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Effect of Surface Preparation of Copper on Self-Assembly of Fullerene Molecules

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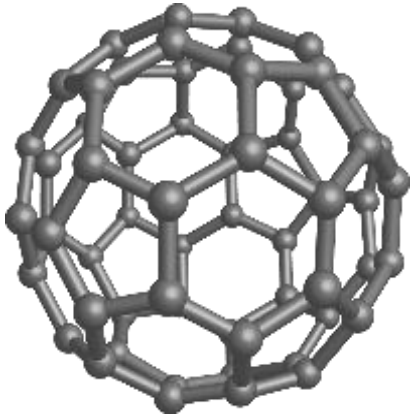
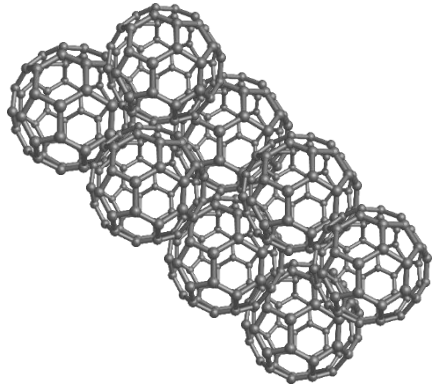
Objective

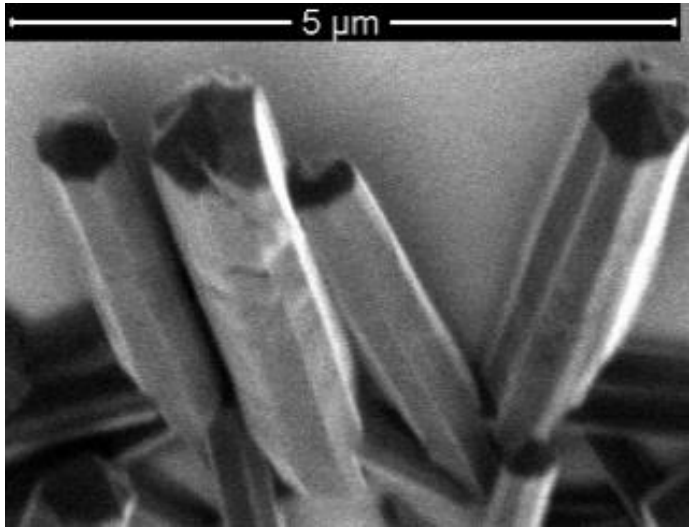
- Effect of surface preparation of copper on:

➢ Substrate mediated controllable self-assembly of **fullerene rods**



C_{60} buckyball



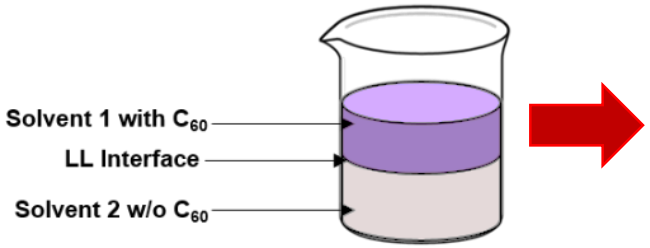


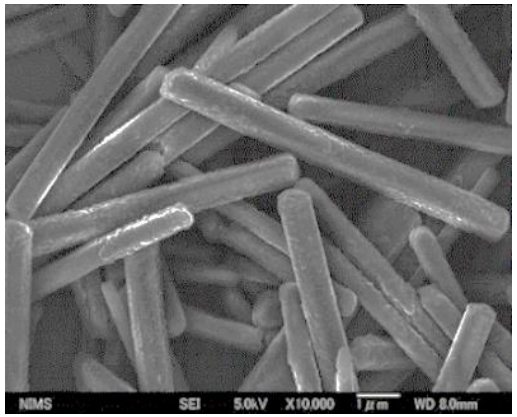
C_{60} nano-rods

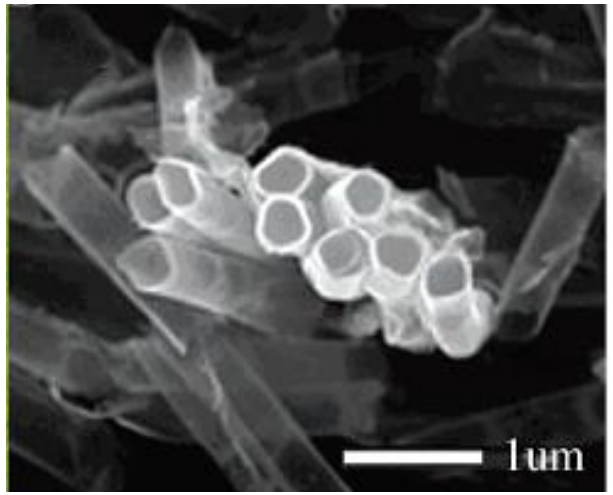
➢ Ultimately enable high-aspect ratio molecular C_{60} wires as interconnects

Background: Conventional Methods for Fullerene Nanostructures

- **Conventional synthesis techniques**
  - Liquid-Liquid Interfacial Precipitation (LLIP): *time consuming (a few hours - two weeks)—no substrate needed.*
  - Template based self-assembly: *longer processing time, expensive and broken nanotubes obtained—Porous alumina template to be infiltrated by fullerene solution.*



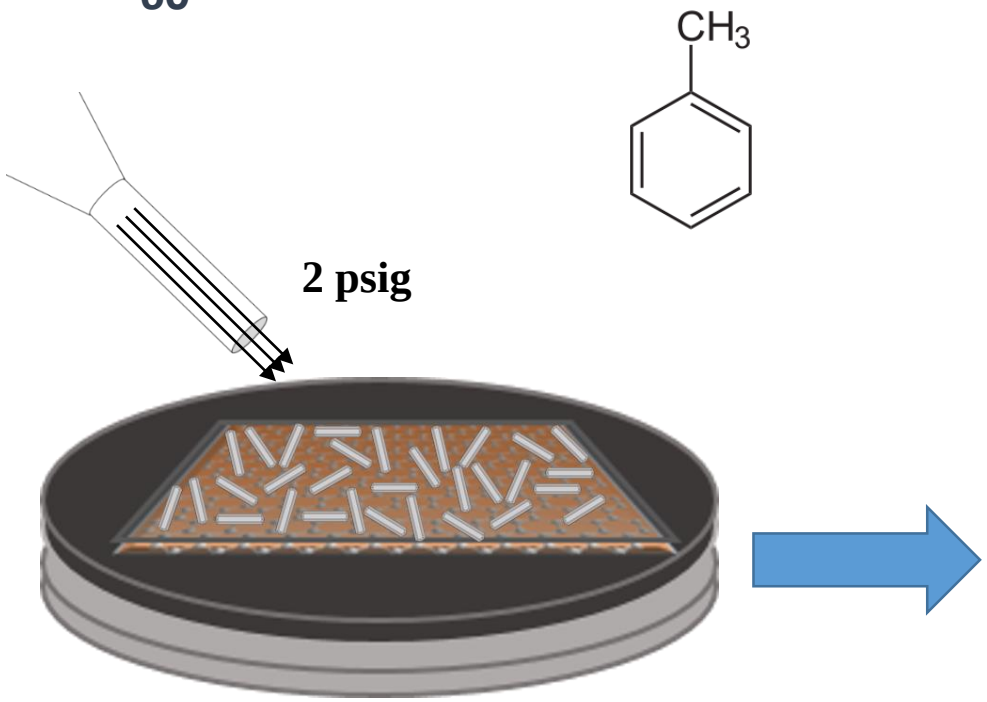


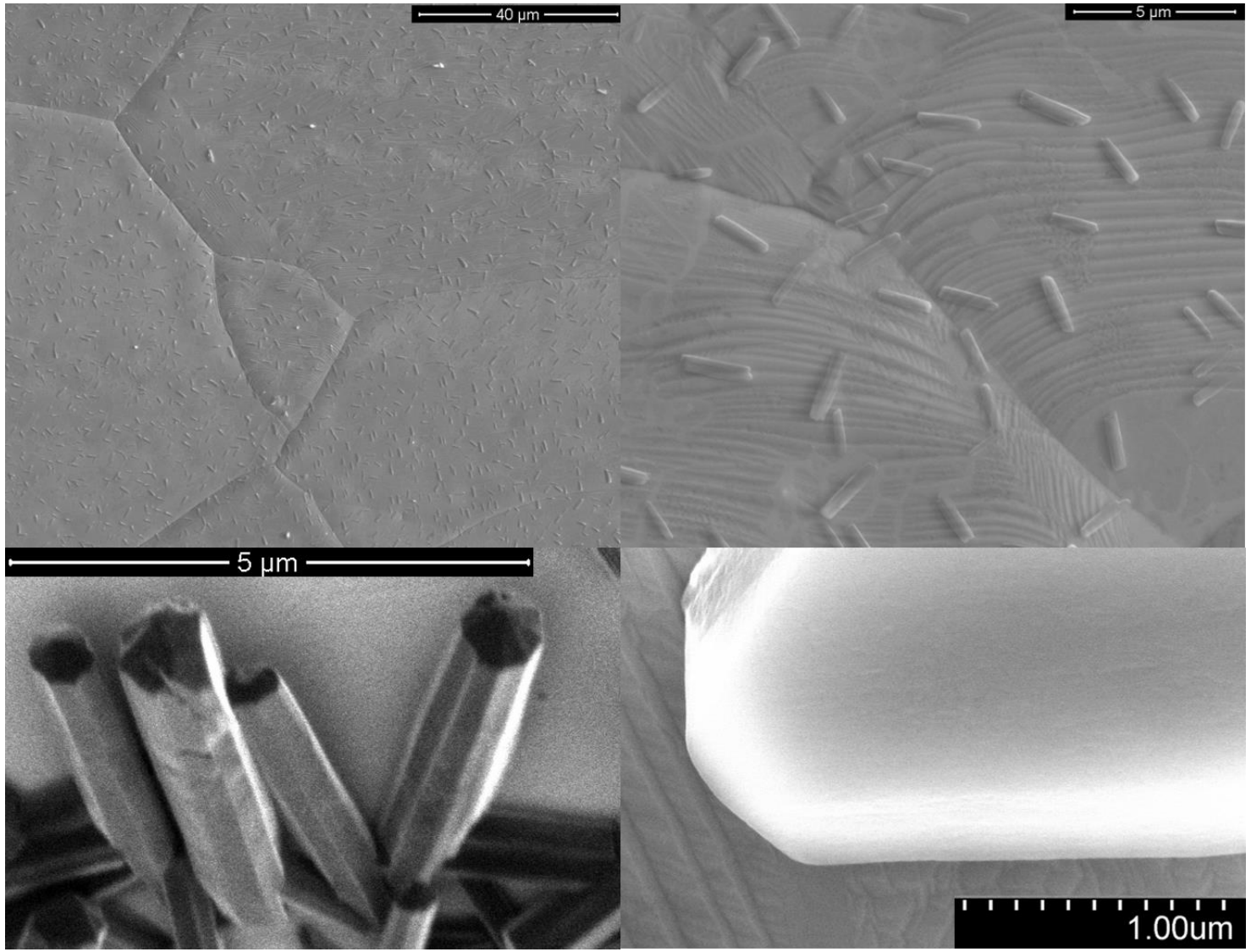


Background: Surface mediated synthesis

Directed Air Stream: leads to fullerene rods

C_{60} dissolved in Toluene





Self-assemblies size:

- **Length: ~2 µm**
- **Width: ~500-700 nm**

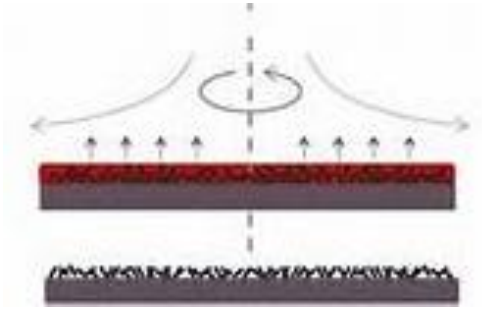
Current Method: Spin coating based substrate mediated route

Substrates	Solution	Spin coating procedure	Spin coating RPM
Cold rolled Cu	Fullerene dispersed in Toluene (2mg/ml)	**1. Dispense solution.** **2. Wait for 1 minute.** **3. Spin substrate at a predetermined RPM.** **4. Spin for 30 seconds.** Repeated 1-4 procedure for total of 4 times.	200-500 RPM
Annealed Cu			
Electropolished Cu			
Graphene coated Cu			

1) Dispense

2) Waiting time

3) Ramp-up spreading



4) 30 seconds RPM. Drying

- **Overall processing time: < 10 minutes for one substrate of size $1\ cm^2$.**

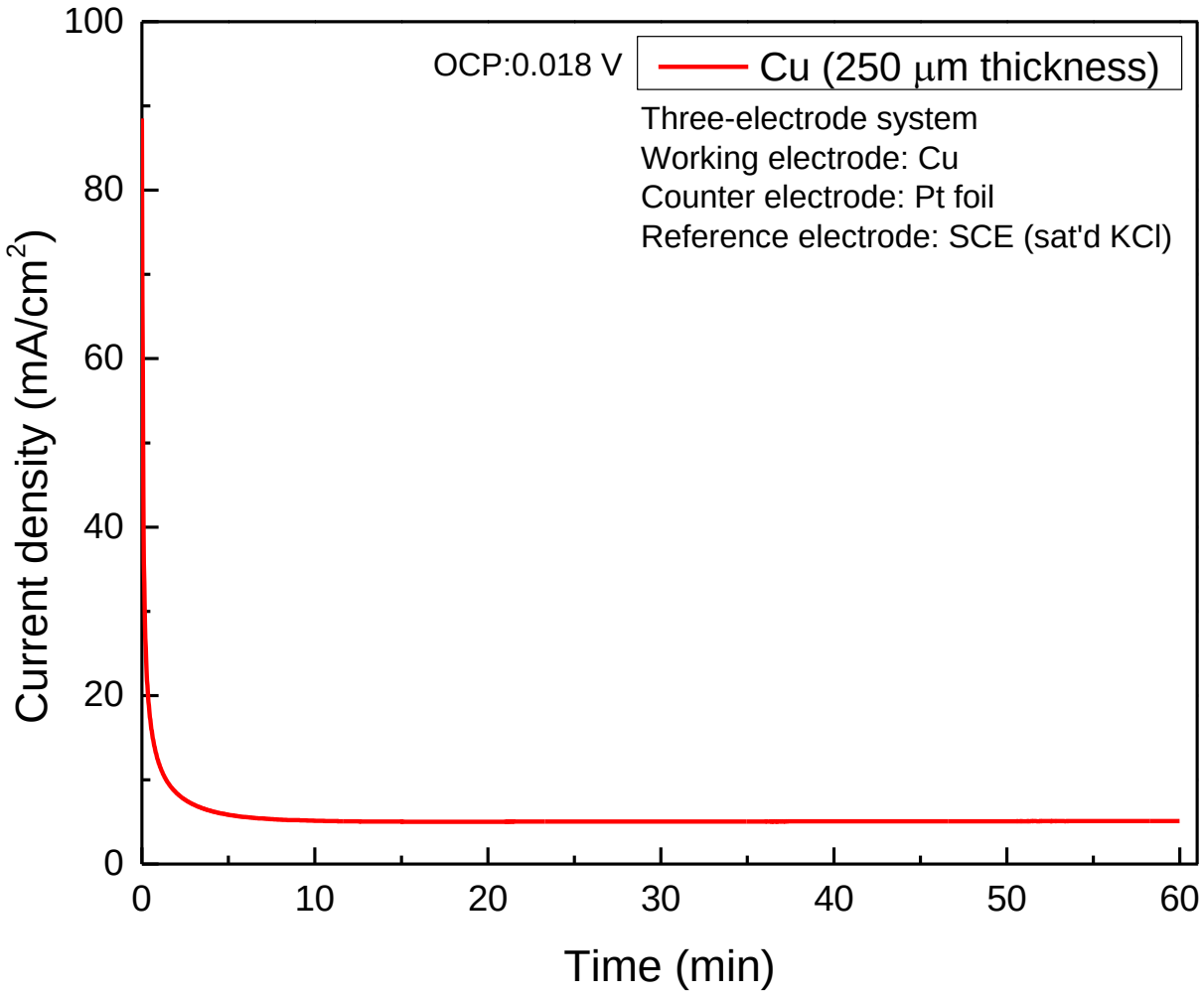
Substrate Preparation

Copper foil (0.25 mm thick, 99.99% metals basis, Alfa Aesar Puratronic®)

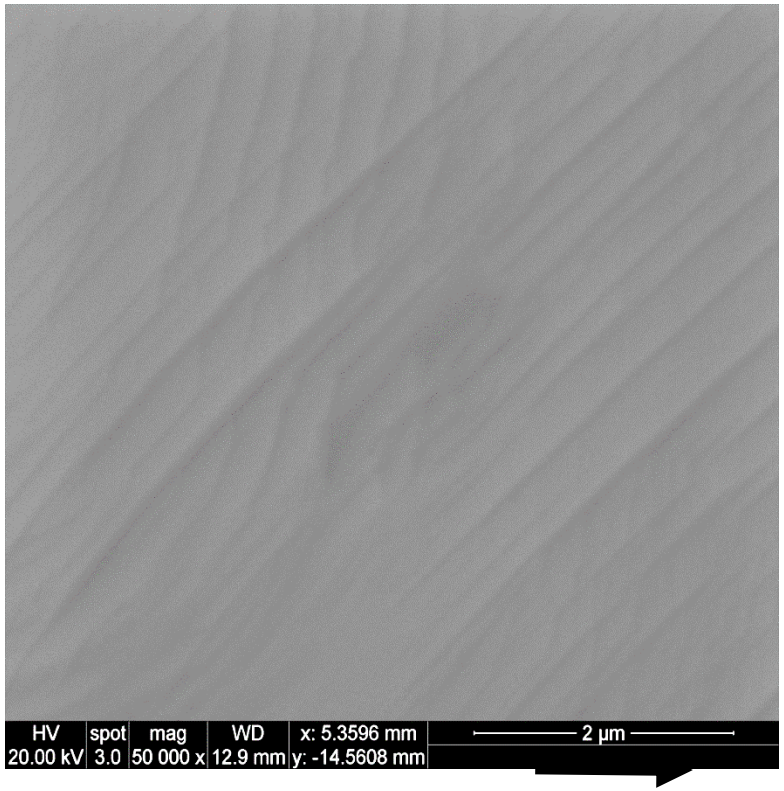
Cold rolled Cu (Contact angle of 72°)	Annealed Cu (Contact angle of 64°)	Graphene on Cu (Contact angle of 80°)	Electropolished Cu (Contact angle of 72°)
Organic impurities removal: IPA rinsed, DI water rinsed, and blown dry with nitrogen.			
	Annealed in a tube furnace (Lindberg Blue M) for 2 hours at 1050°C.	Graphene on Cu via chemical vapor deposition (CVD).	Acetic acid treatment: 1) Immersed in 2M acetic acid solution at 60°C for 10 min. 2) DI water rinsed and blown dry with nitrogen. *Electropolishing procedure shown on next slide.*

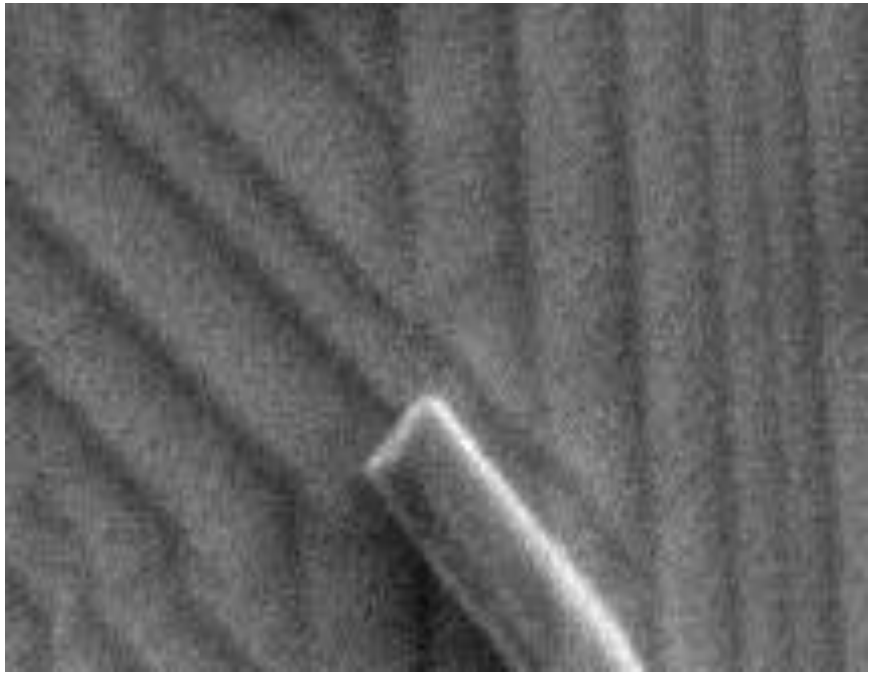
Preparation of Substrates: Electropolishing Procedure

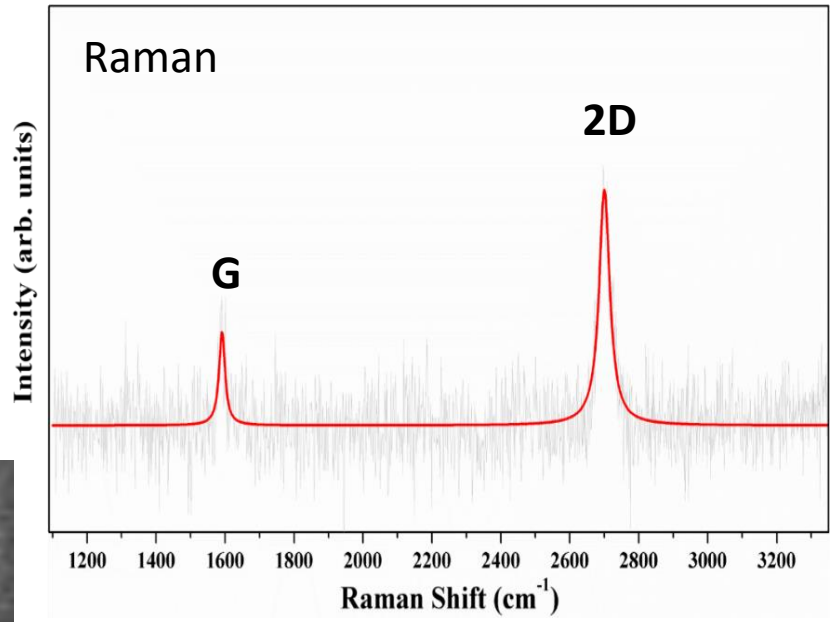
- Solution: 85% phosphoric acid.
- Applied a constant potential of 1.5 V vs. SCE for 1 hour.



