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End-to-End Assembly of CTAB-Stabilized Gold Nanorods by Citrate Anions

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Introduction

- ➢Metal nanostructures - their shape-dependent SPR
- ➢Gold nanorods (GNRs) : their length and aspect ratio (AR) can be easily controlled through a chemical reduction process
- ➢Self-assemble in a smectic-like fashion during evaporation of the solvent.
- ➢End to end assembly more interesting
- ➢End to end assembly using particular molecules such as biotin and streptavidin, 3-mercaptopropionic or 11-mercaptoundecanoic acids, dithiols, or phosphatidylcholine reported.

In this paper ……..

The end-to-end assembling phenomenon of gold nanorods is studied using transmission electron microscopy (TEM) associated with selected area electron diffraction (SAED). The GNRs with ARs of 3 and 16 were synthesized by chemical reduction methods, followed by connecting them at their end positions. The SPR properties of the connected GNRs were also investigated with optical extinction measurement.

Experimental

1) Preparation of GNRs with Different Aspect Ratios

GNRs with an AR of 3 were prepared using a one-step-seeding method described by Nikoobakht et al.

GNRs with an AR of 16 were prepared using a three-stepseeding method developed by Jana et al.

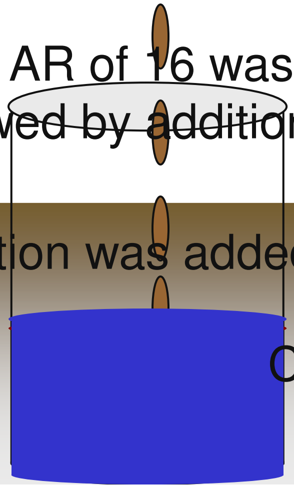
Citrate-stabilized gold nanospheres (GNSs) were also prepared.

CTAB-stabilized GNSs were also prepared by adding 200 μL of 0.1 M CTAB solution to 2 mL of the citrate-stabilized GNS solution.

2) End-to-End Connection of GNRs.

GNRs were centrifuged at 15000 rpm and the supernatant was discarded. The residue was diluted to the initial volume using distilled water.

The solution of GNRs with an AR of 16 was aged for 2 weeks to spontaneously precipitate the particles, followed by additional substitution of Milli-Q water for the solvent.



1 mM sodium citrate

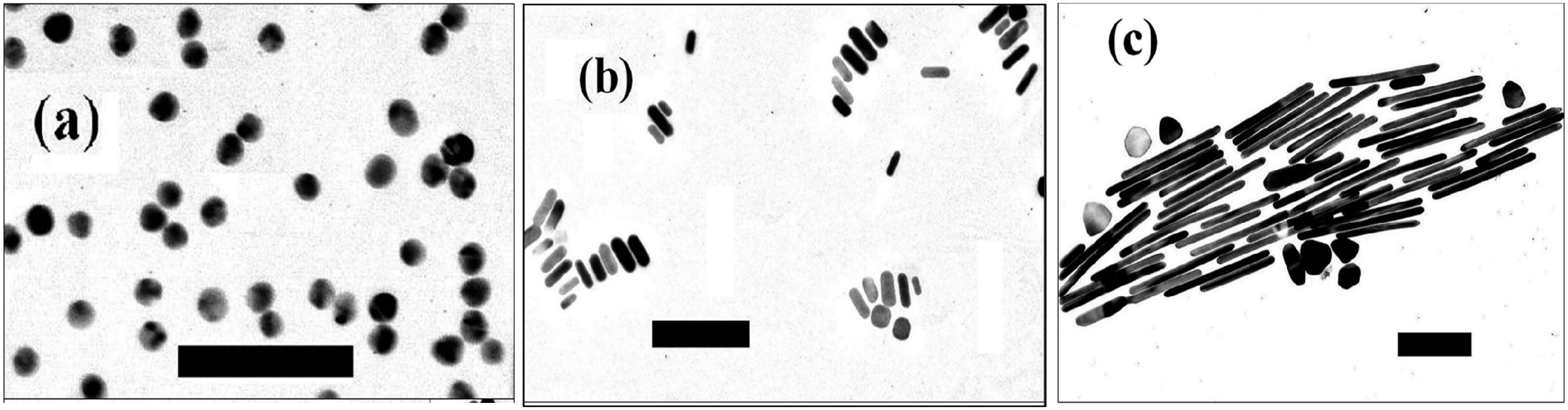
5 mL of the solution of GNRs

0.5 mL of 40 mM CTAB solution was added in order to suspend the color change.

Color change from reddish to bluish violet.

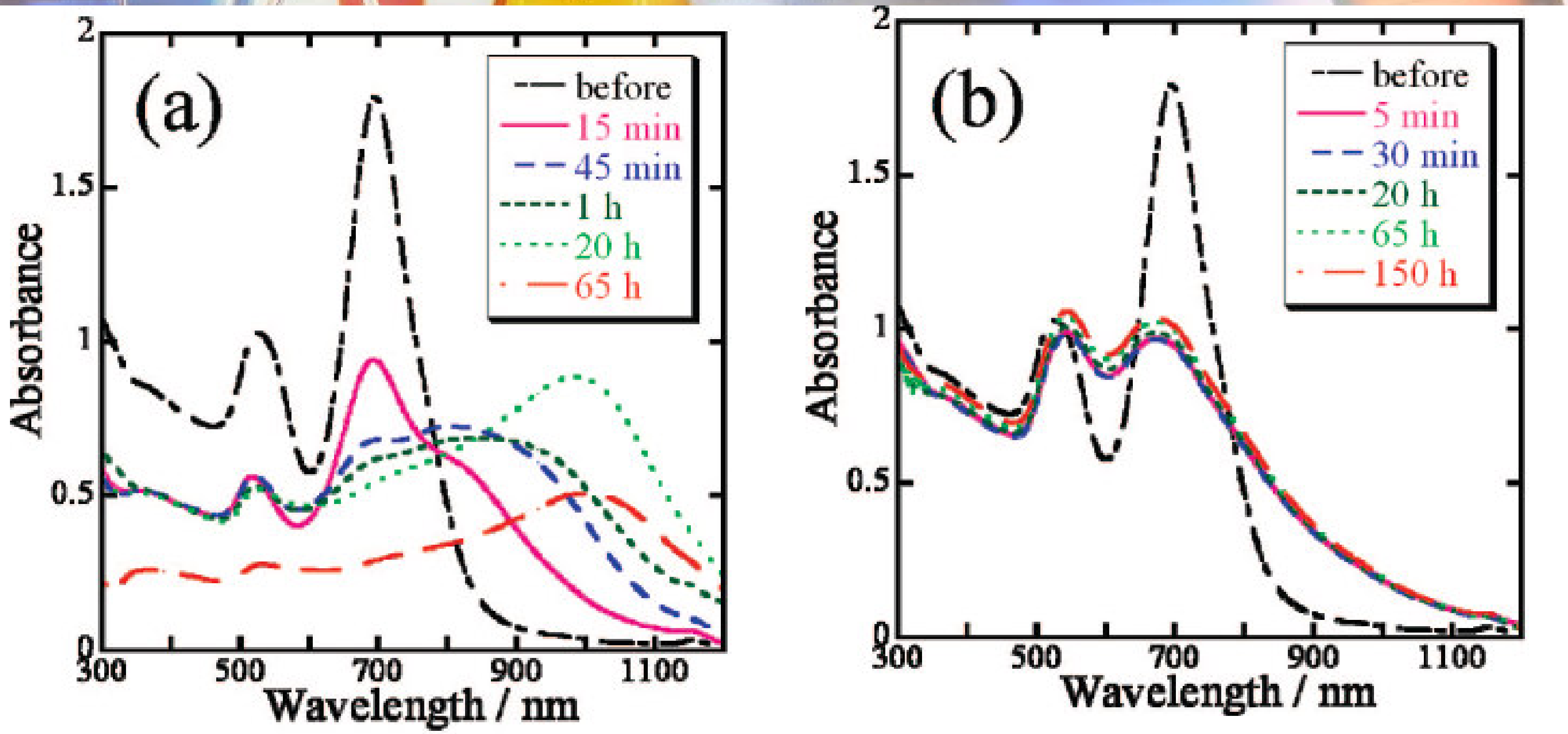
Results and Discussion

Assembly of GNRs with Various Aspect Ratios.

