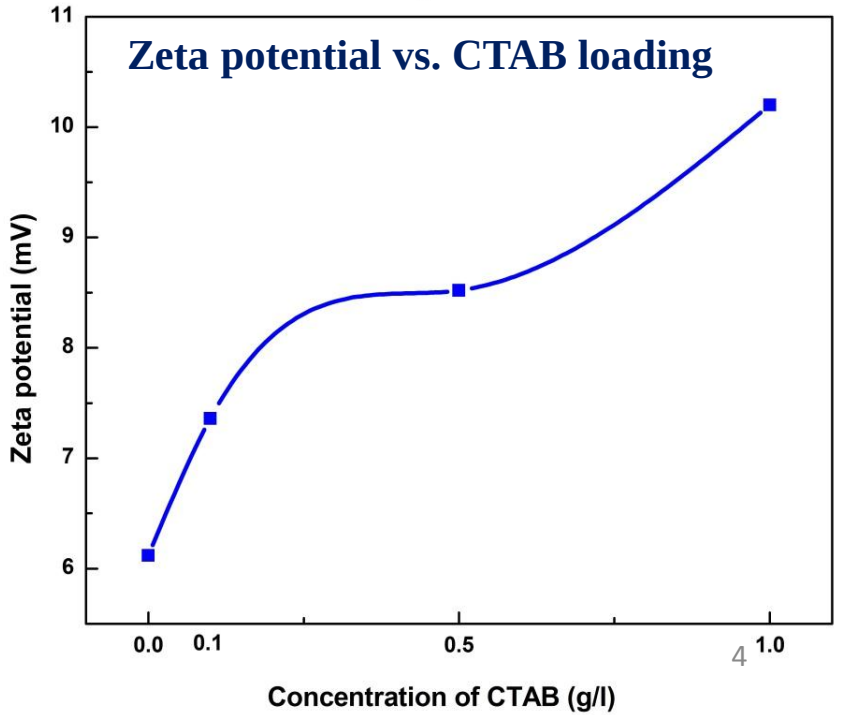
The Electrolyte pH < IEP

- **To avoid possible agglomerations of ZrO_2**
- **Uniform codeposition of ZrO_2 particles**

Size ranges from 13−37 nm





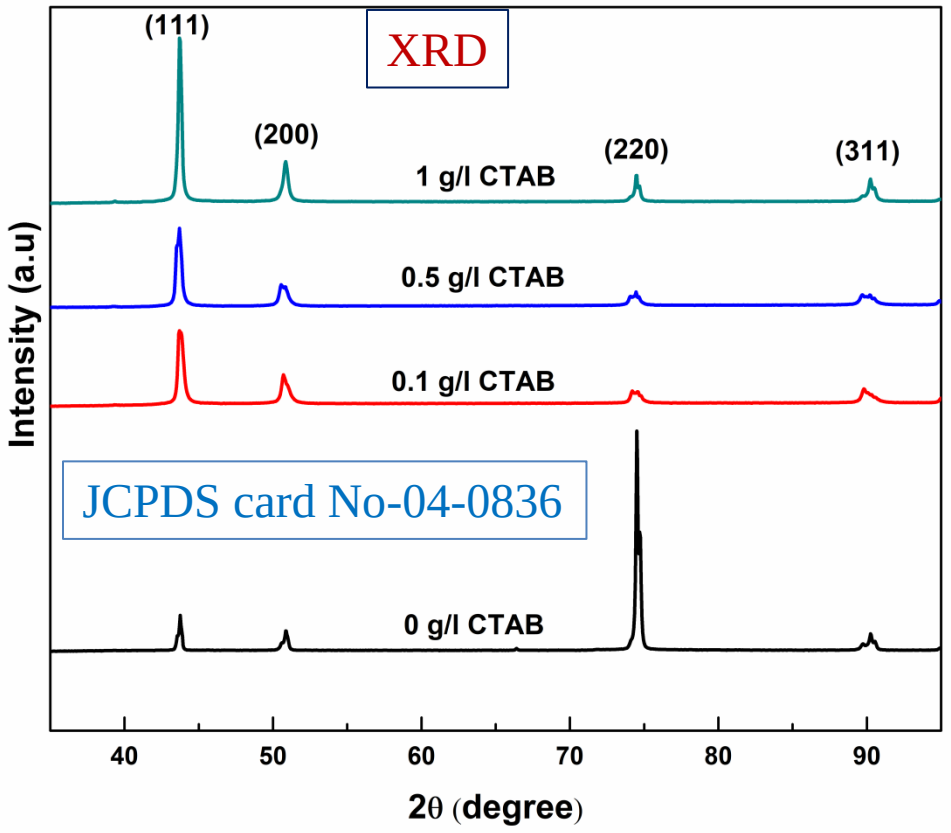


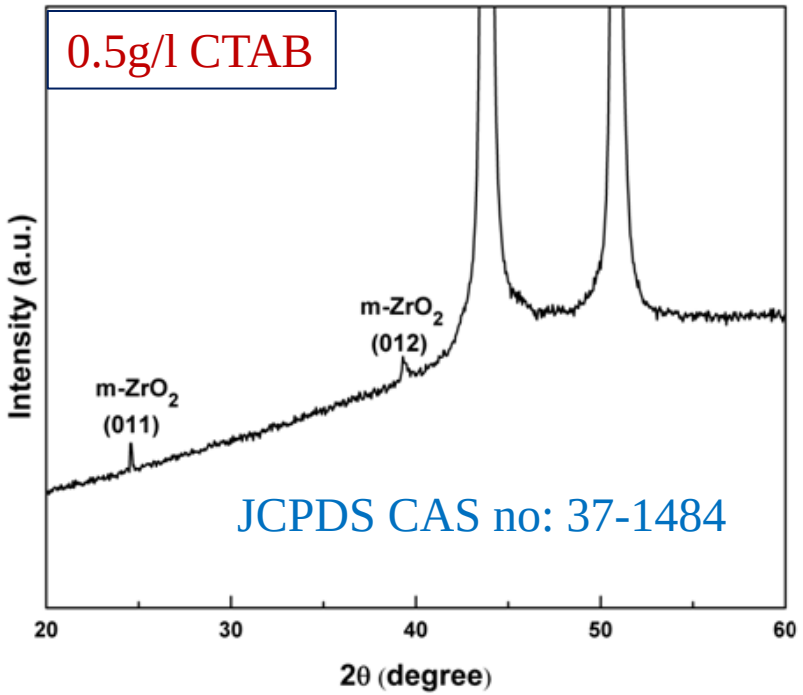
XRD analysis:

$$RTC_{(hkl)} = \frac{I_{(hkl)} / I_{0(hkl)}}{\sum (I_{(hkl)} / I_{0(hkl)})} \times 100\%$$