Graphene grown *via* chemical vapor deposition (CVD)





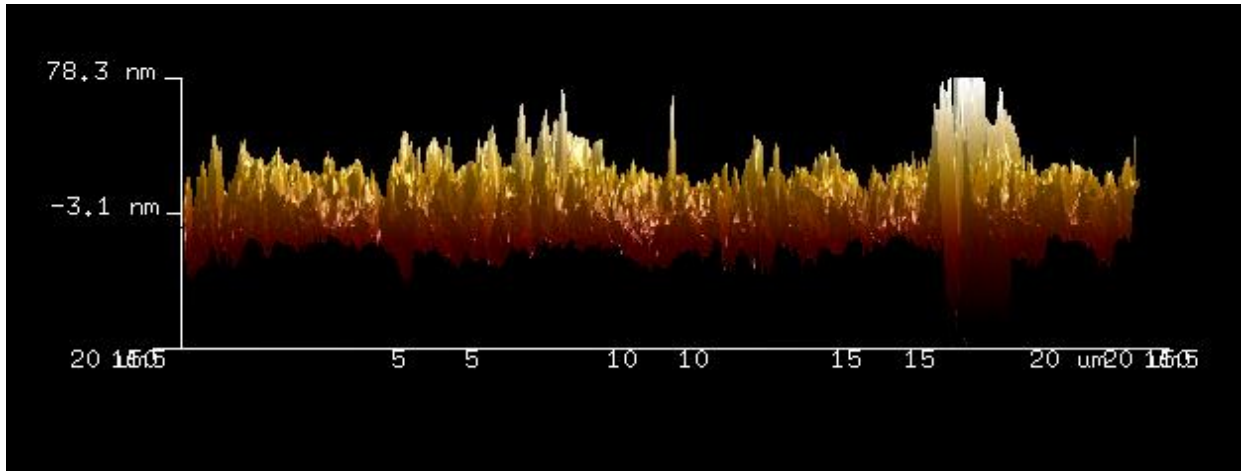


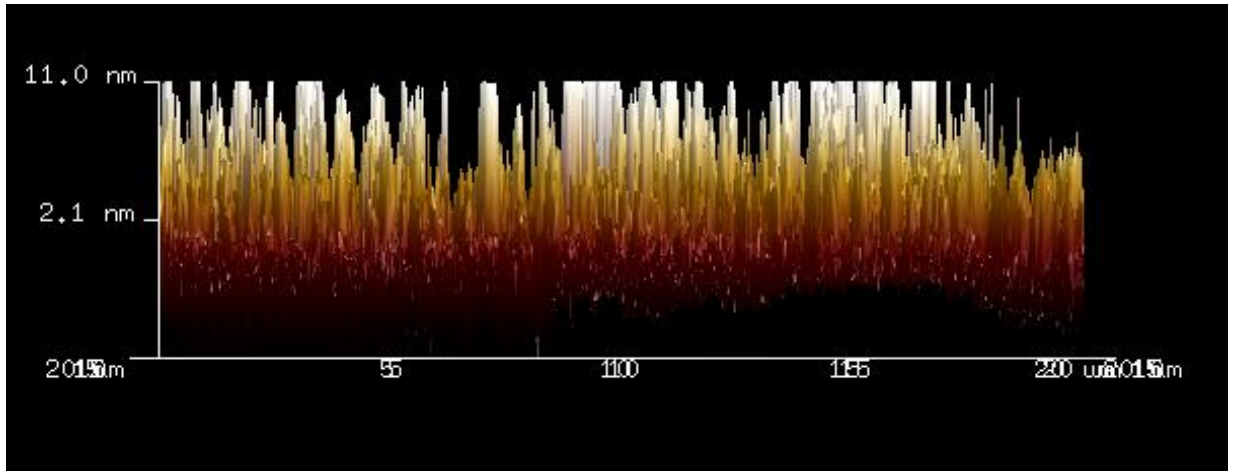
- CVD grown graphene shows characteristic ripple structure.

CVD conditions:
Pressure of 200 mTorr
Temperature of 1050°C
100 sccm Argon
60 sccm Hydrogen
20 sccm Methane

SURFACE CHARACTERIZATION

Surface Roughness of Cold Rolled Cu and Electropolished Cu an AFM Analysis

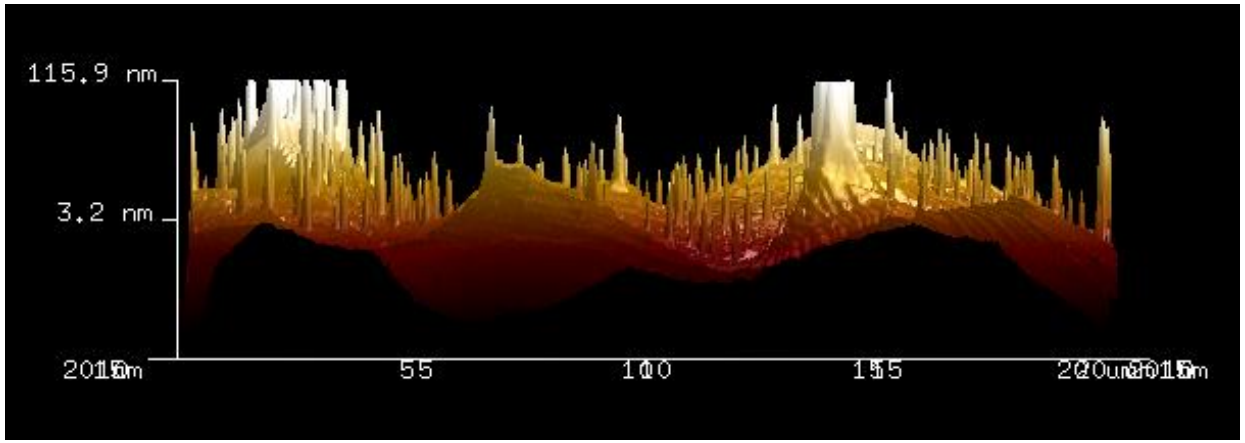


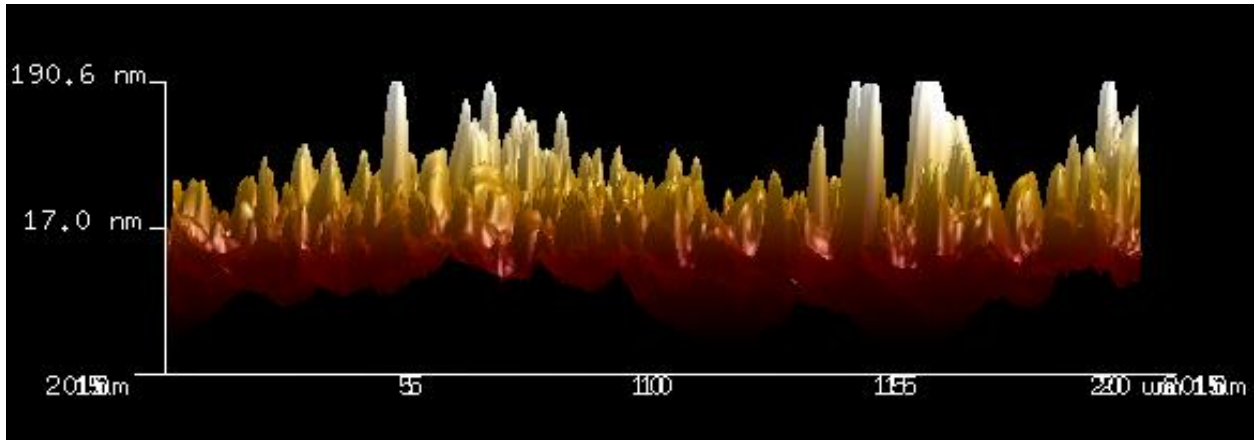


Cold rolled Cu
(**surface roughness rms : 15.5nm**)

Electropolished Cu
(**surface roughness rms: 4.7nm**)

Surface Roughness of Annealed Cu and Graphene Coated Cu an AFM Analysis





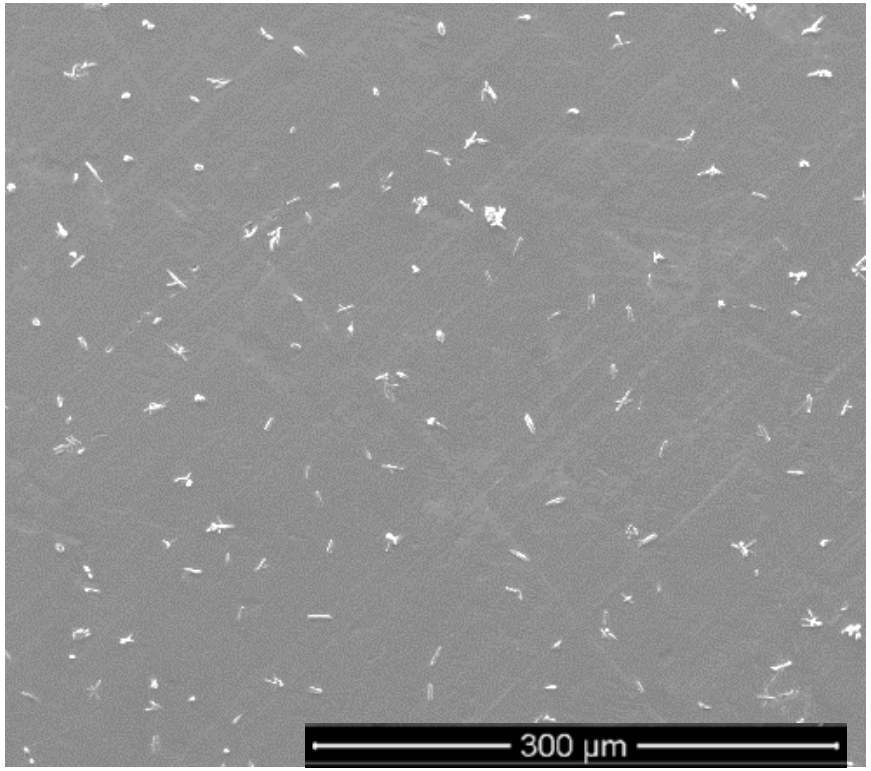
Annealed Cu
(**surface roughness rms: 53.3nm**)