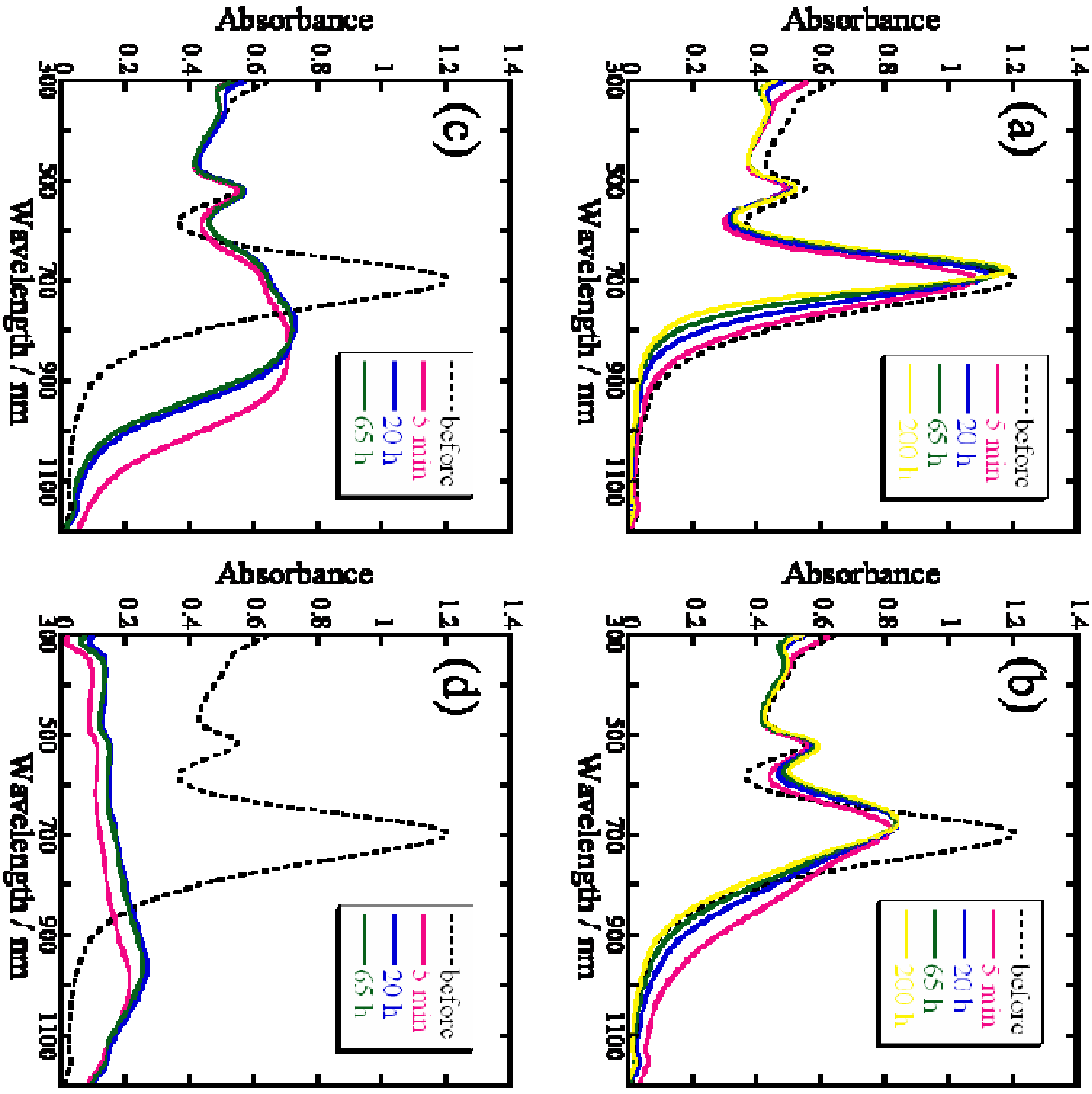


TEM images of the prepared gold nanoparticles with a diameter of ~10 nm and ARs of 1 (a), 3 (b), and 16 (c). Scale bars in parts a and c are 200 nm. The scale bar in part b is 100 nm.

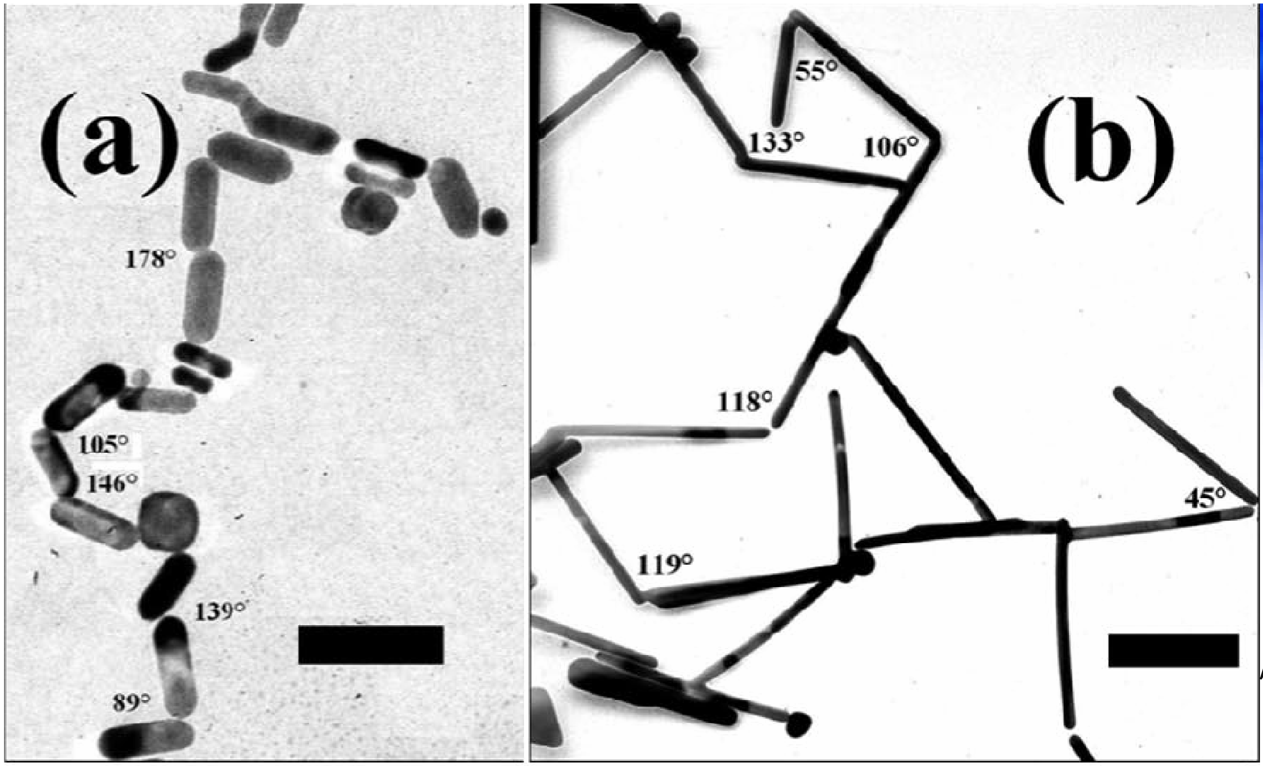
Formation of End-to-End Assembled GNRs



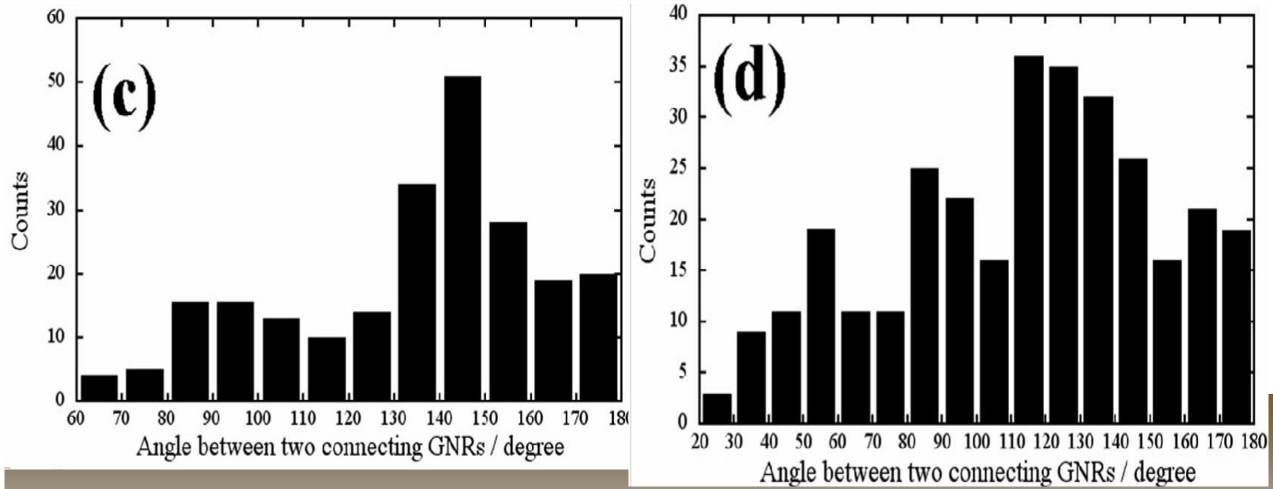
Optical extinction spectra of the solution of GNRs with an AR of 3 prepared by adding 40 μL of 1 mM sodium citrate (a), and adding 0.5 mL of 40 mM CTAB 5 min after the addition of 60 μL of 1 mM sodium citrate (b). The described times in parts a and b are the time intervals after the addition of sodium citrate and CTAB, respectively



Arresting the assembly by CTAB

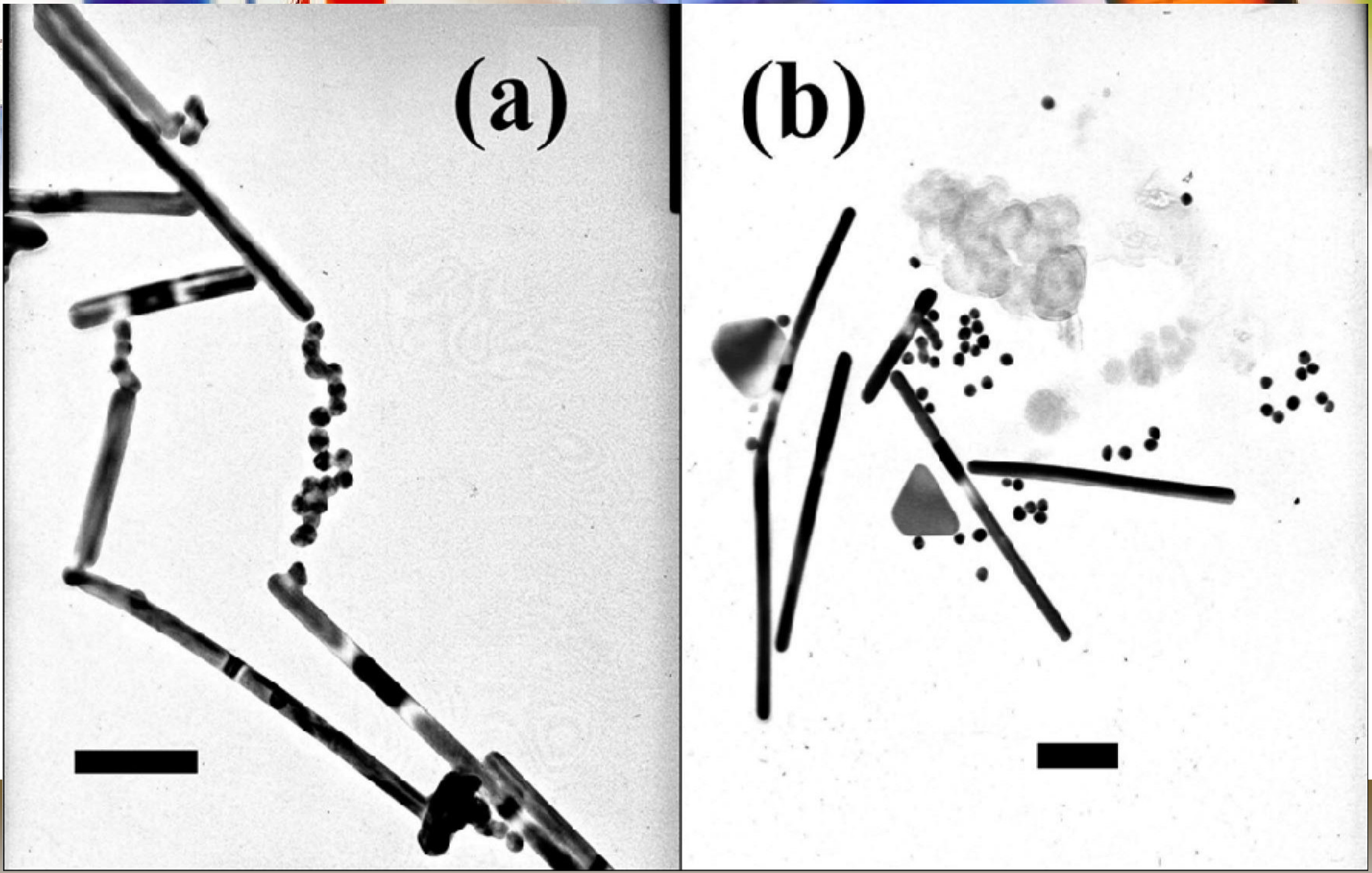


TEM images of the end-to-end connected GNRs with ARs of 3 (a) and 16 (b). Scale bars in parts a and b are 50 and 200 nm, respectively.



c and d are the corresponding distributions of the angles between two connecting GNRs shown in parts a and b, respectively.