(220) —CTAB→ **(111)**

(Low atomic density) (High atomic density)





Relative Texture Coefficients:

Sample Details	$RTC_{(hkl)}$%			
	(111)	(200)	(220)	(311)
Without CTAB	03	04	85	08
0.1g/l (CTAB)	28	24	22	26
0.5g/l (CTAB)	45	21	20	14
1.0g/l (CTAB)	34	19	30	17

Microstructures:

Coarse

0.1g/L ↓

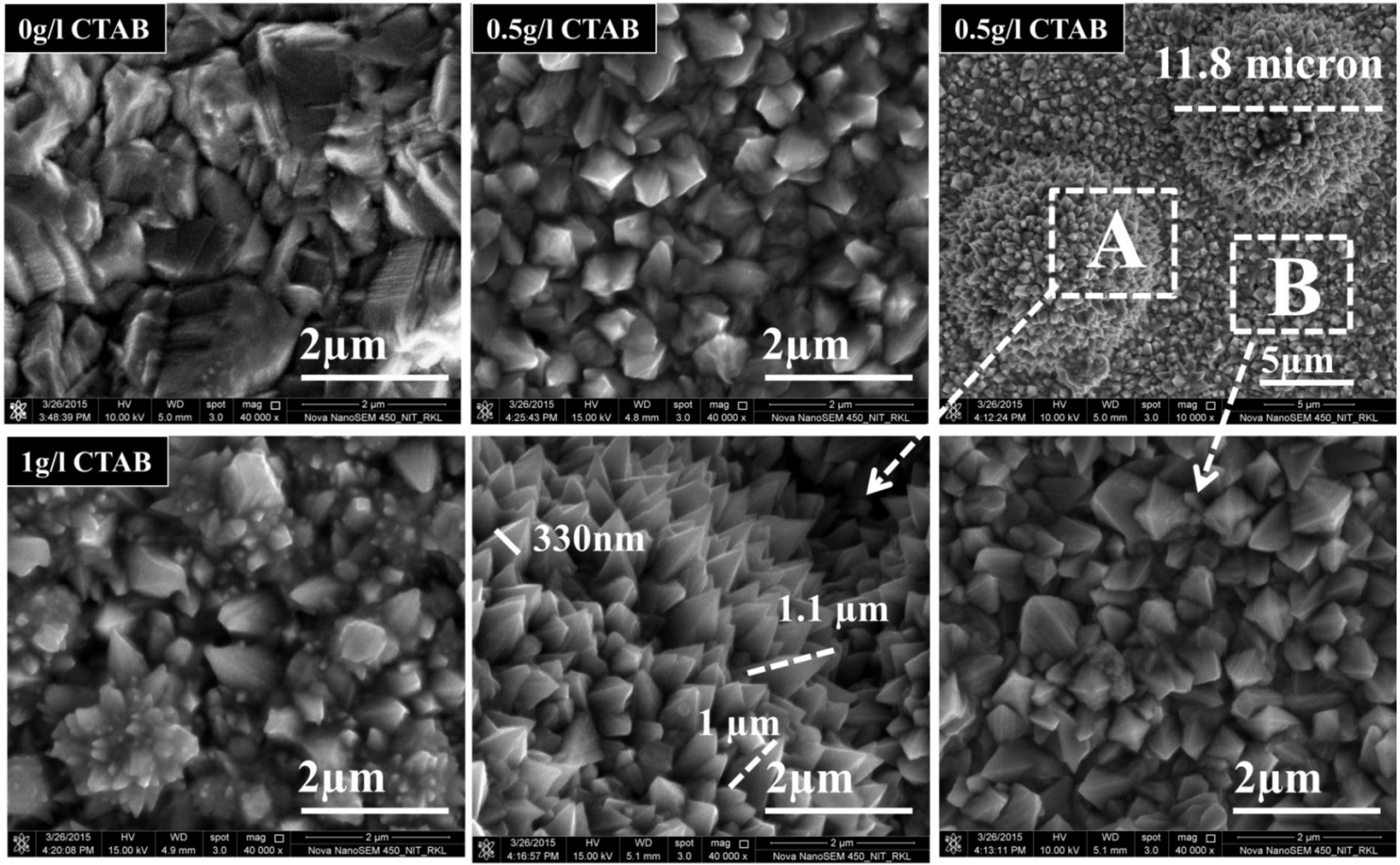
Finer nano-cone

0.5g/L ↓

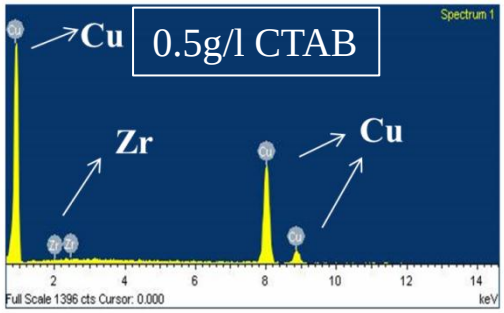
Duplex hemispherical with hierarchical nano-cone