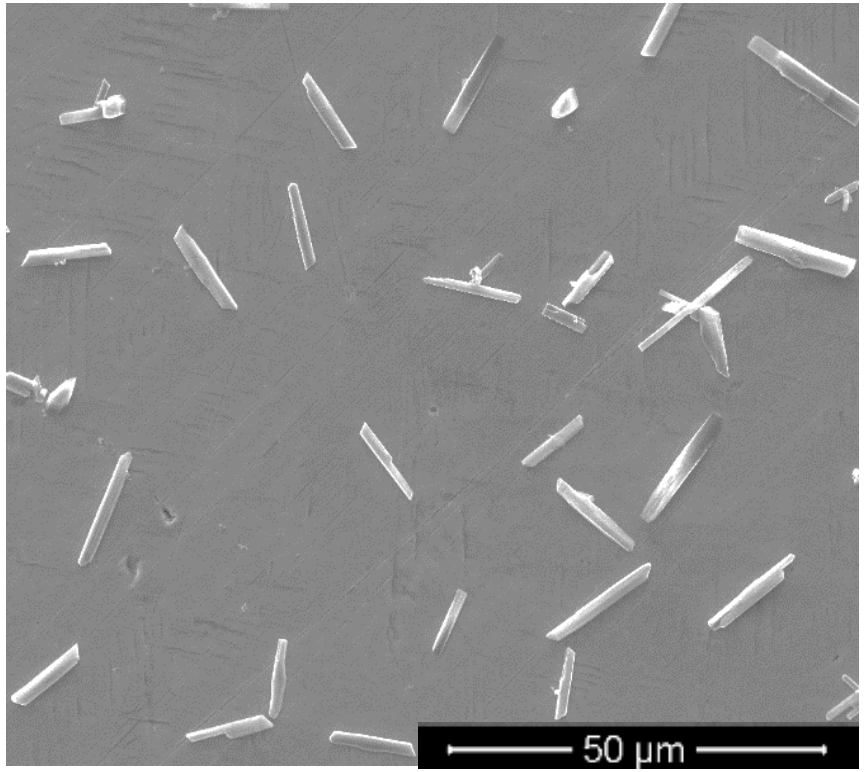
Graphene Coated Cu
(**surface roughness rms: 41.5nm**)

Results and discussion

Substrates	Solution
Cold rolled Cu	▪ Fullerene dispersed in Toluene (2mg/ml)
Annealed Cu	
Electropolished Cu	
Graphene coated Cu	

Uniform distribution of Rod-like C_{60} Self-Assemblies on Cold Rolled Cu Substrate

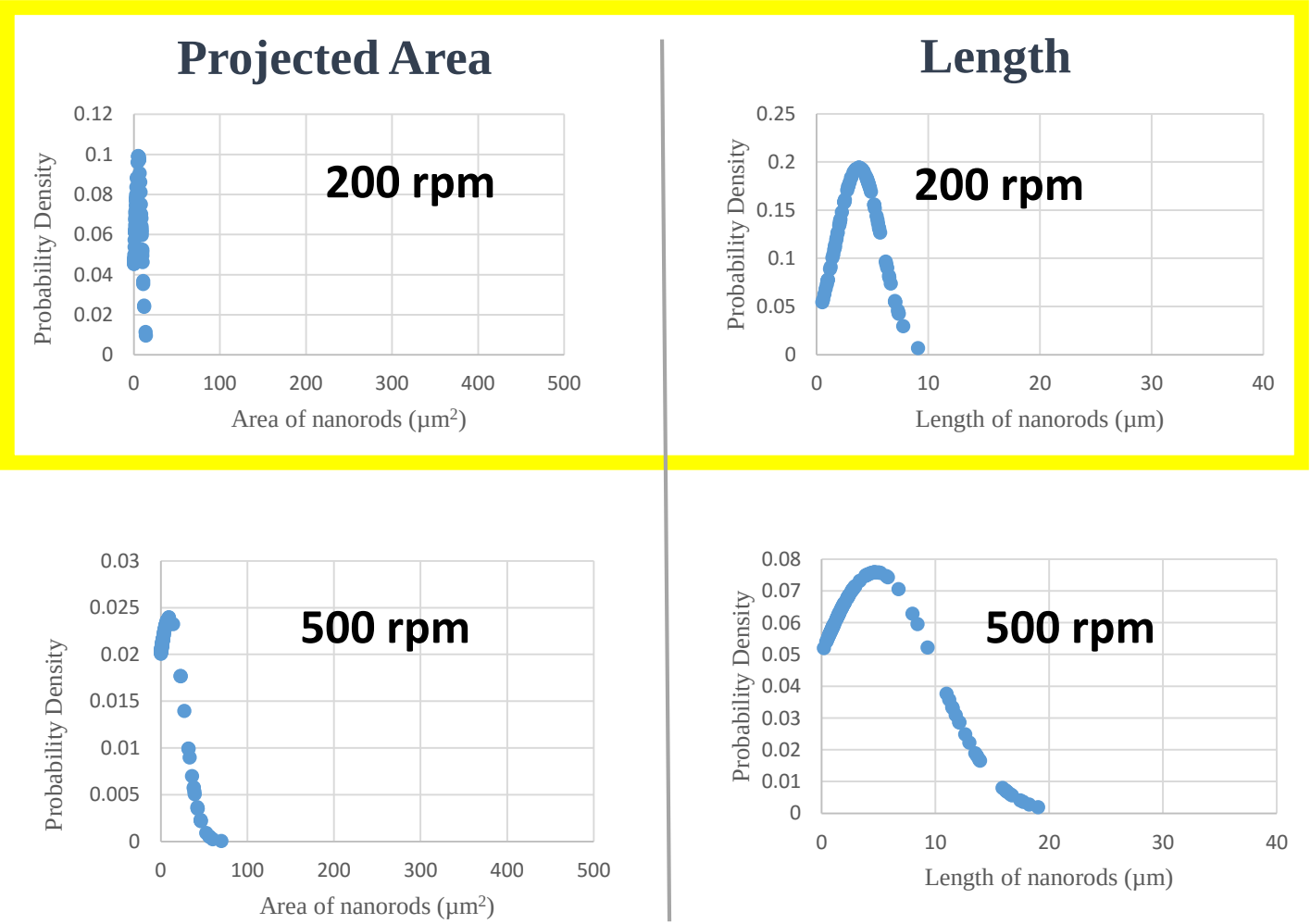




- Average length of fullerene self-assemblies (FSA) at 200 rpm: ~5 µm.

➢ **Good control over size and morphology of fullerene rods at lower rpm (next slide).**

Size Analysis : Projected Area and Length Distributions of C_{60} rods on Cold Rolled Cu Substrate

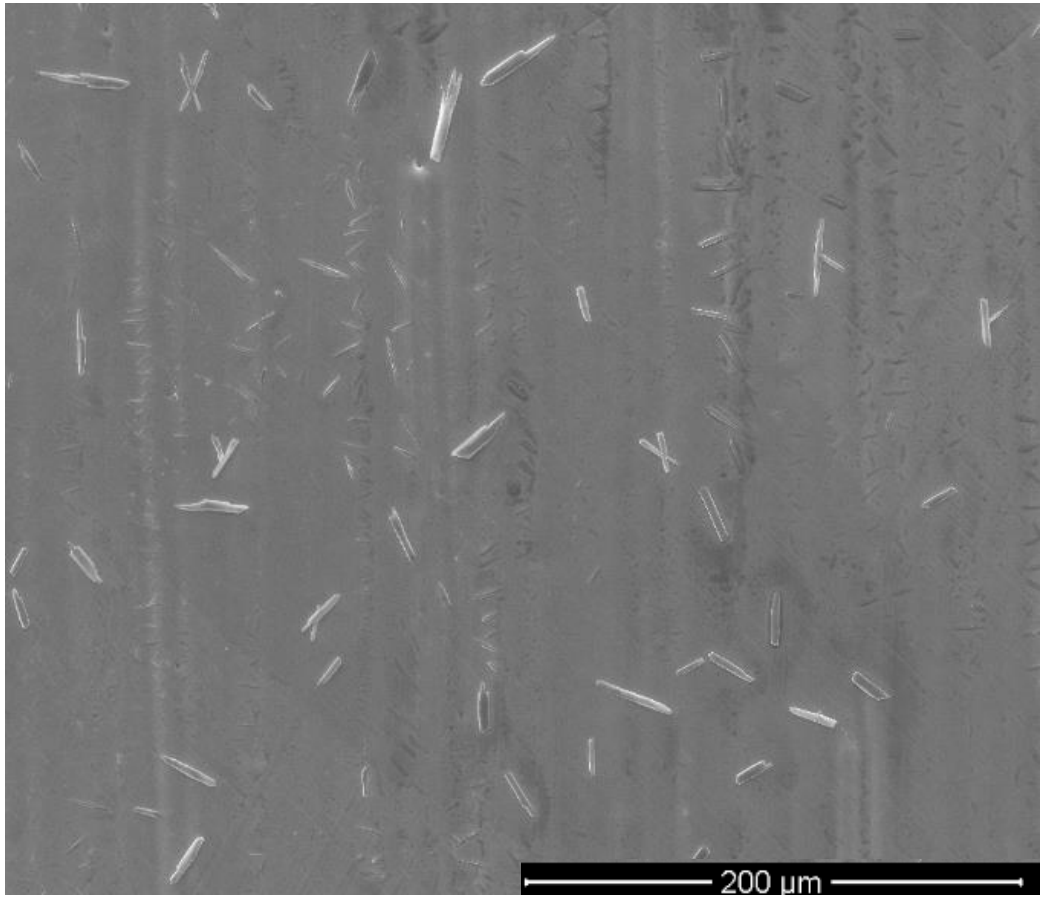


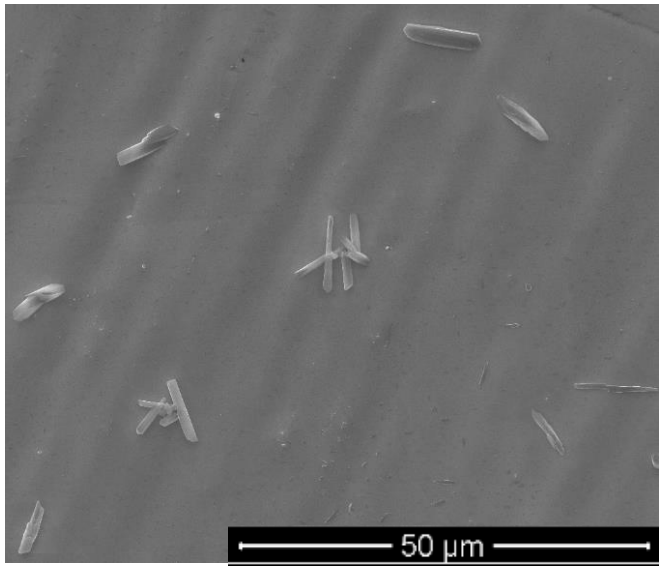
- Best distribution of rods at 200 rpm.
- Average length of fullerene self-assemblies at 200 rpm is ~5 µm.