Effect of sodium citrate on the endto-end assembly



TEM images of the CTAB-covered GNRs reacted with the citrate-stabilized GNSs (a) and the CTAB-stabilized GNSs (b). Scale bar is 100 nm.

Four hypothesizes behind the mechanism of the end-to-end assembly of GNRs

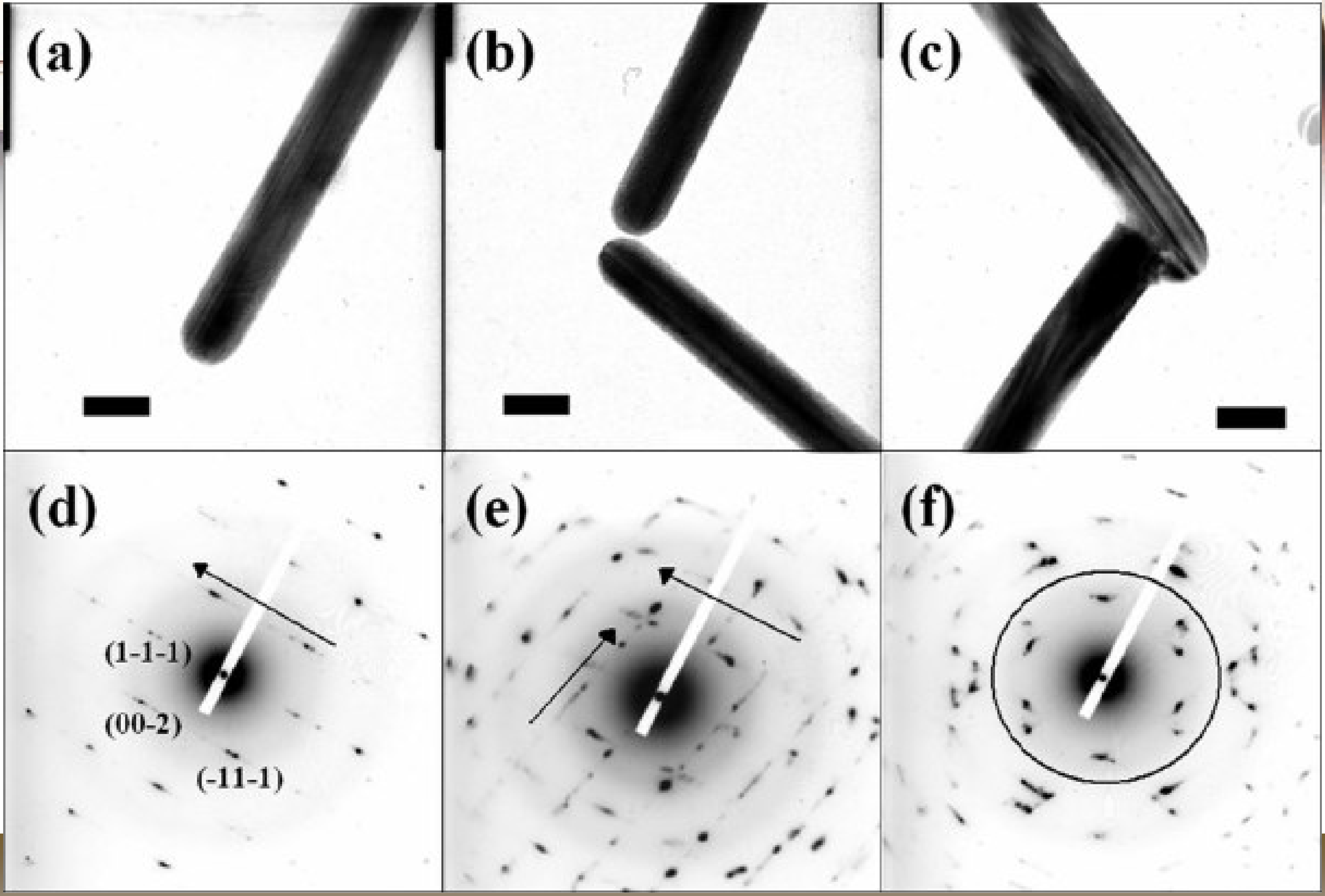
(i) the adsorption of citrate anions (negatively charged) to the ends of CTAB-modified GNRs (positively charged) neutralizes the electric charge on the surface, resulting in the aggregation of the GNRs at the end positions

(ii) the low covering rate of CTAB on the GNR ends causes interdigitations of carboxyl groups of Citrate at the gap of GNRs to assemble them.

(iii) the cationic head groups of CTAB and citrate anions adsorbed on the GNR ends attract each other electrostatically

(iv) the carboxyl groups of sodium citrate form intermolecular hydrogen bonds at the GNR ends in nonpolar hydrophobic environment provided by the long alkyl chains of CTAB adsorbed on the GNR surface.

Welding of End-to-End Connected GNRs.

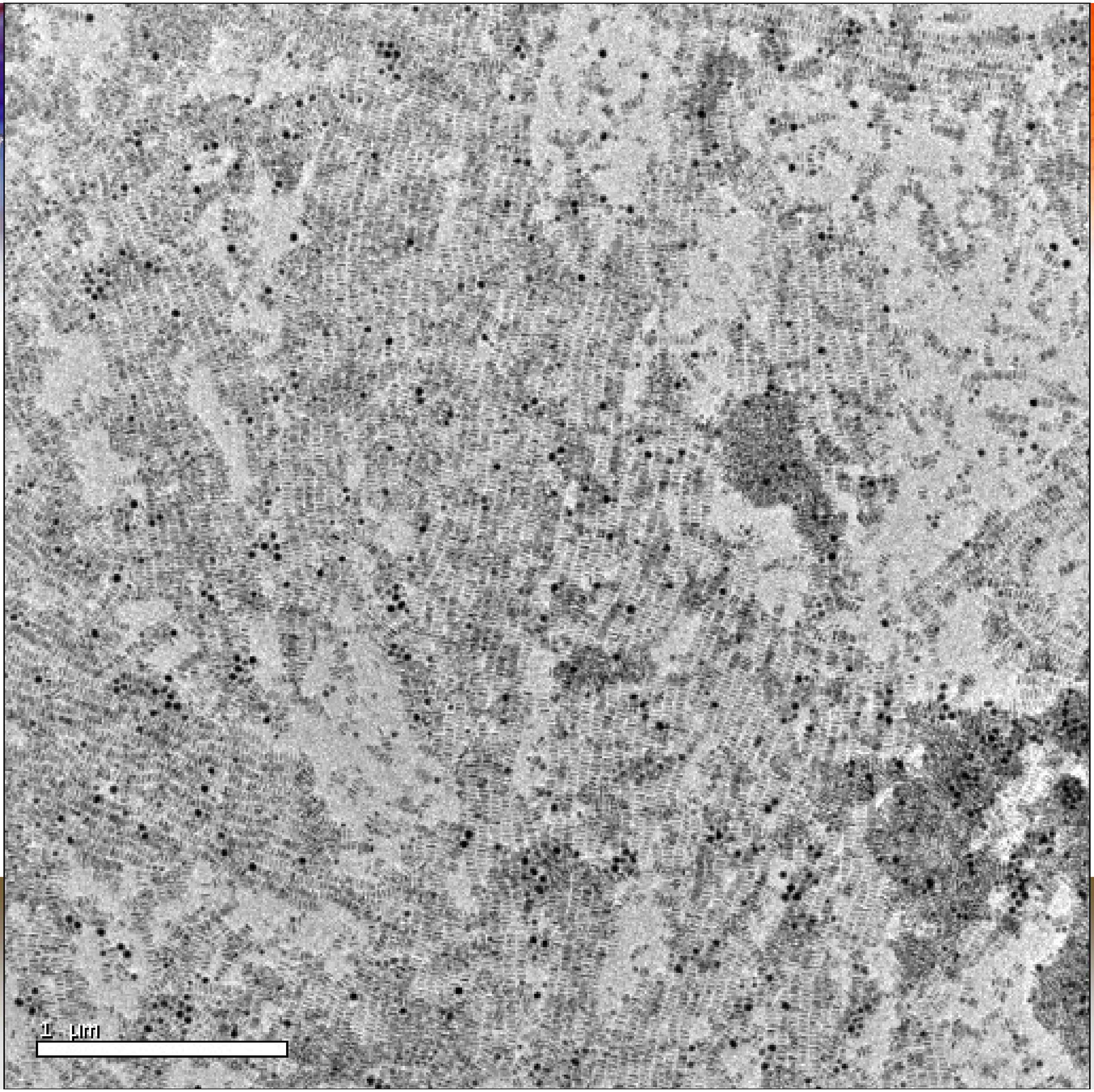


TEM images of the isolated (a), loosely (b), and tightly connected GNRs (c). (d-f) Corresponding SAED patterns of parts a-c, respectively. Scale bar is 20 nm.

Conclusions

- ➢GNRs with an AR of 3 are assembled in an end-to-end fashion by adding sodium citrate
- ➢The SPR properties of GNRs changes by the end-to-end assembly
    - LSPR band is shifted to longer wavelength region as the GNRs interact with each other at their end positions.
- ➢Red shift can be suspended by adding CTAB
- ➢As citrate-modified GNSs are preferentially adsorbed on the GNR ends, citrate anions are considered to neutralize the surface charge of the GNRs at their end positions so that the end-to-end connection is promoted.
- ➢GNRs with an AR of 16 are assembled in an end-to-end fashion by only decreasing CTAB concentration in the solution. The further decrease of the CTAB concentration leads to the formation of end-to end aggregated GNRs in the solution.