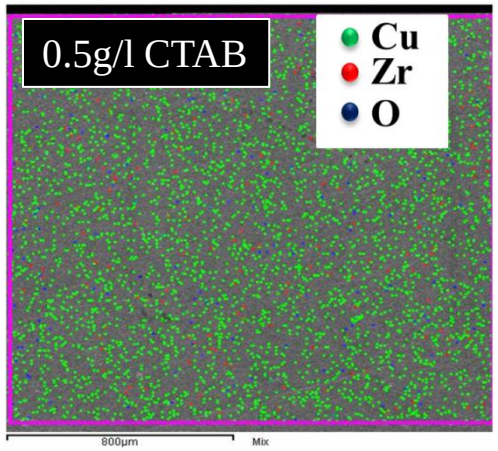
1g/L ↓

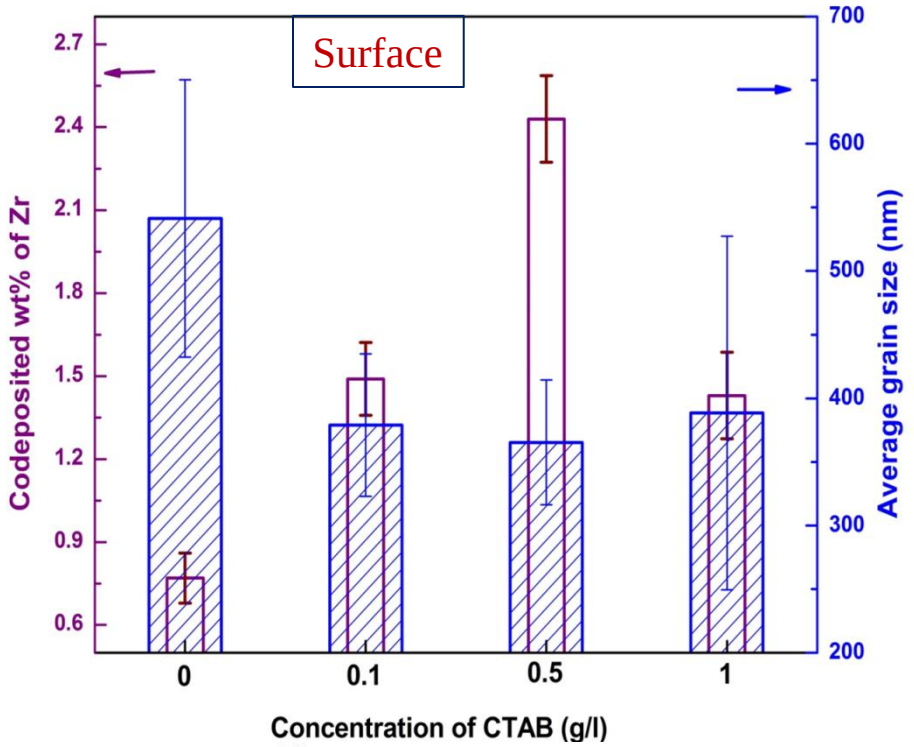
Dual structured flowery appearance with hierarchical nano-cone



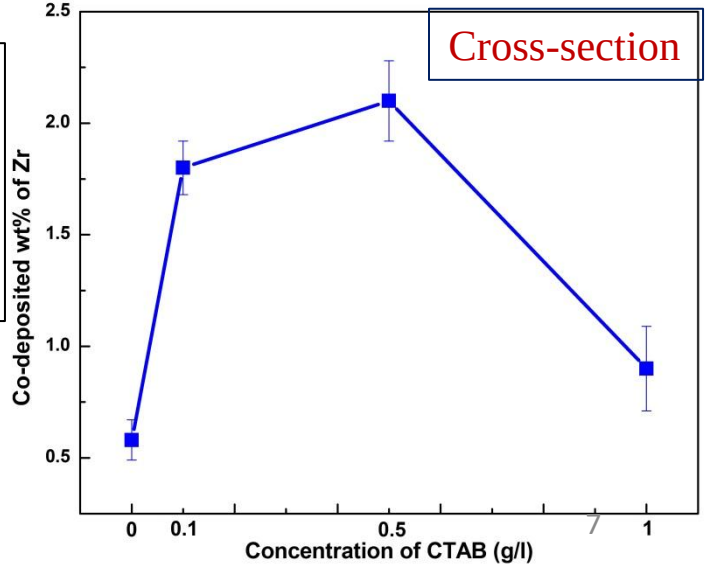
Compositional analysis:





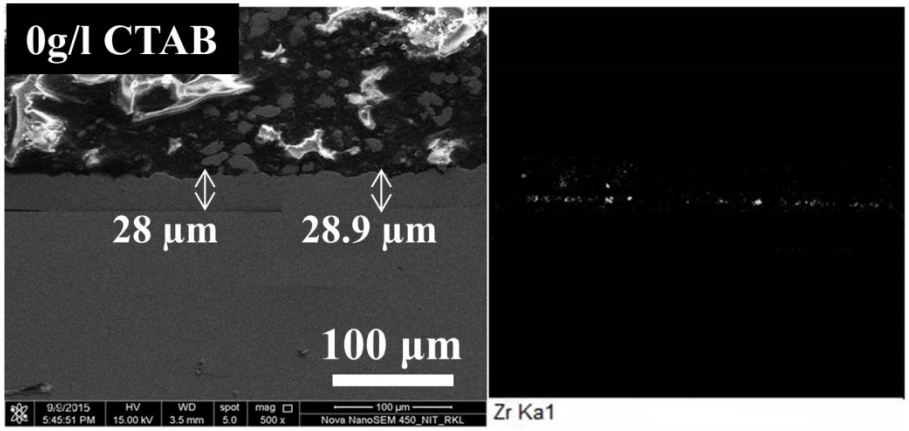


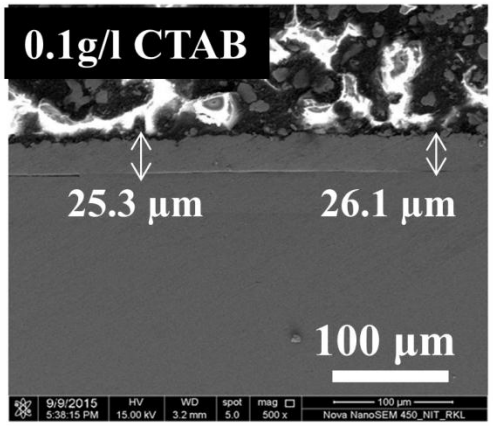
- Confirmation of presence and uniform distribution of Zr along with O in Cu matrix
- CTAB addition up to 0.5g/l facilitates ZrO_2 codeposition.