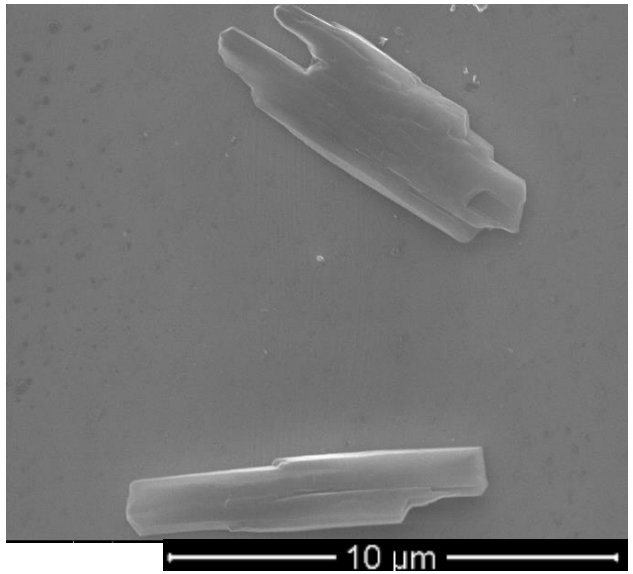
Results and discussions

Substrates	Solution
Cold rolled Cu	▪ Fullerene dispersed in Toluene (2mg/ml)
Annealed Cu	
Electropolished Cu	
Graphene coated Cu	

C_{60} Self-Assemblies on Annealed Cu Substrate: larger variations in size and morphology



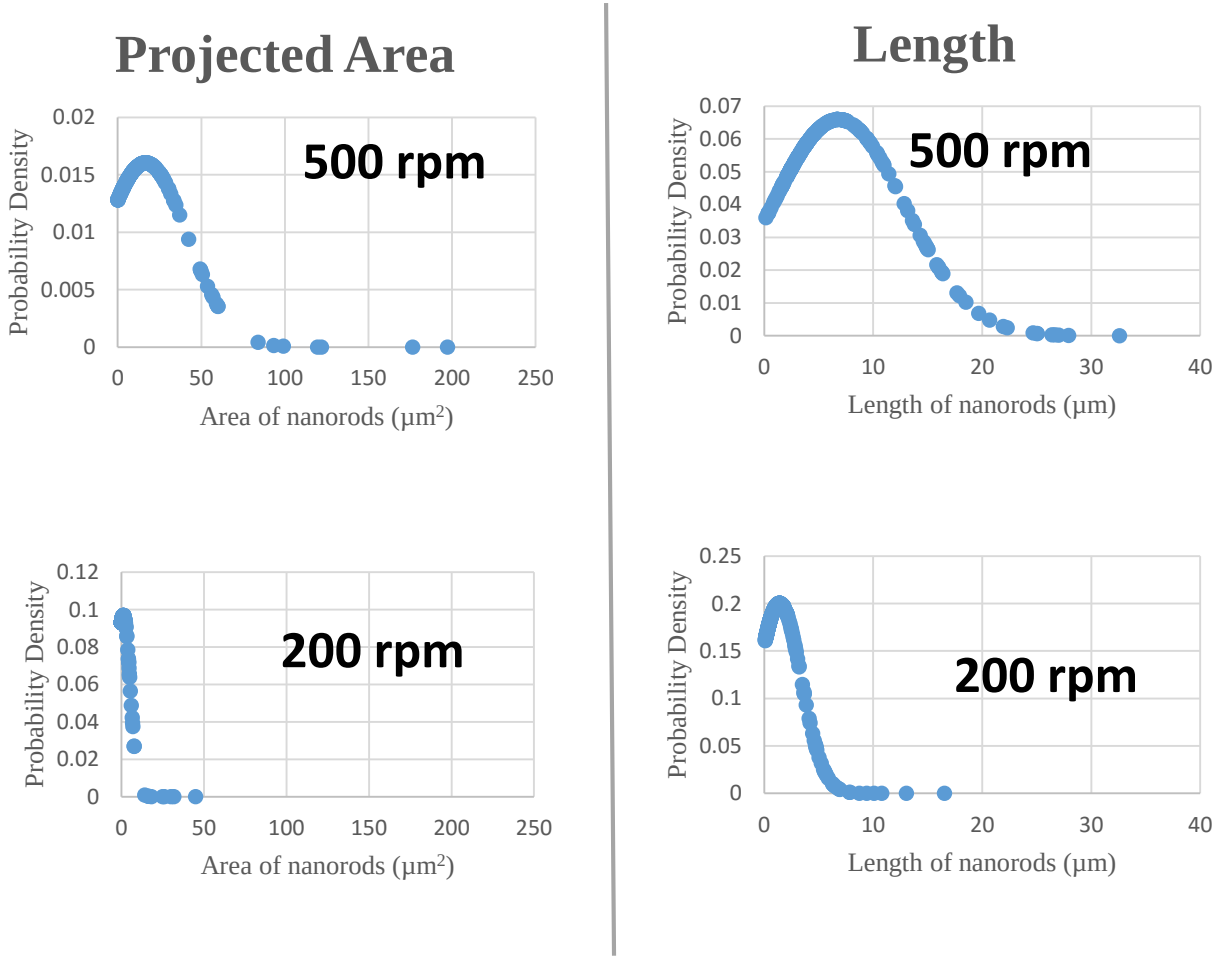




- Average length of FSA is ~5 µm.

➢ Less control over size and morphology of fullerene rods at lower rpm.

Size Analysis: Projected Area and Length Distribution of C_{60} self-assemblies on Annealed Cu Substrate

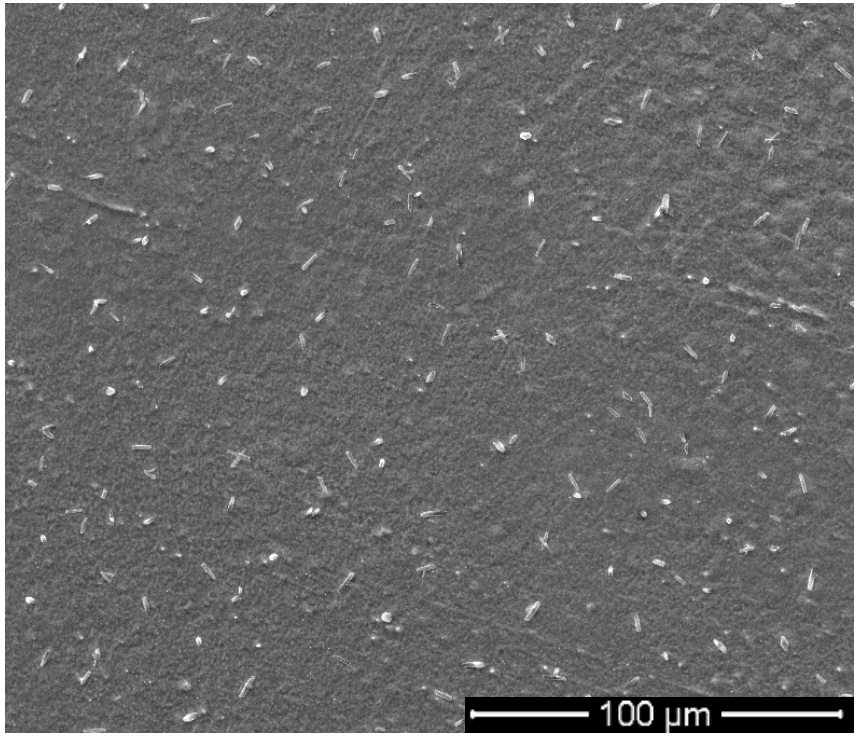


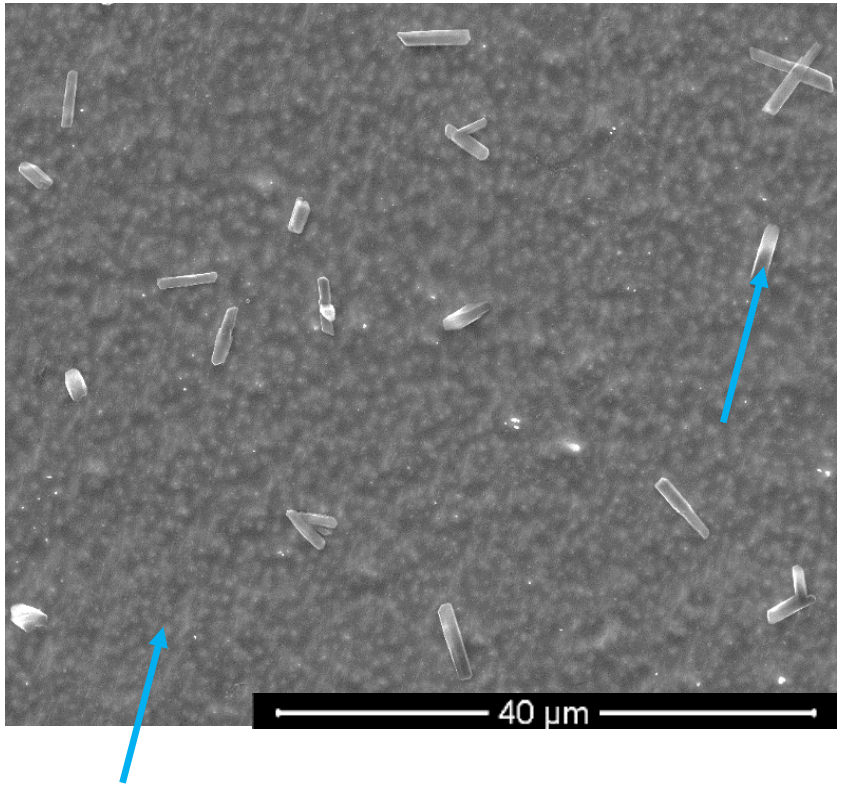
- Poor distribution at low and high spinning speeds.
- Average length of 5 µm and projected area of 18 µm² at 200 rpm.