Thanks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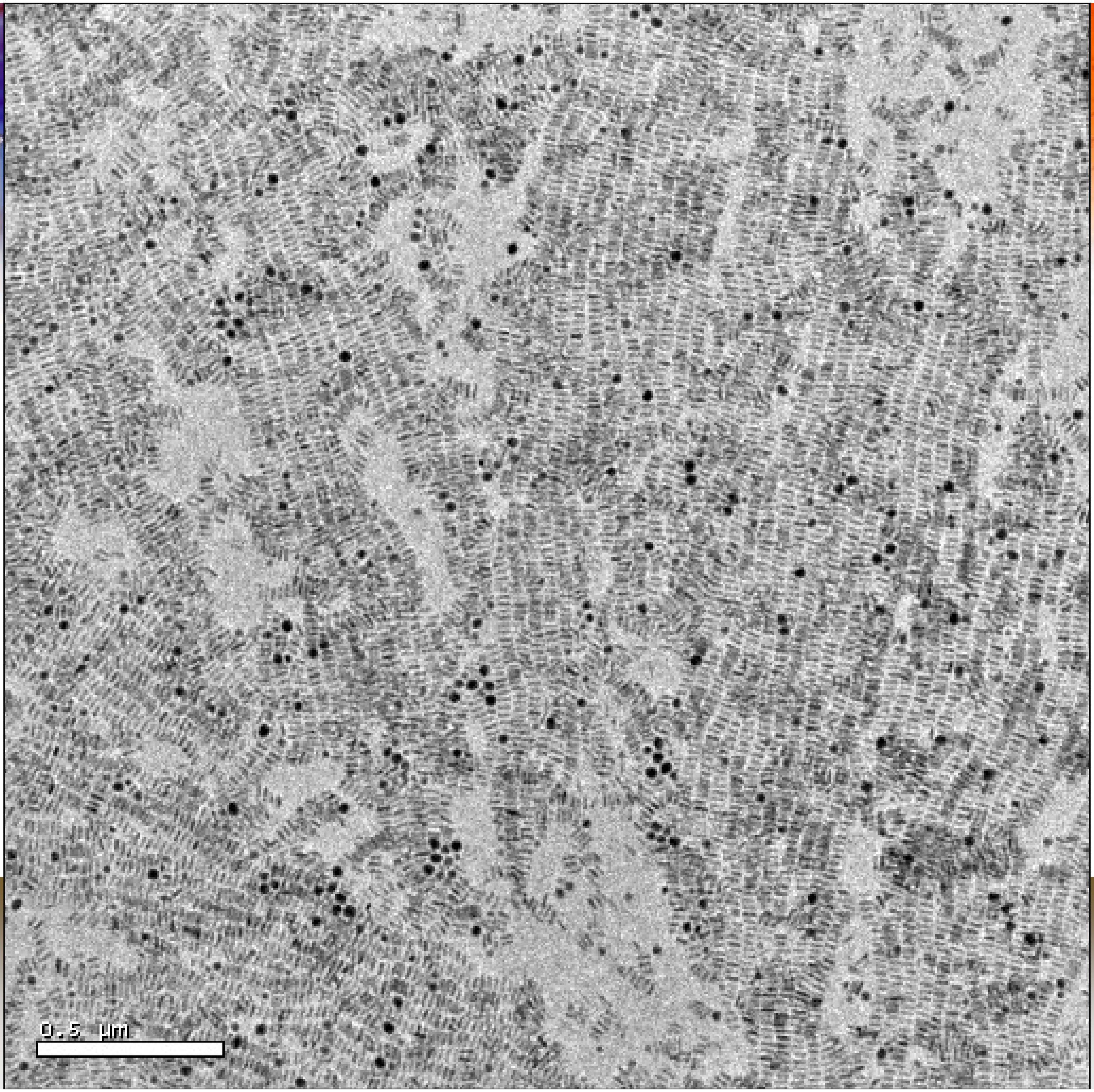
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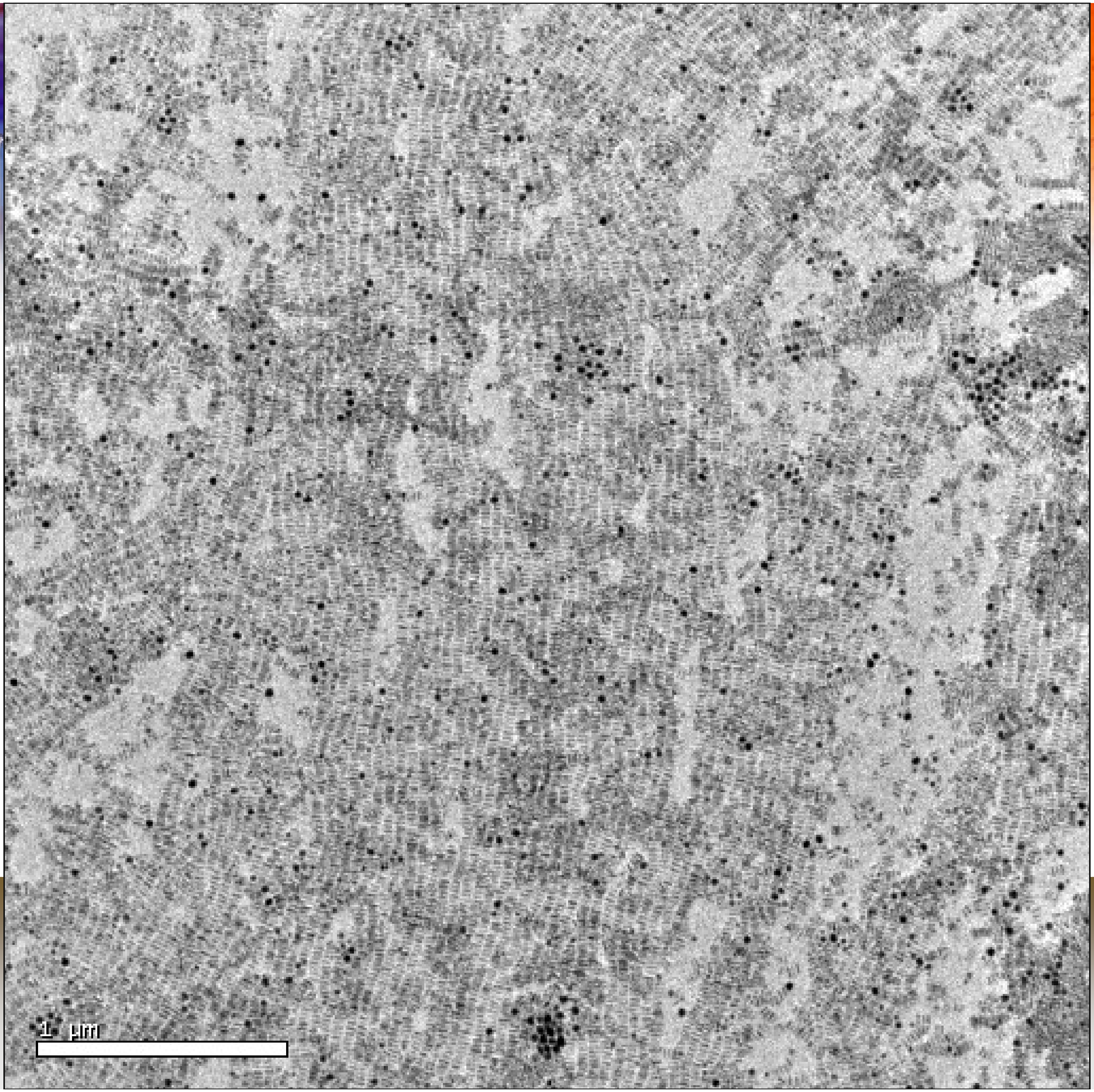
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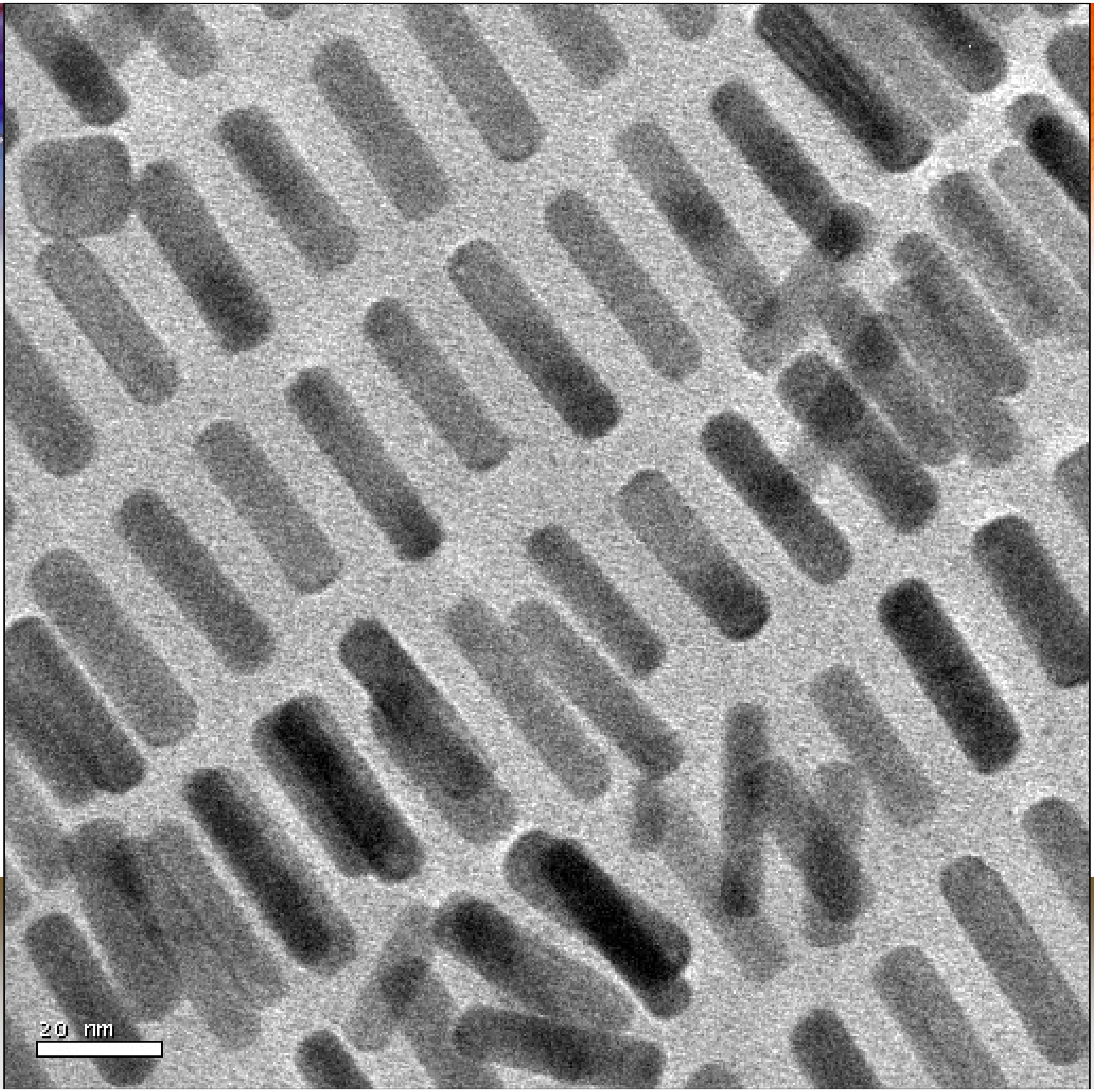