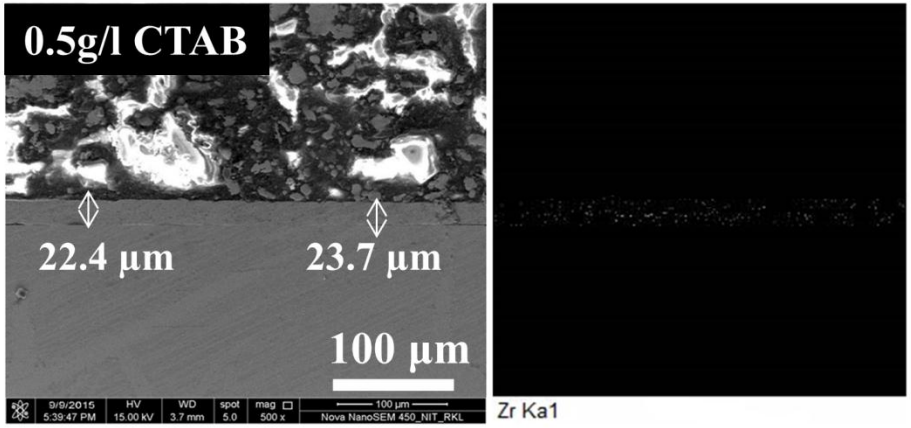


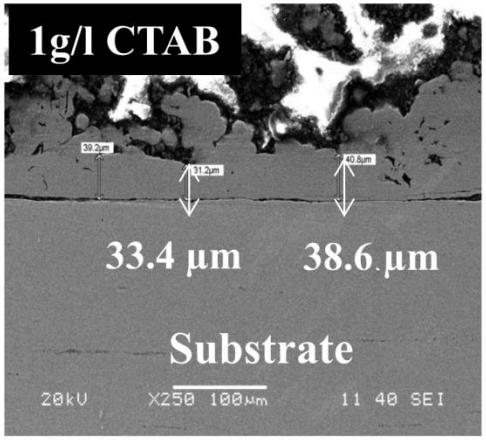
Coating thickness:

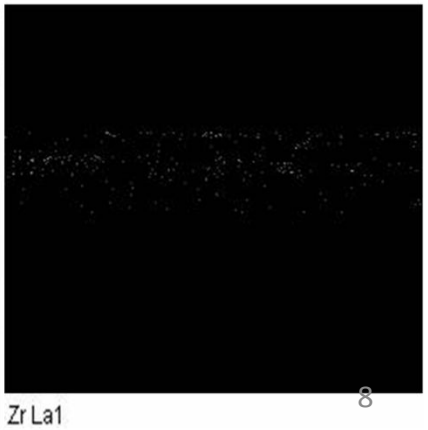
- Zr mapping of cross-sections also confirm the ZrO_2 codeposition.
- CTAB concentration (up to 0.5g/l) is proportional to $\frac{1}{Film\ thickness}$
- Coating thickness ~ crystallographic orientation ~ nucleation growth ~ ZeO_2 content







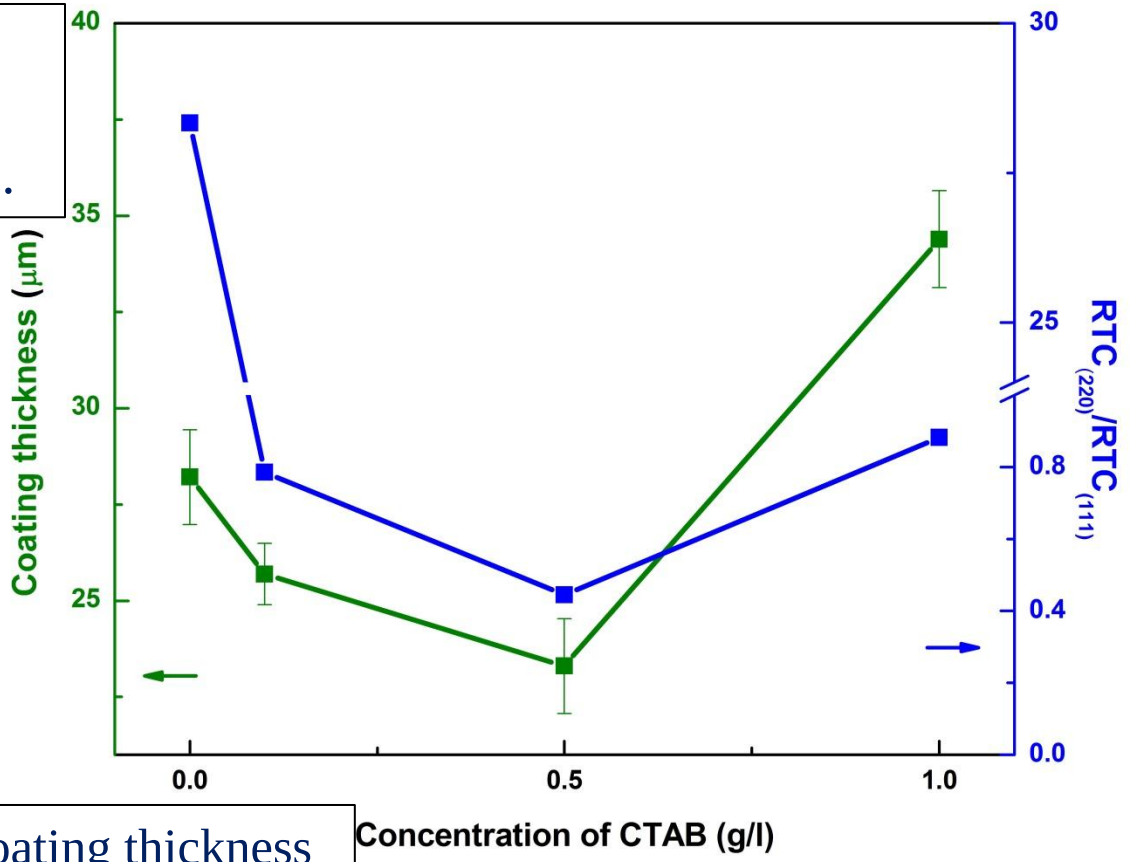




CTAB addition in electrolyte up to 0.5g/l may lower the Cu deposition rate and decrease the film thickness.