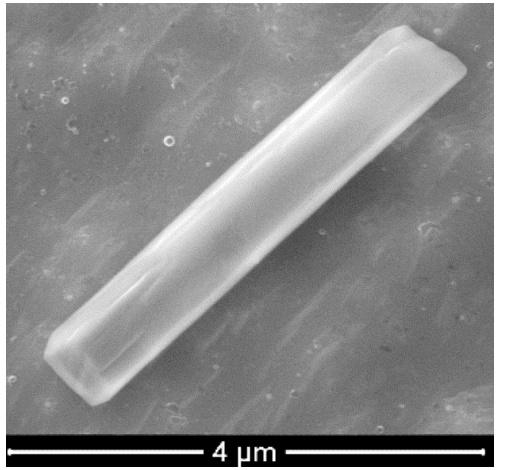
Results and discussions

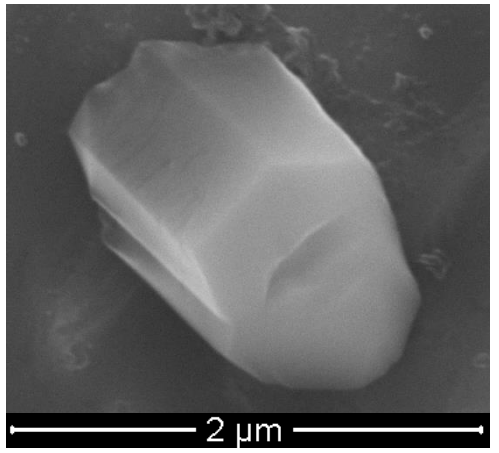
Substrates	Solution
Cold rolled Cu	▪ Fullerene dispersed in Toluene (2mg/ml)
Annealed Cu	
Graphene coated Cu	
Electropolished Cu	

C_{60} rods on Graphene Coated Cu Substrate: Two distinct morphologies







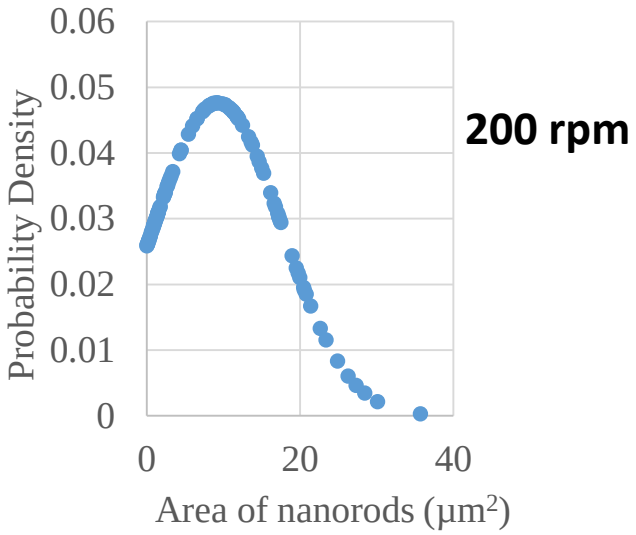


- **Good control over distribution and morphology of fullerene nanorods at 200 rpm.**

- **average length ~ 5 µm.**

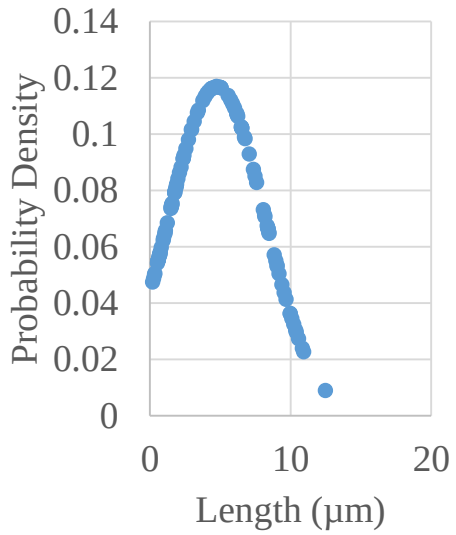
Size distribution of larger rods: Projected Area and Length Distribution on Graphene Coated Cu Substrate

Projected Area



200 rpm

Length



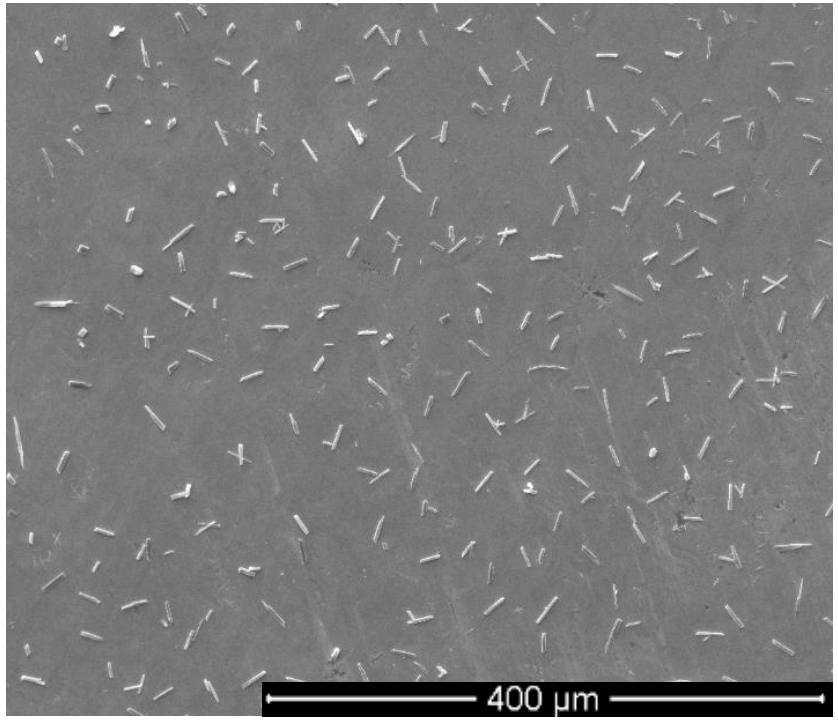
200 rpm

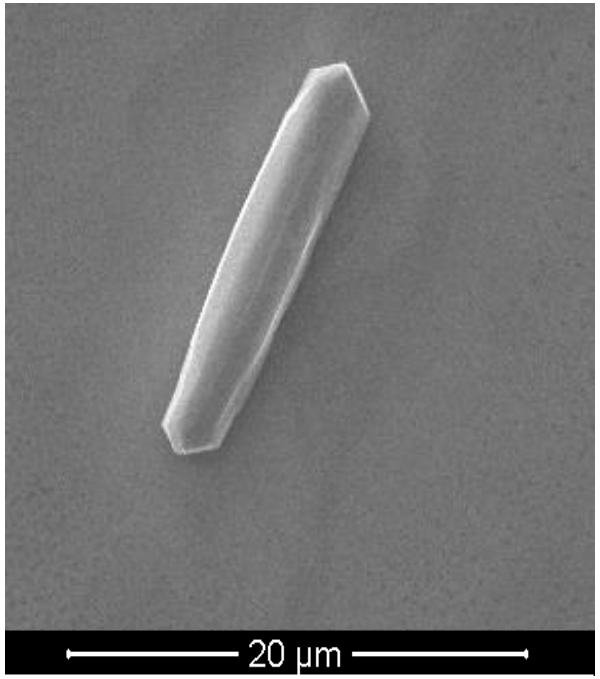
- Projected area of 10 µm² with length of 5 µm.

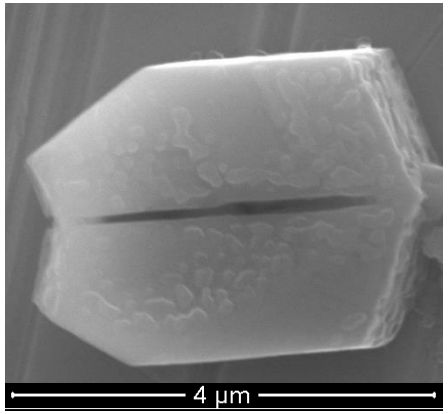
Results and discussions

Substrates	Solution
Cold rolled Cu	▪ Fullerene dispersed in Toluene (2mg/ml)
Annealed Cu	
Graphene coated Cu	
Electropolished Cu	