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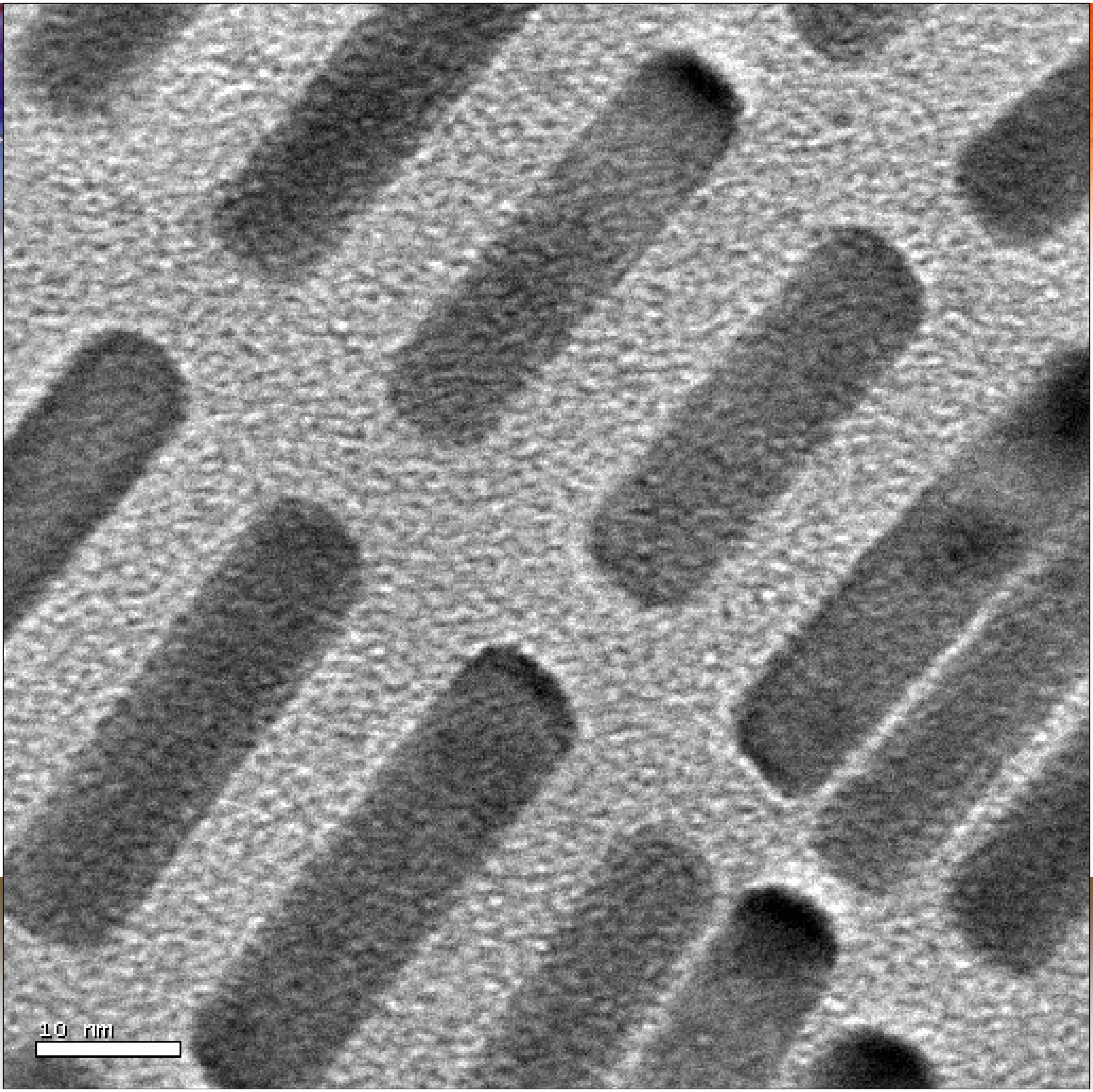
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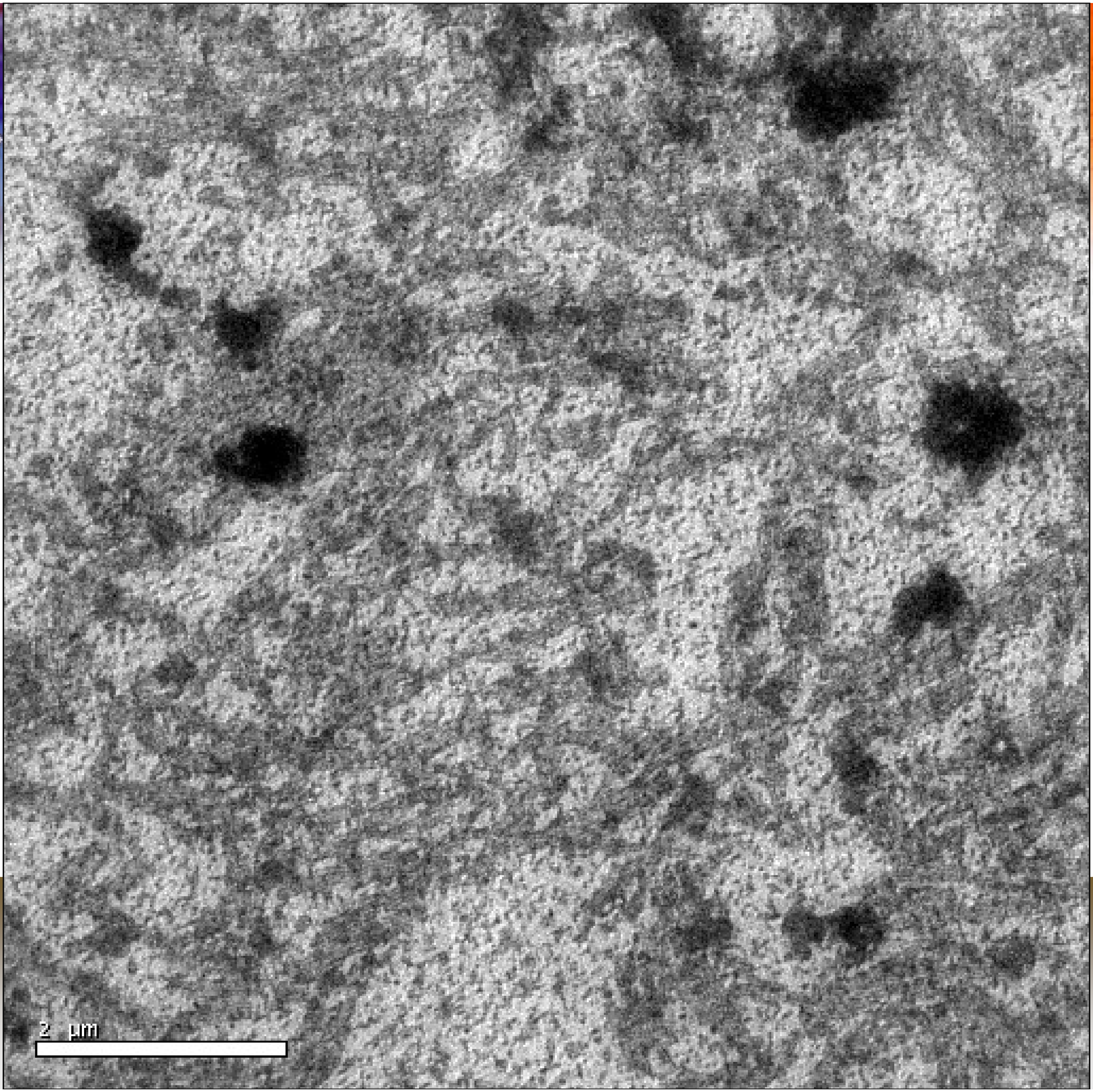
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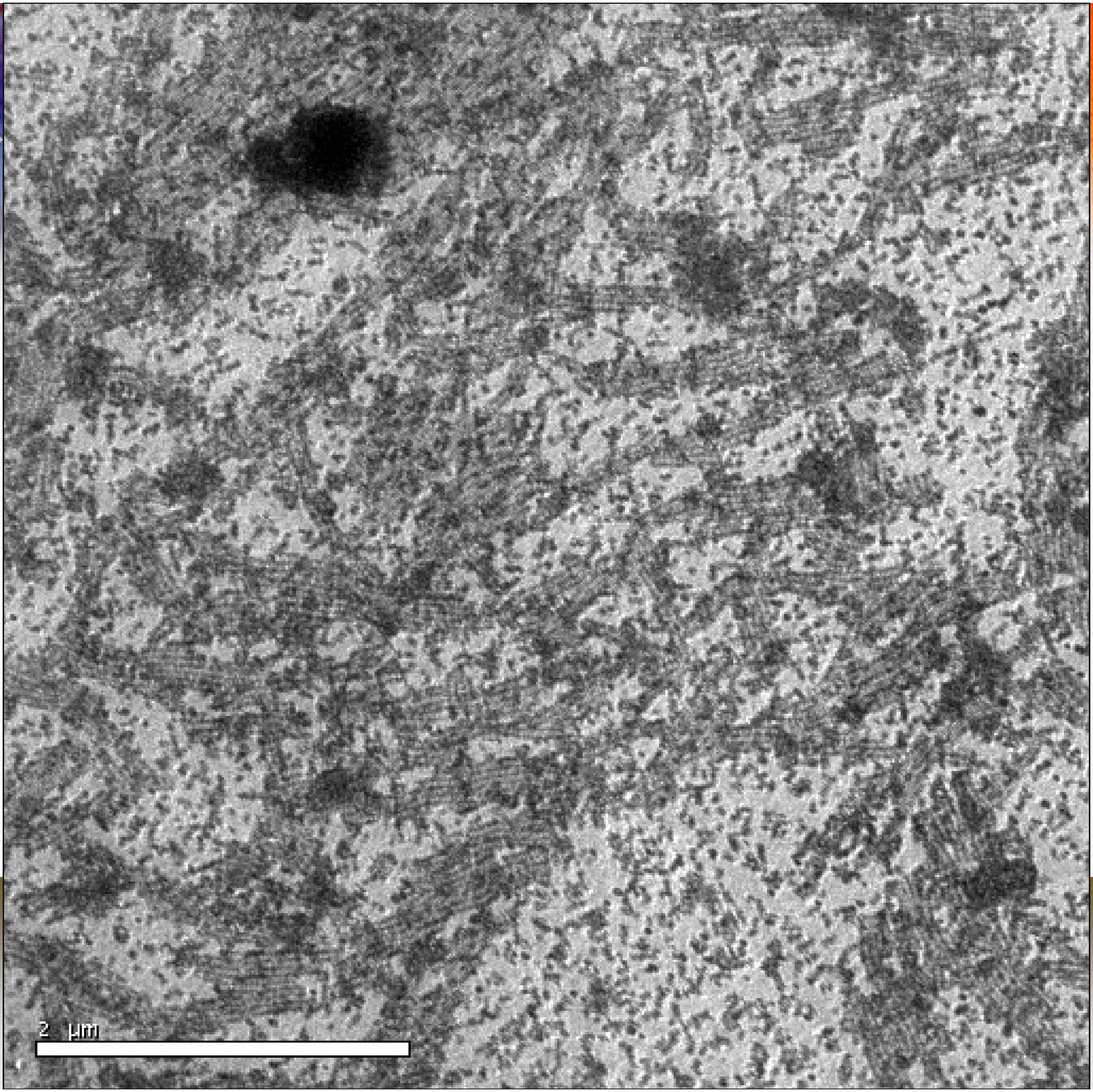