(111) Orientation ↑

Coating thickness ↓



$RTC_{(220)}/RTC_{(111)}$ is proportional to coating thickness

Decrease of film thickness.

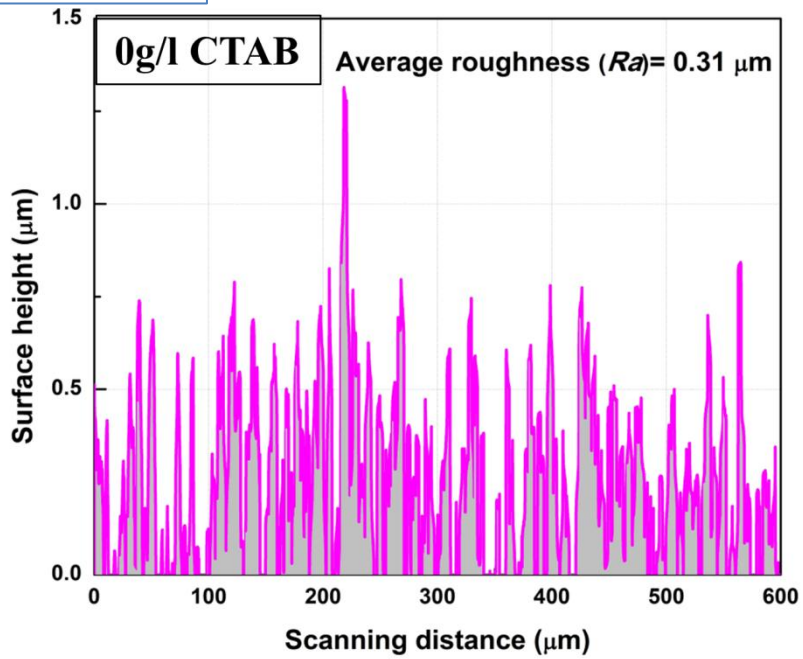
↓

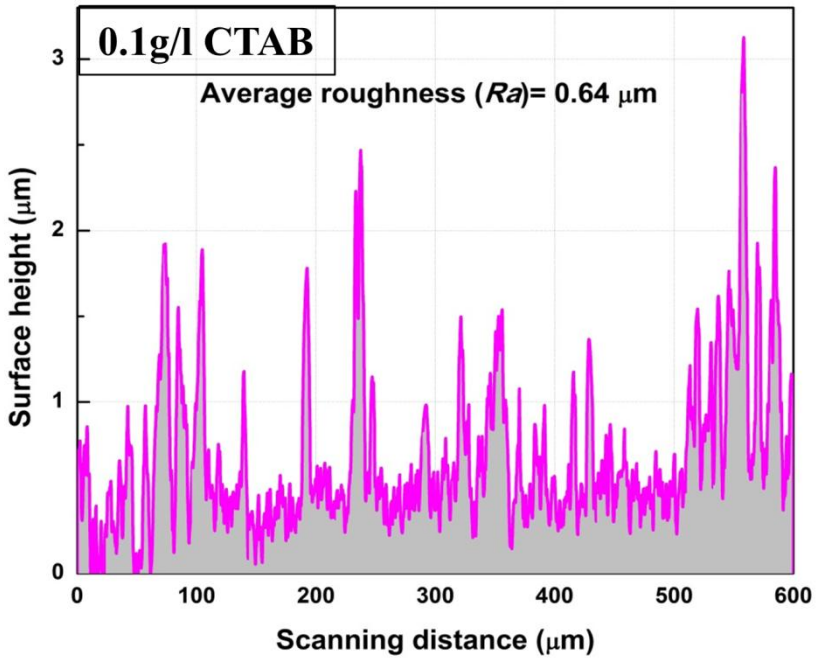
Decreasing amount of strain energy may be accommodated.