Highly controllable synthesis of C_{60} rods on Electropolished Cu Substrate



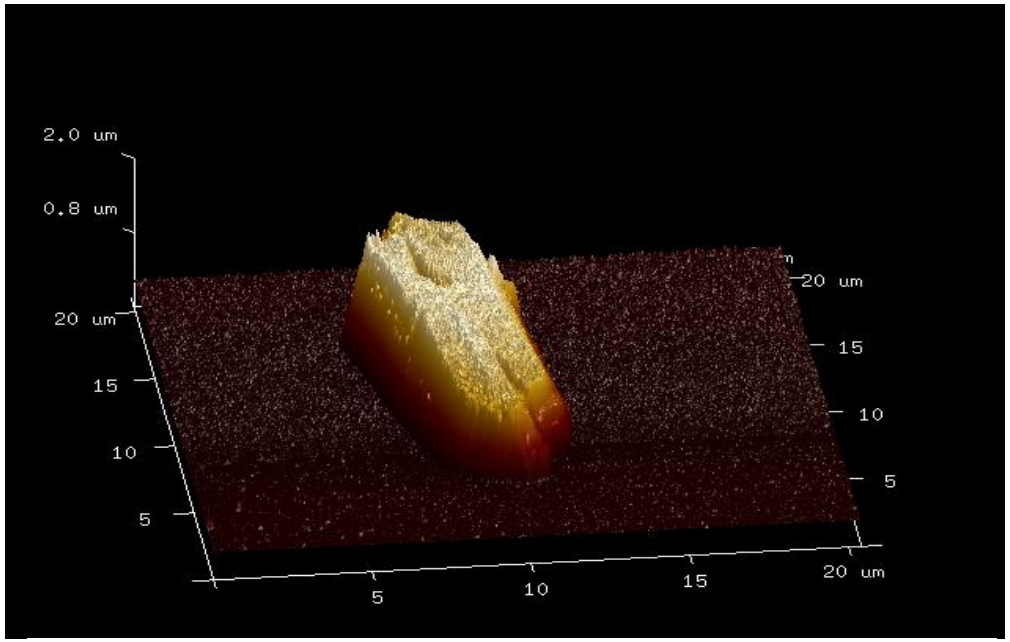


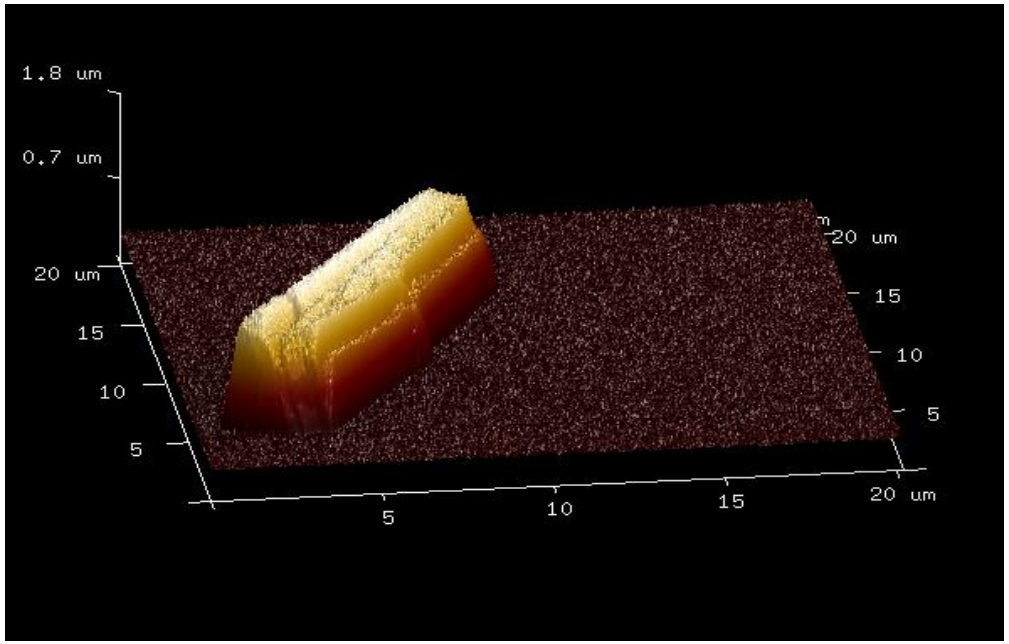


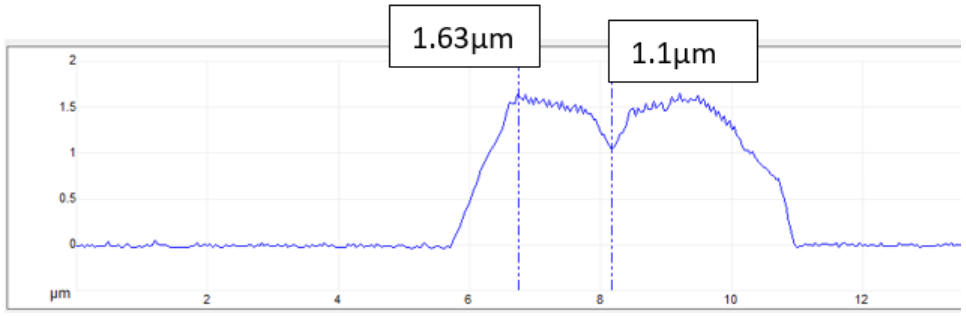
- Length of rod : ~10 µm

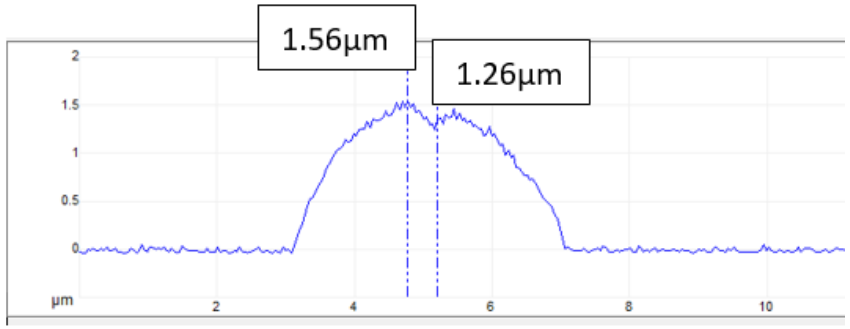
➢ **Excellent control over size and morphology of fullerene nanorods at lower rpm.**

C_{60} rods on Electropolished Cu (200 rpm) by AFM Analysis



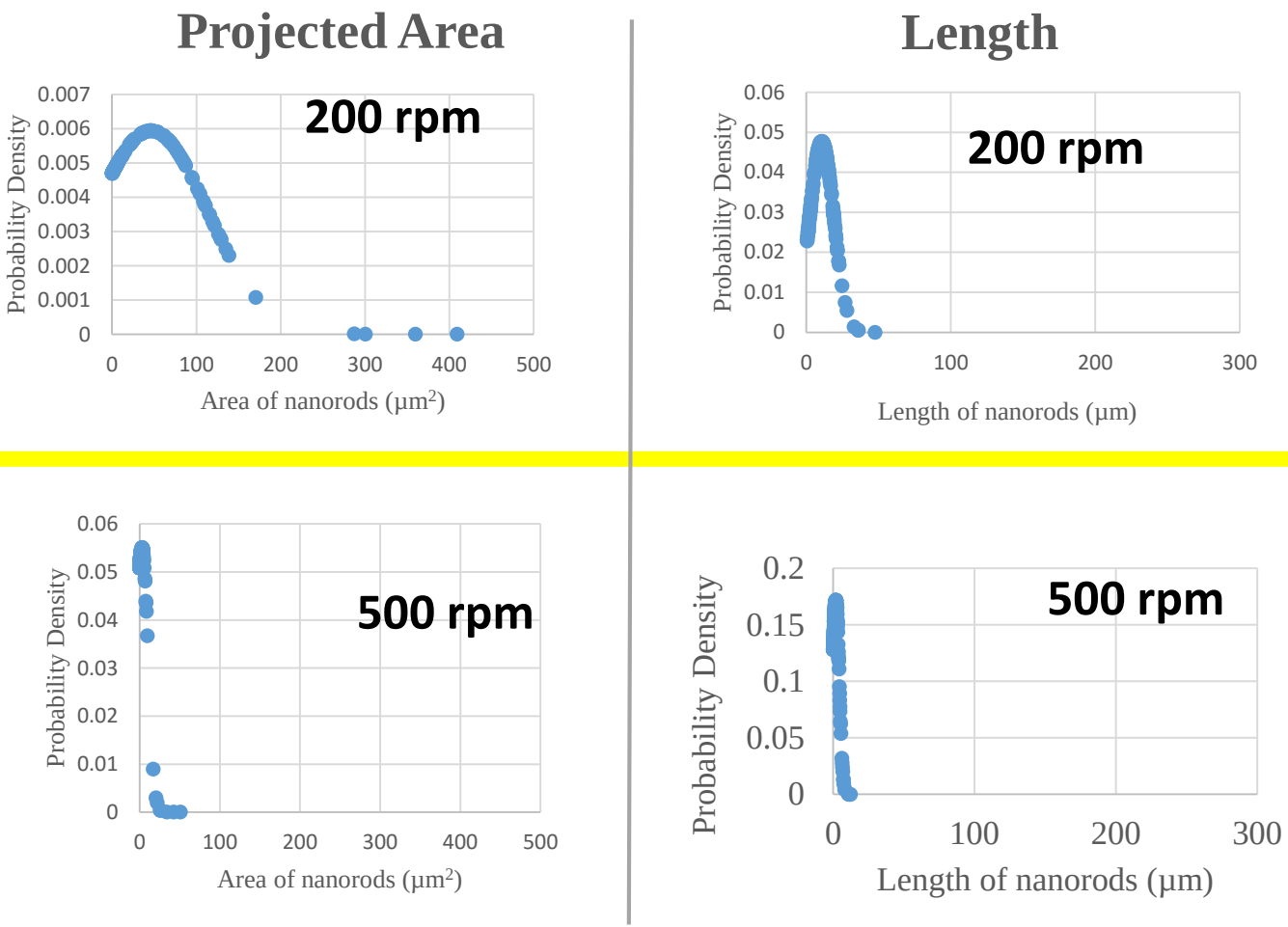






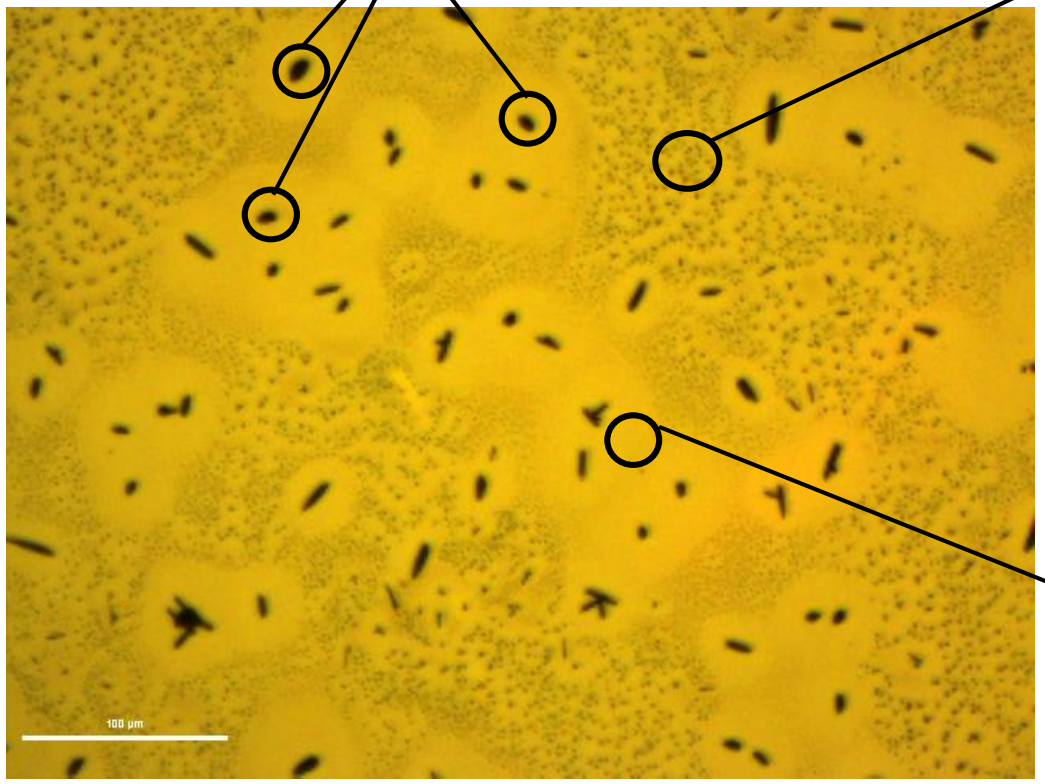
- Length of nanorods is ~14 µm with diameter of ~1.5 µm.