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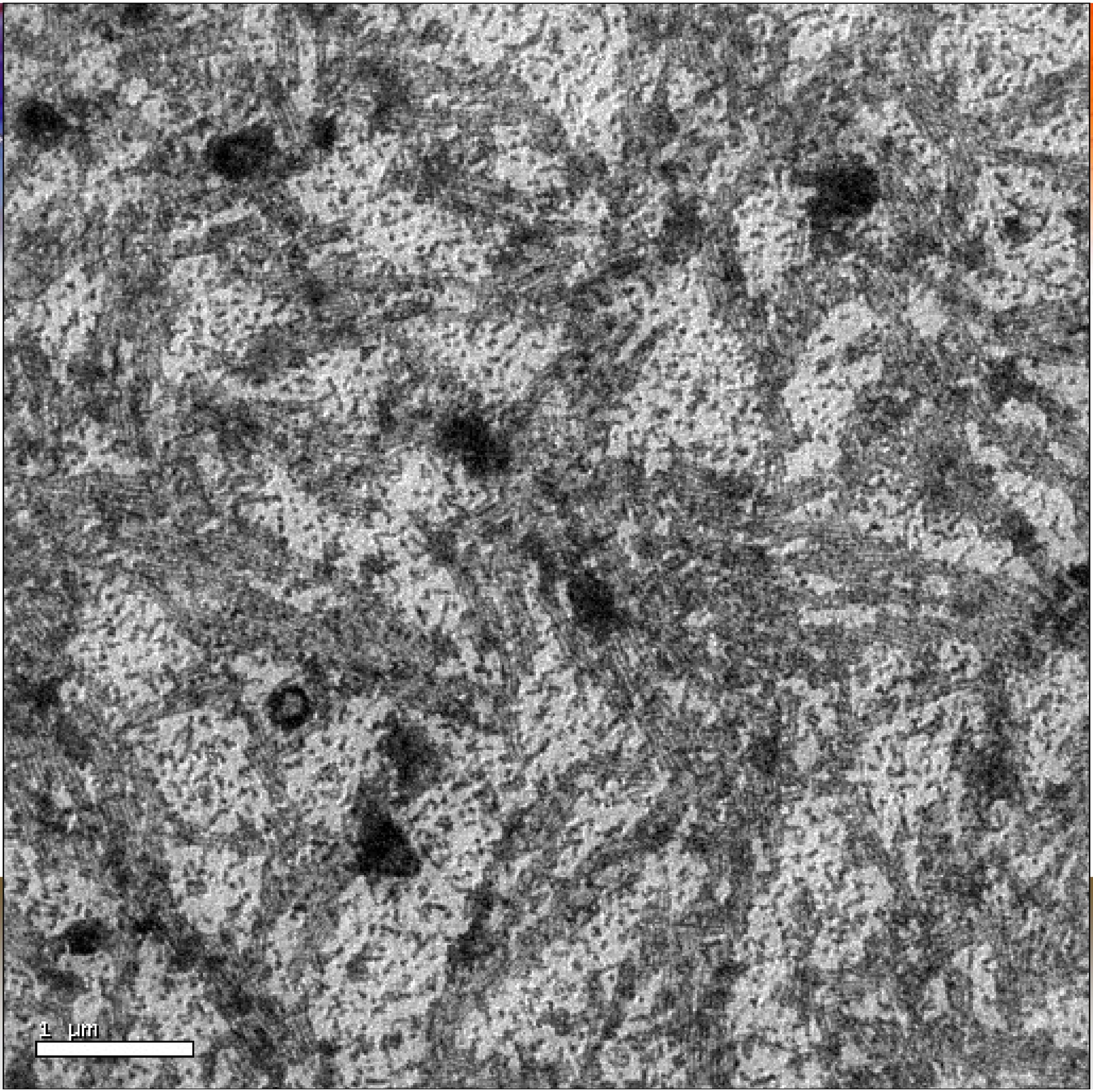
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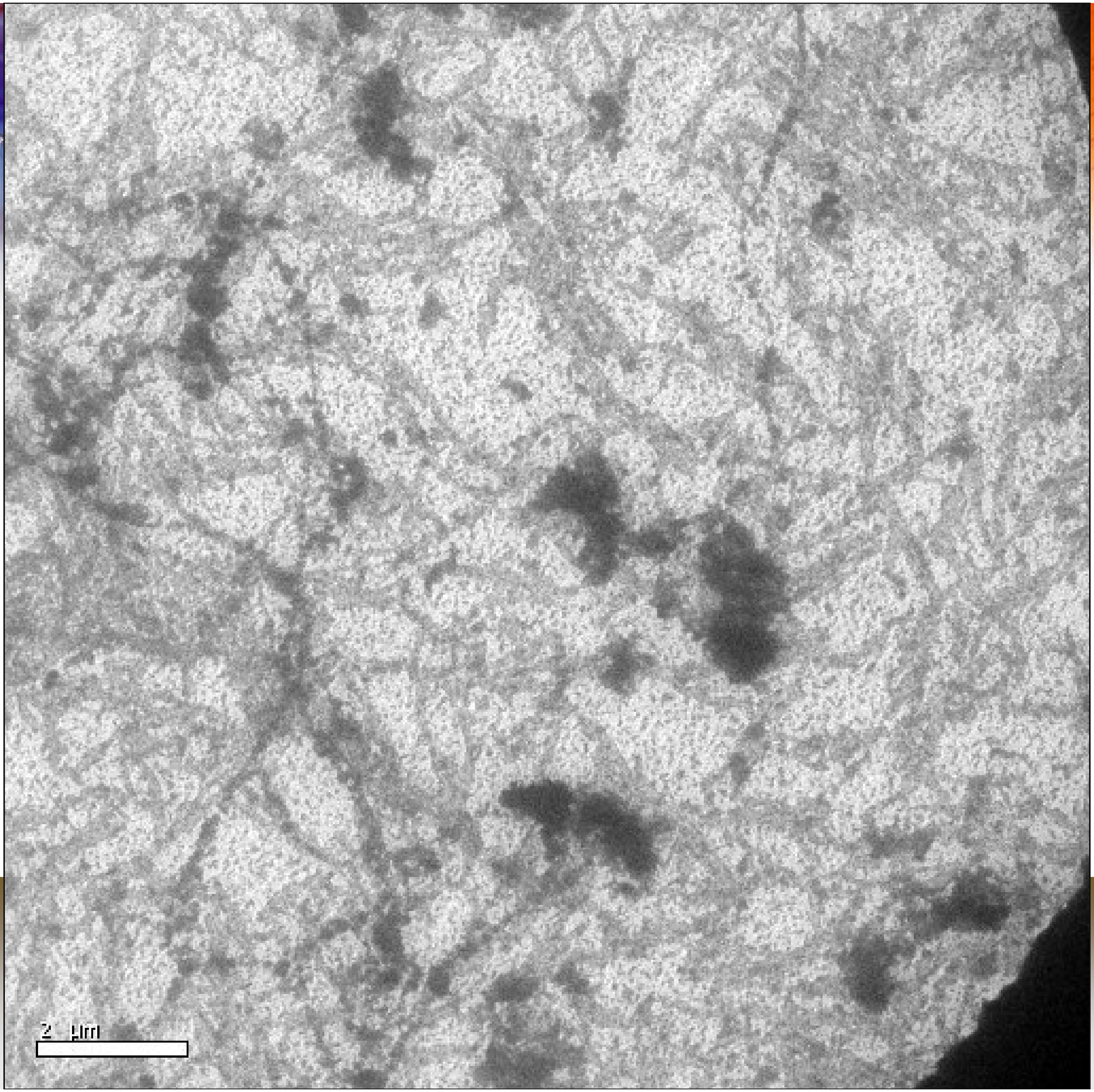
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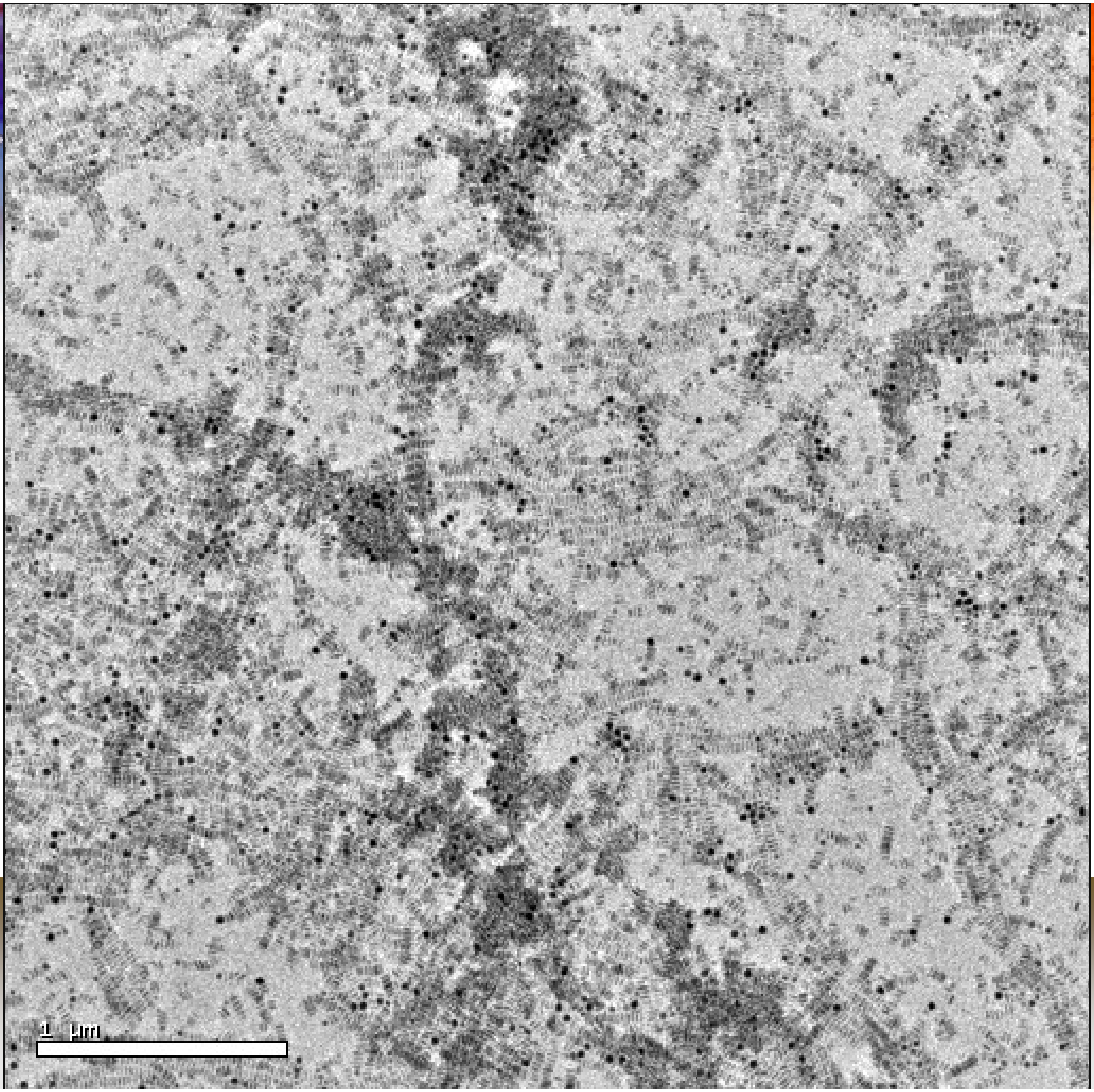