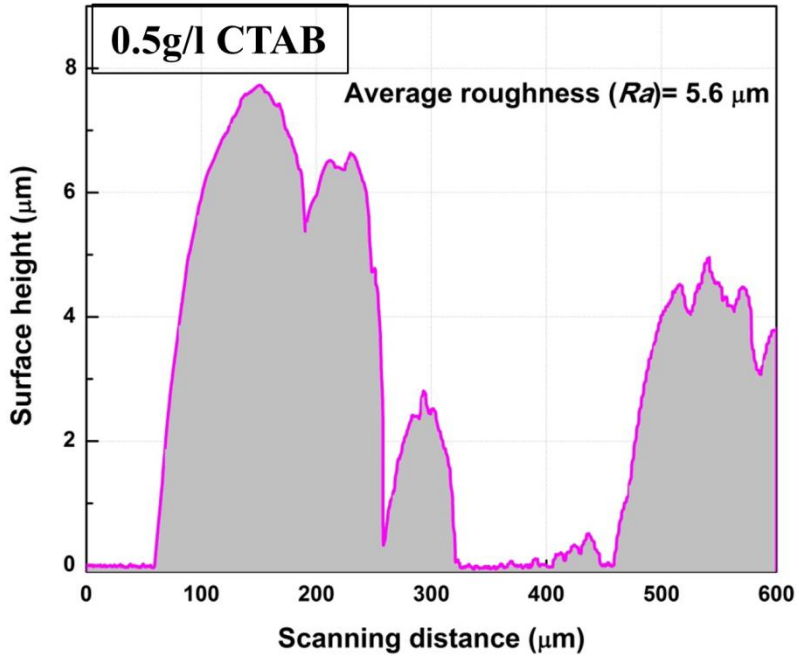
↓

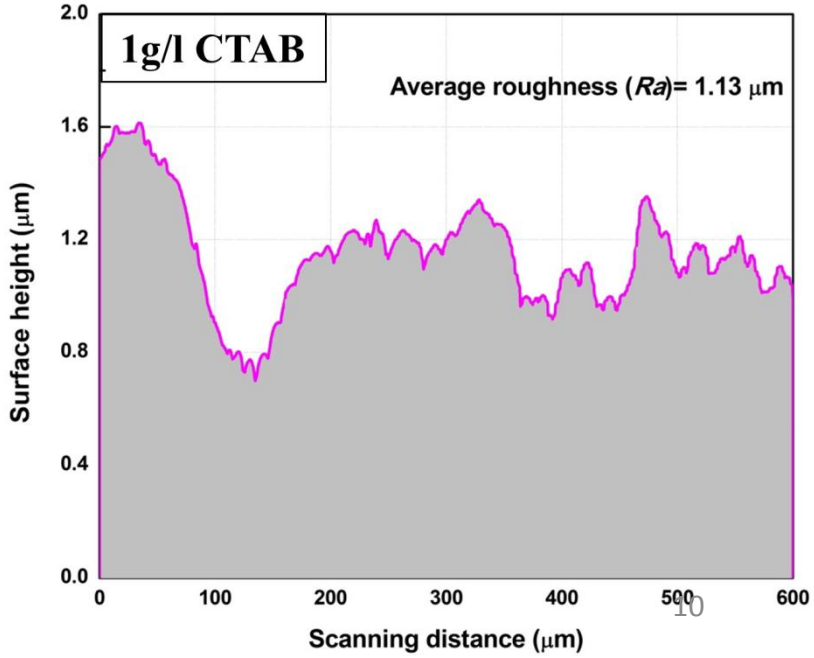
The (111) texture is favoured (Because (111) planes accommodate lesser strains than (220) planes).

Surface roughness:









Hardness:

Dual hardness

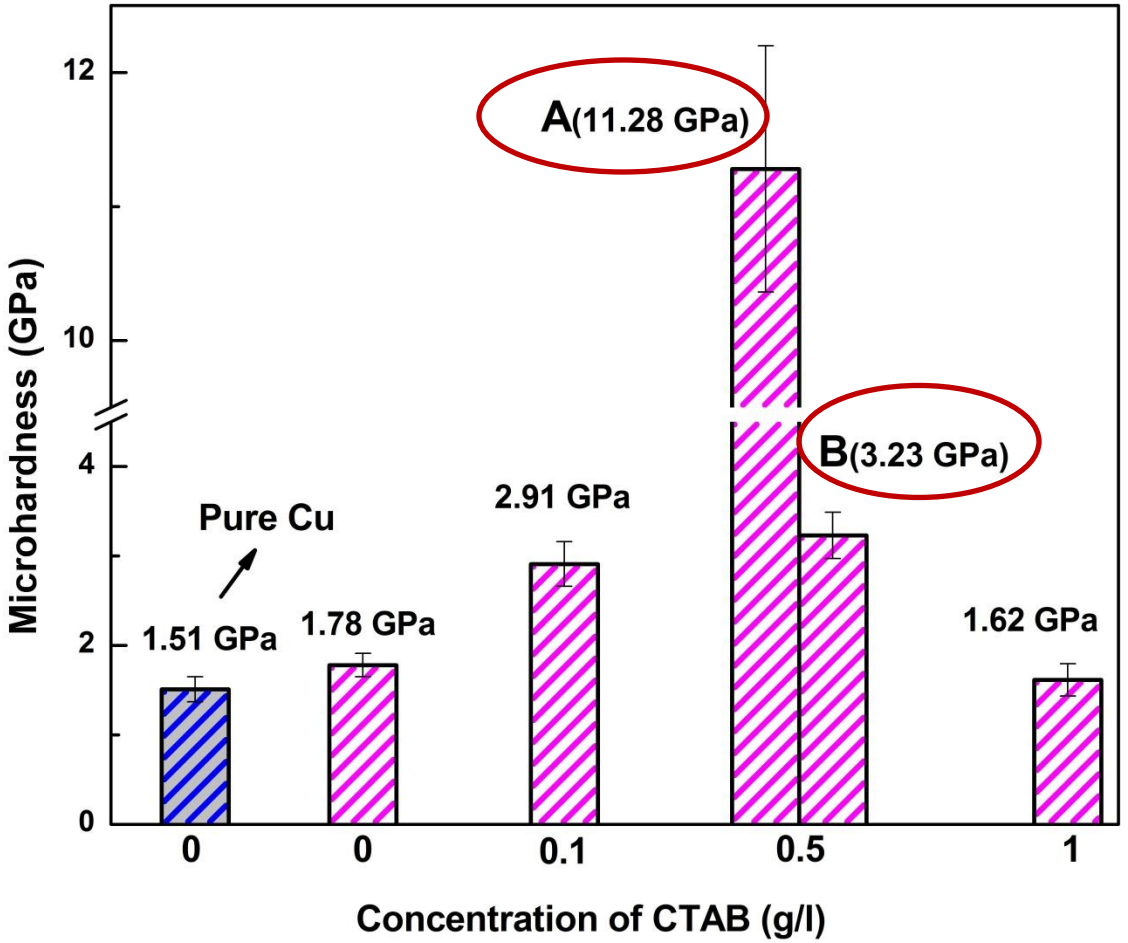
↓

0.5g/l CTAB added coating

Higher hardness of Cu-ZrO_2 coating

↓

- Codeposition of ZrO_2 particle
- Preferred (111) orientation
- Conical coating structure



Lowest hardness of 1.0 g/l CTAB coating among all composite coatings

↓

- Coarser matrix compared to 0.1 and 0.5 g/l CTAB added coating.
- Smaller value of $RTC_{(111)}$ and lower value of ZrO_2 content in the coating.