Size analysis: Projected Area and Length Distribution of rods on Electropolished Cu Substrate

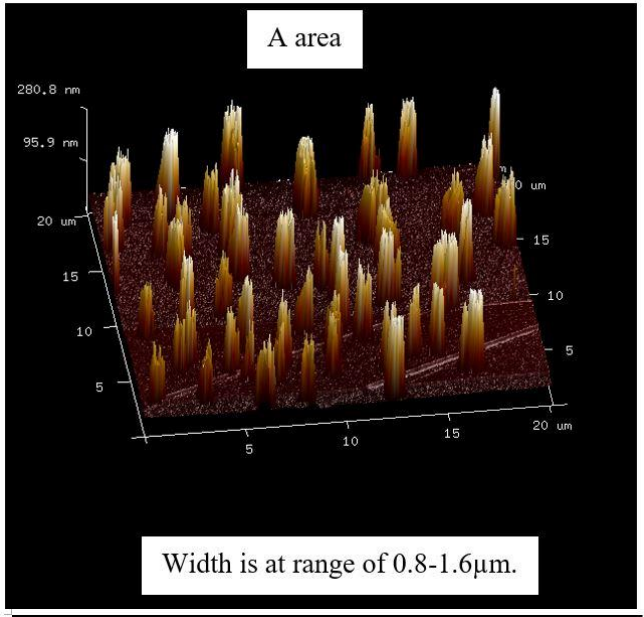


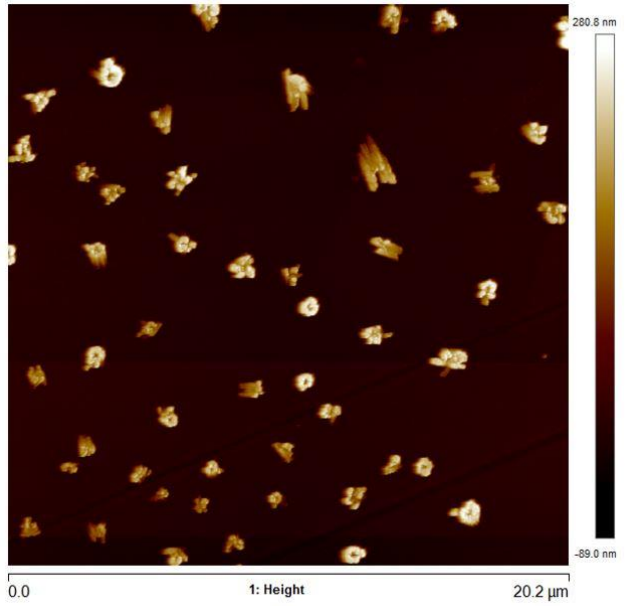
- Best distribution and morphology of rods at 200 rpm.
- Length of fullerene self-assemblies is ~10 µm.

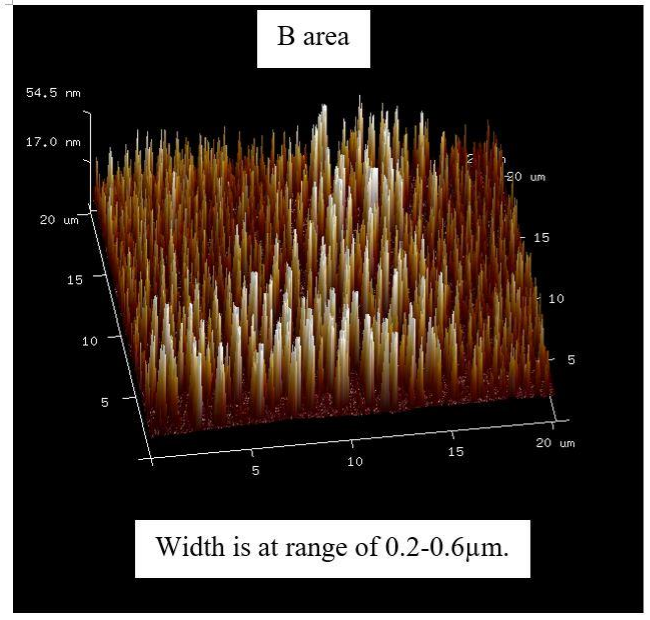
Distinct Nanowire bundles in areas without C_{60} rods on electropolished Cu

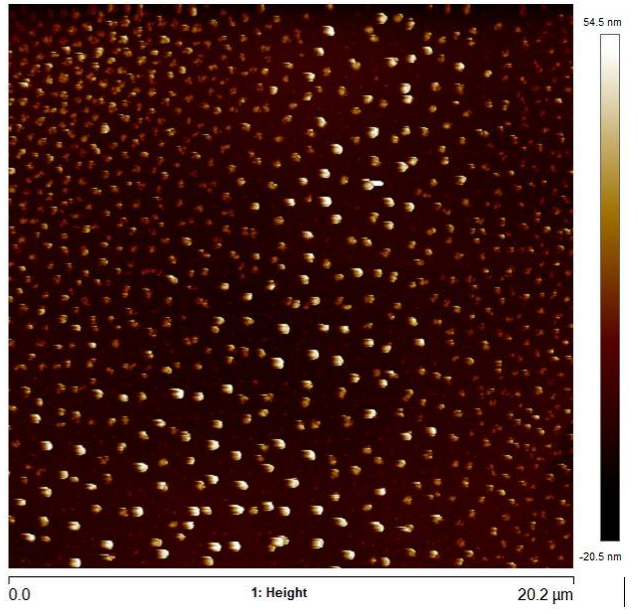


C_{60} self-assemblies on electropolished Cu (200 rpm).

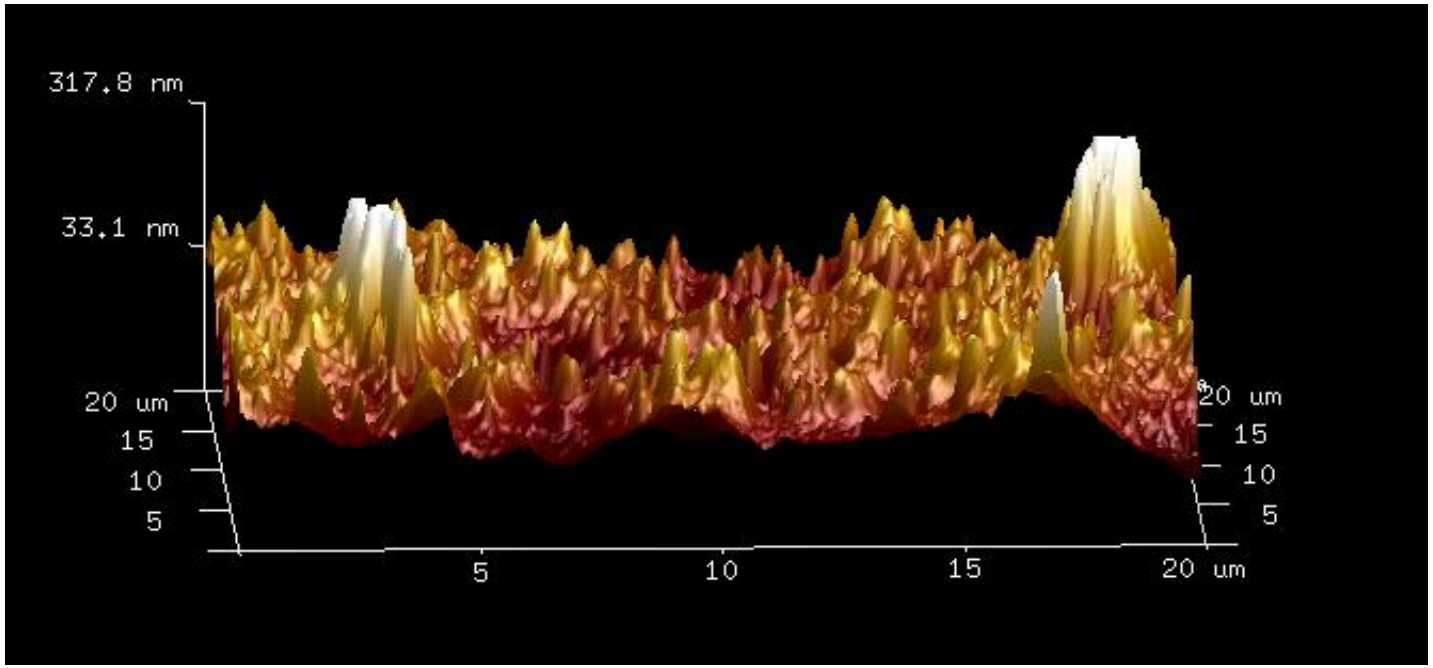








In contrast,
No well-defined nanowires in Graphene Coated Cu (200 rpm)



Areas without nanorods are not well defined as one on EP Cu substrate.

Discussion

- **It has been shown from DFT calculations that surface defects on Cu as well as graphene corrugations serve as strong adsorption sites for C_{60} molecules**

  - Well defined adsorption sites on electropolished Cu and graphene on Cu lead to more control on size, shape, morphology of C_{60} rods

  - Bigger rods are formed via nucleation and growth during the waiting time of 1 minute prior to ramp-up spreading
  - The nanowires are formed after the ramp-up as a result of ‘coalescence’ between the remaining C_{60} molecules
  - The coalescence is initiated due to C_{60}-C_{60} interaction arising as a result of spinning

  - The presence of intrinsic surface defects on annealed and cold-rolled Cu leads to less control of C_{60} morphology

Conclusions and Future Outlook

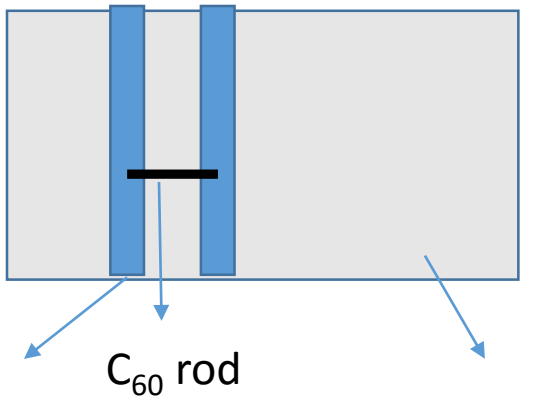
- A simple, wet-chemistry based spin-coating method developed for obtaining c_{60} rods and nanowires in a controllable fashion
- The size, shape and morphology of the C_{60} structures are intimately linked to the substrate on which they are formed.
- The developed method provides a new avenue to achieve high aspect ratio C_{60} molecular wires based interconnects as well as devices with tunable electrical properties (see next slide)

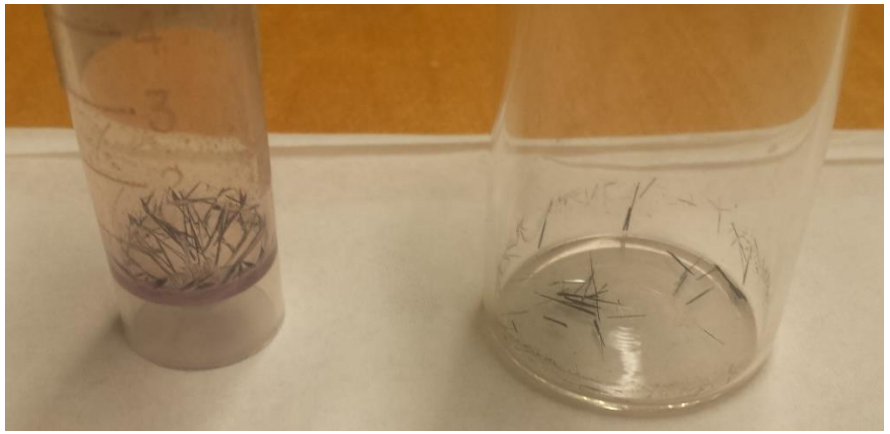
C60 milli-rods: electrical conductivity

Electrical conductivity of millimeter long C_{60} rods (aspect ratio = 10:1) formed from CS_2 solution within a glass/polycarbonate vial

$$\sigma_{rod} = 0.1(\Omega cm)^{-1}$$

$$\sigma_{C60\ film} = 10^{-6}(\Omega cm)^{-1}$$





Polycarbonate Glass