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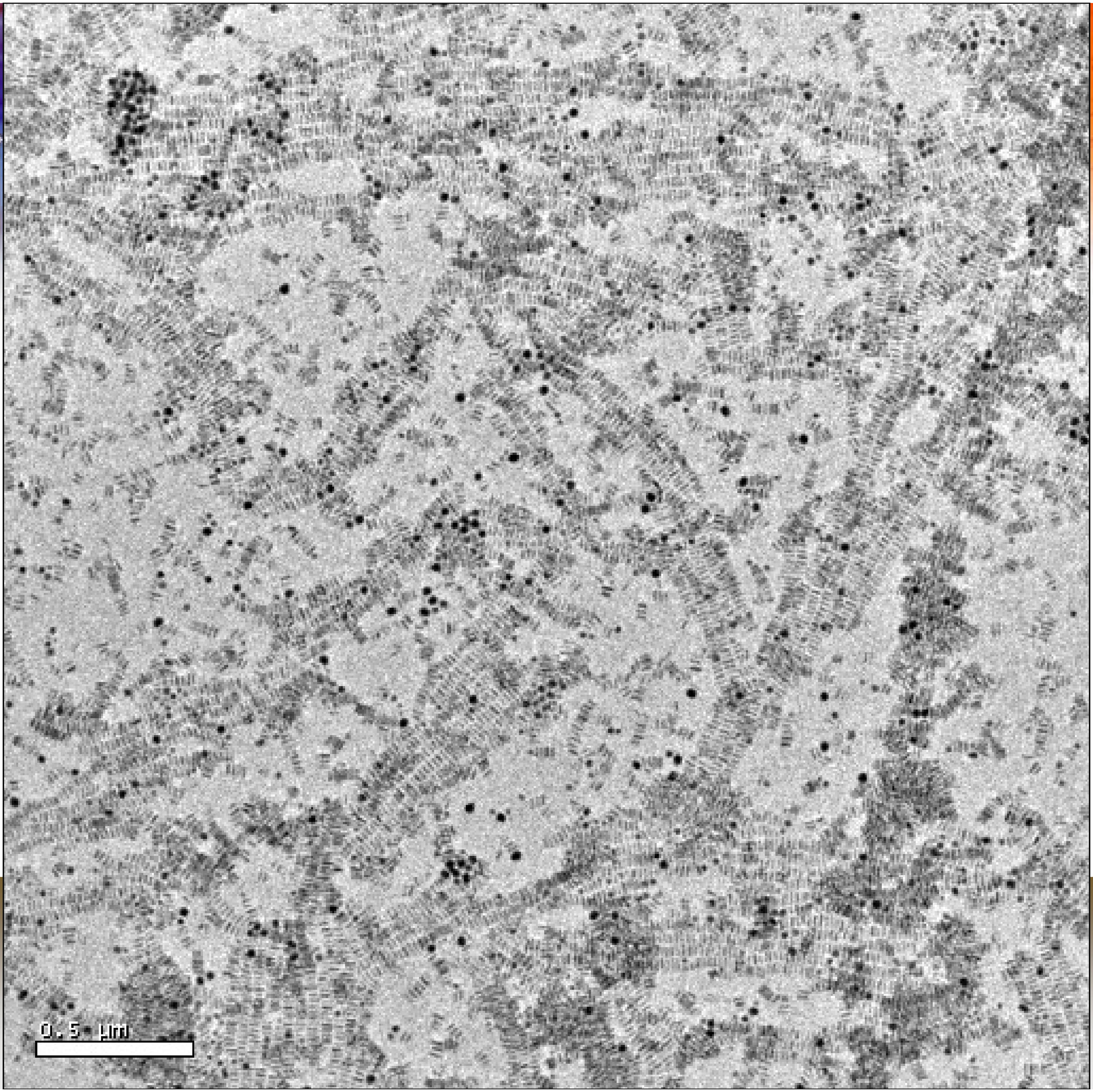
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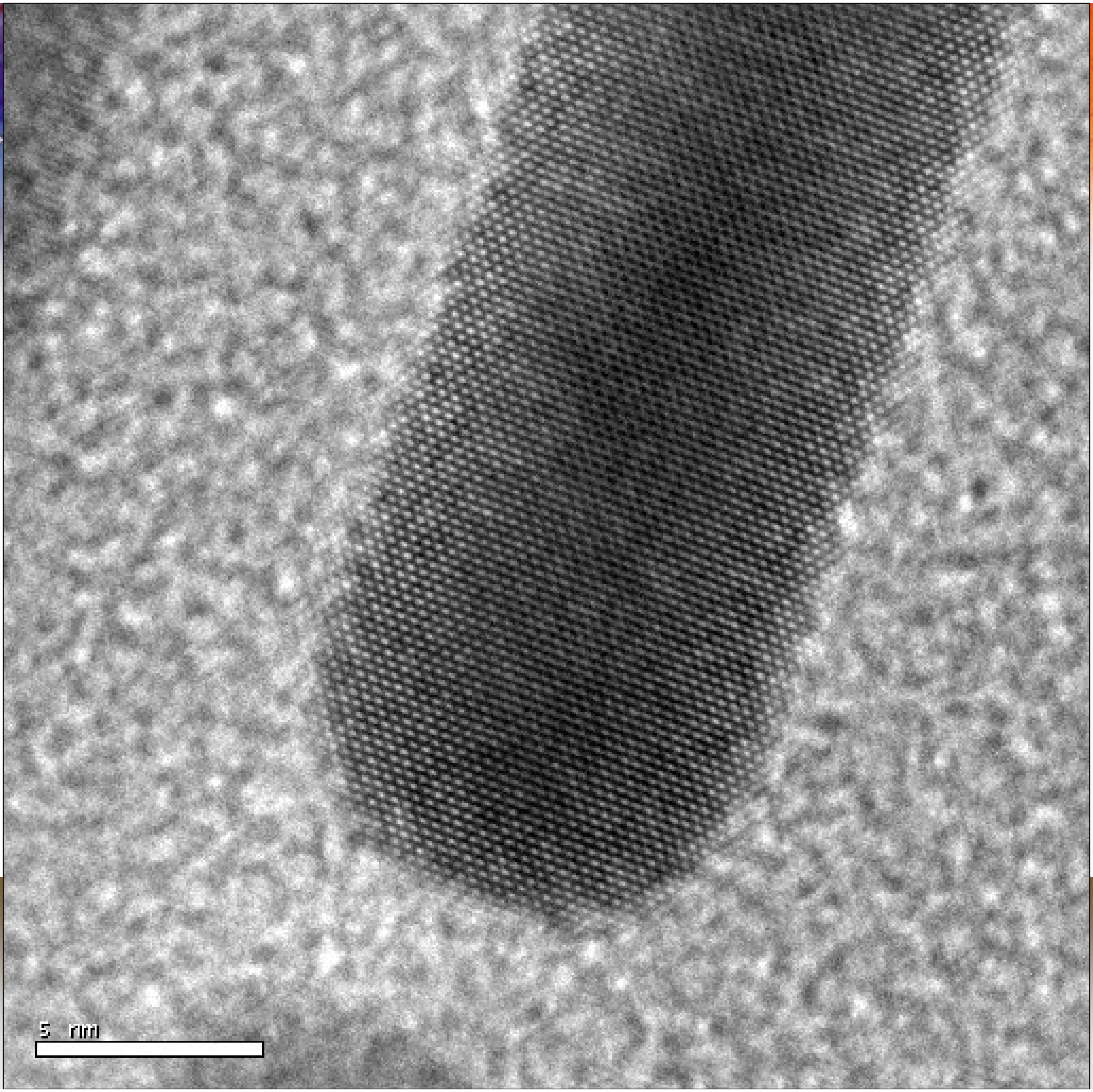
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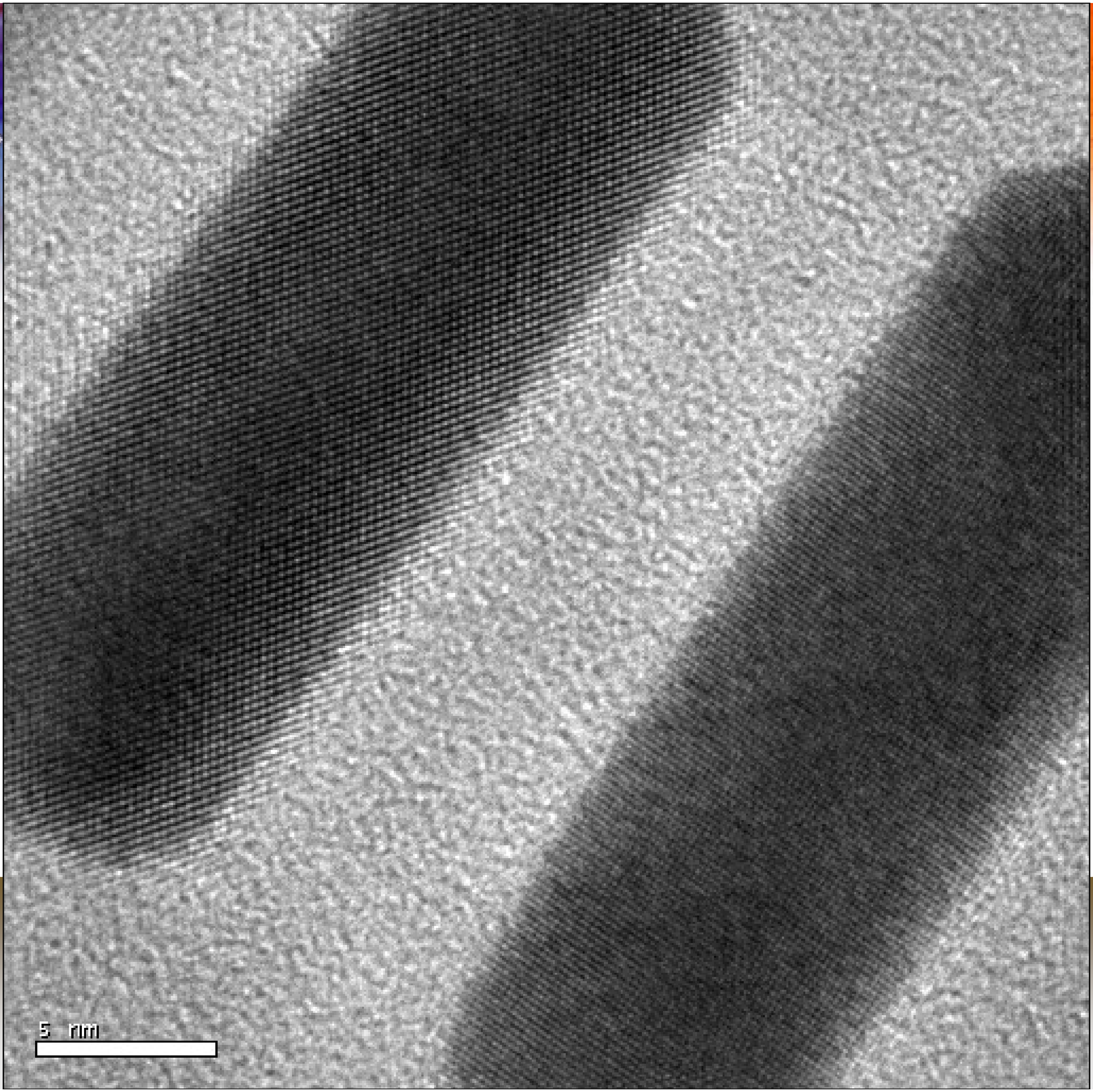