Wear analysis:

Lowest wear depth → 0.5g/l CTAB added coating

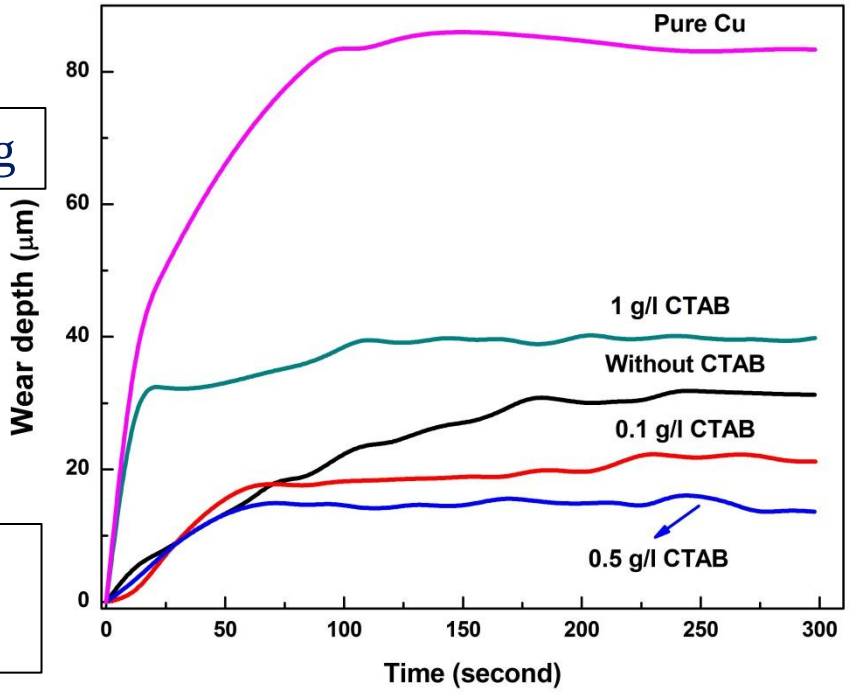
Wear depth result is similar to hardness trend.
Penetration rate also depict similar trend.

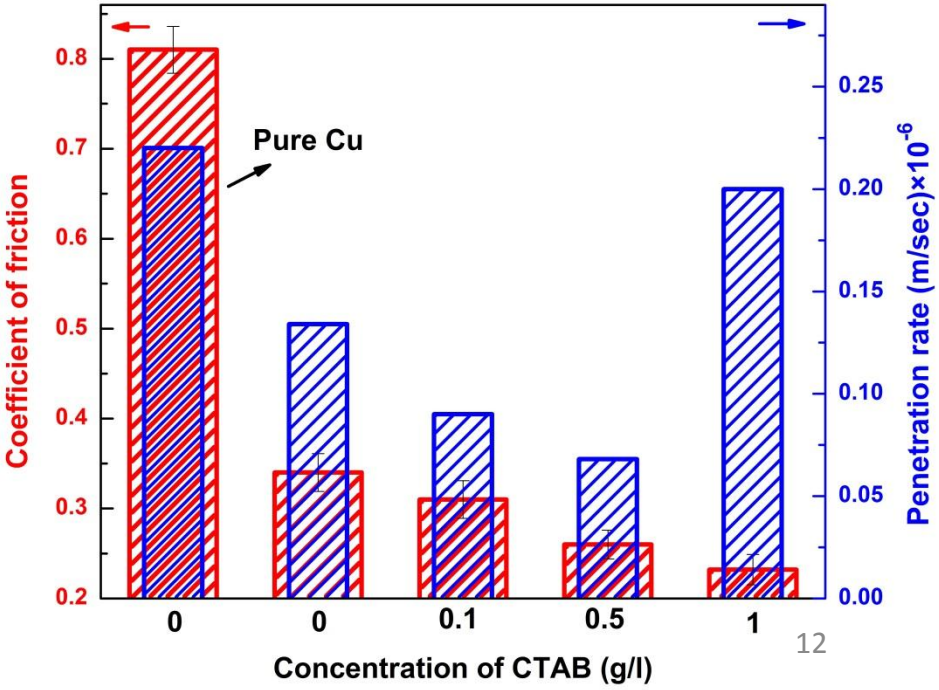
- Coefficient of friction (COF) is proportional to CTAB loading.

Lowest COF of 1g/l CTAB added coating
(in spite of lower wear resistance and hardness)

↓

Due to less contact between indenter and coating surface



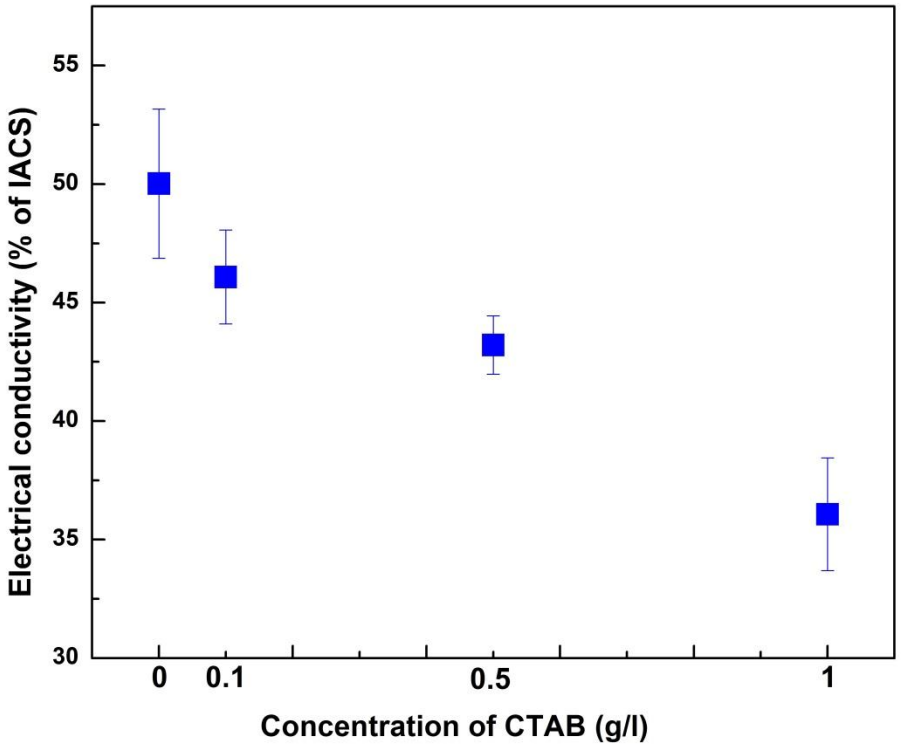


Electrical conductivity:

Without CTAB coating = 50.2% of IACS

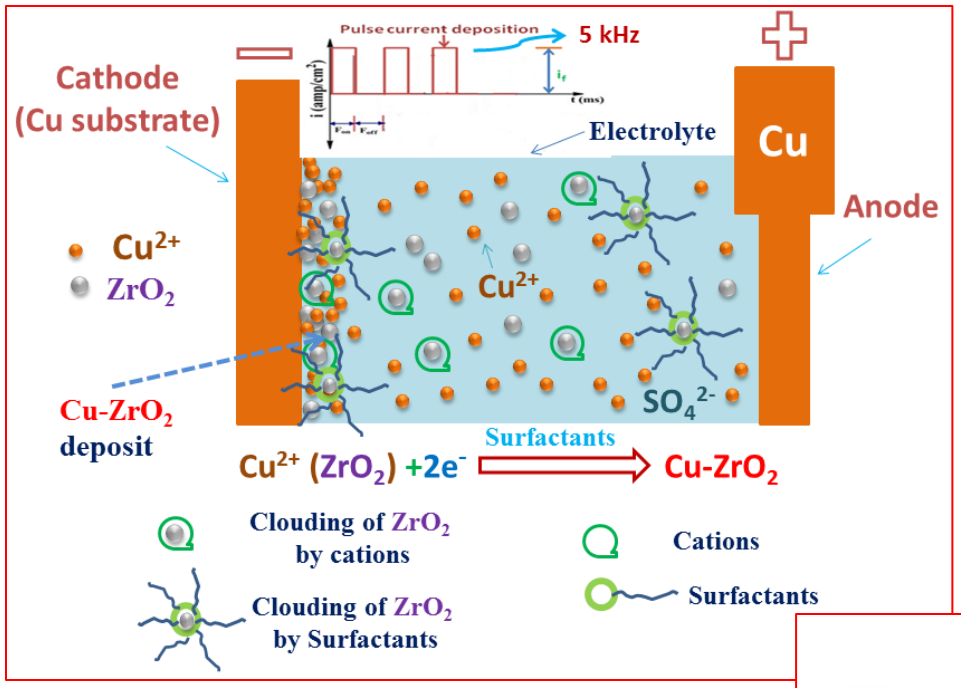
CTAB added coating = 36.3-46% of IACS

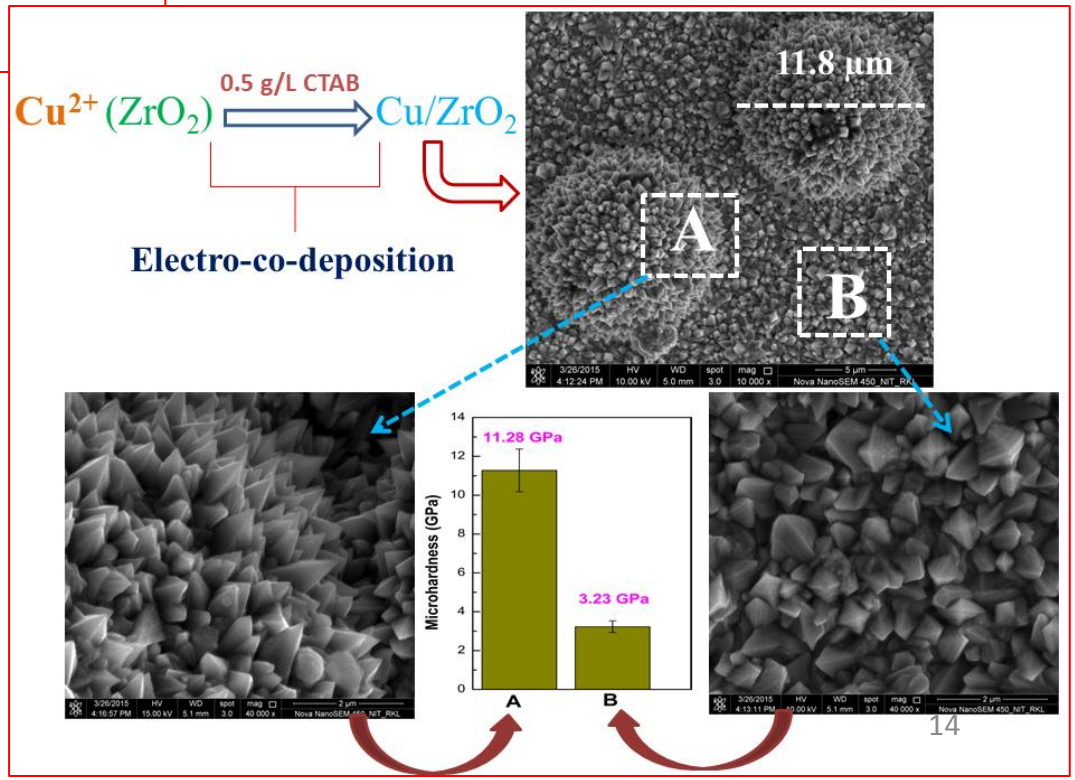
Lower electrical conductivity
(0.5 and 1g/l CTAB added coating)



- Insulating ZrO_2 codeposition
- Duplex structure

Higher surface roughness ⟶ Lower contact area ⟶ Lower electrical conductivity


Pulse current deposition
5 kHz
i (amp/cm²)
t (ms)
Cathode
(Cu substrate)
Electrolyte
Cu
Anode
Cu2+
ZrO2
Cu2+
SO4 2-
Cu-ZrO2
deposit
Surfactants
Cu2+ (ZrO2) +2e-
Cu-ZrO2
Clouding of ZrO2
by cations
Cations
Clouding of ZrO2
by Surfactants
Surfactants


Cu2+ (ZrO2)
0.5 g/L CTAB
Cu/ZrO2
Electro-co-deposition
11.8 µm
A
B
11.28 GPa
3.23 GPa
Microhardness (GPa)
0
2
4
6
8
10
12
14
A
B

Conclusions:

- After addition of CTAB in the electrolyte the developed Cu-ZrO_2 composite coating shows unique nano-cone structures.
- By considering all the properties, 0.5 g/l CTAB assisted Cu-ZrO_2 coating was considered as best among all developed coatings.
- Hardness obtained in the present study was quite high compared to earlier reported literatures. These observations are attributed towards nano-cone structure, amount of ZrO_2 added to the coating and crystallographic orientation.
- Coating obtained with CTAB shows marginal drop in electrical conductivity compared to non CTAB assisted composite specimen. The coatings obtained in the present study can be used for possible electrical applications with better surface mechanical property.

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