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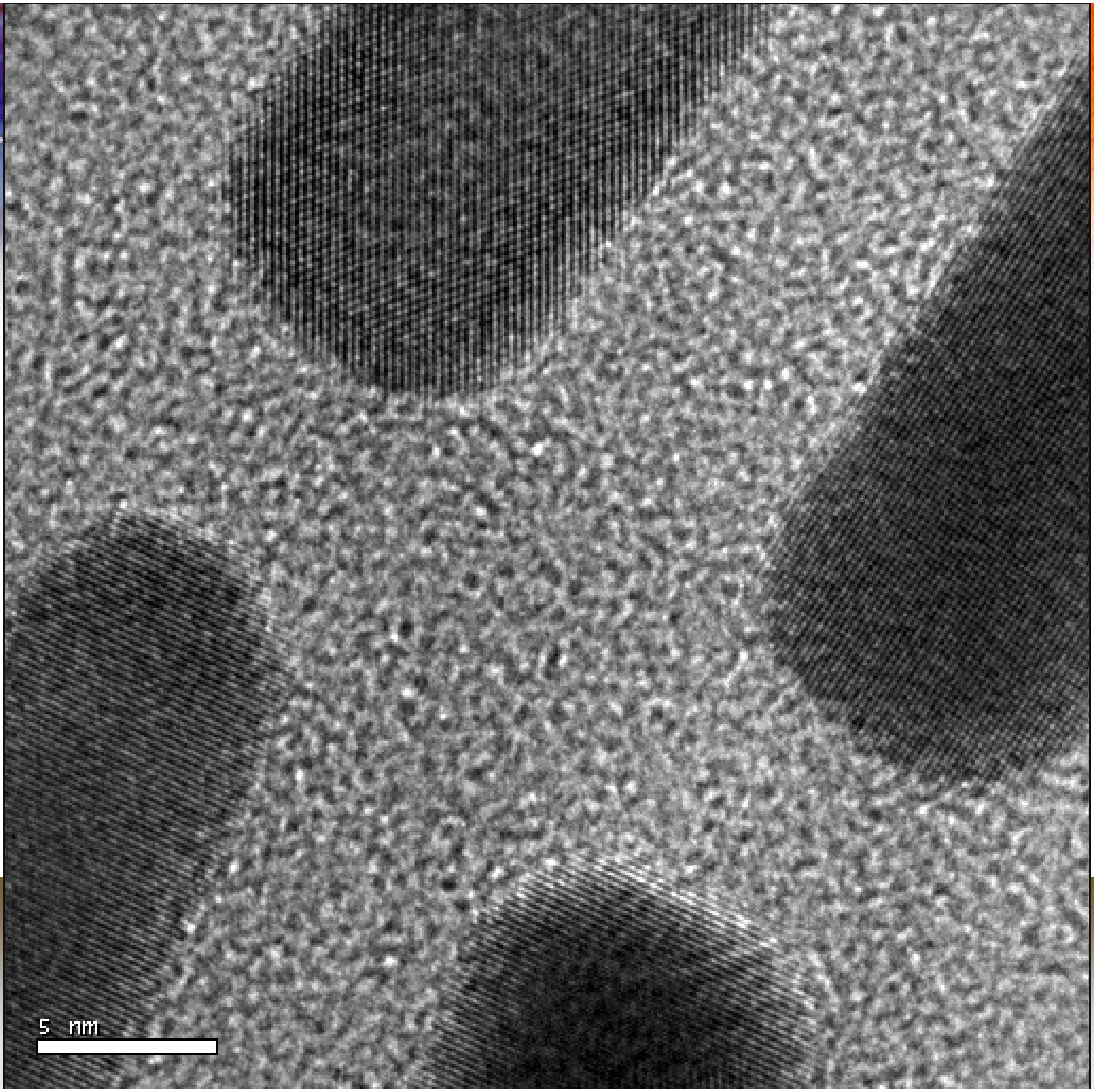
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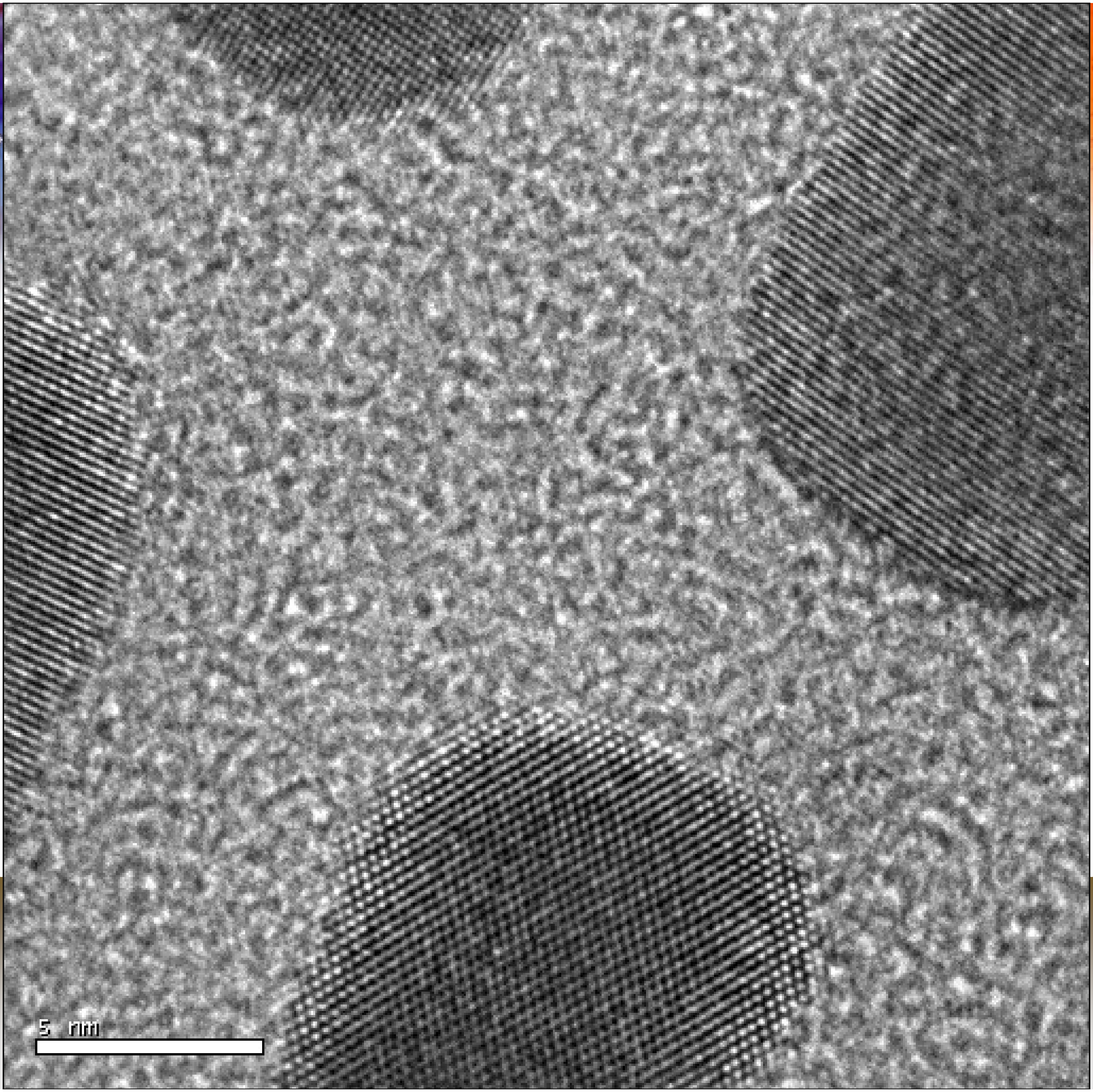
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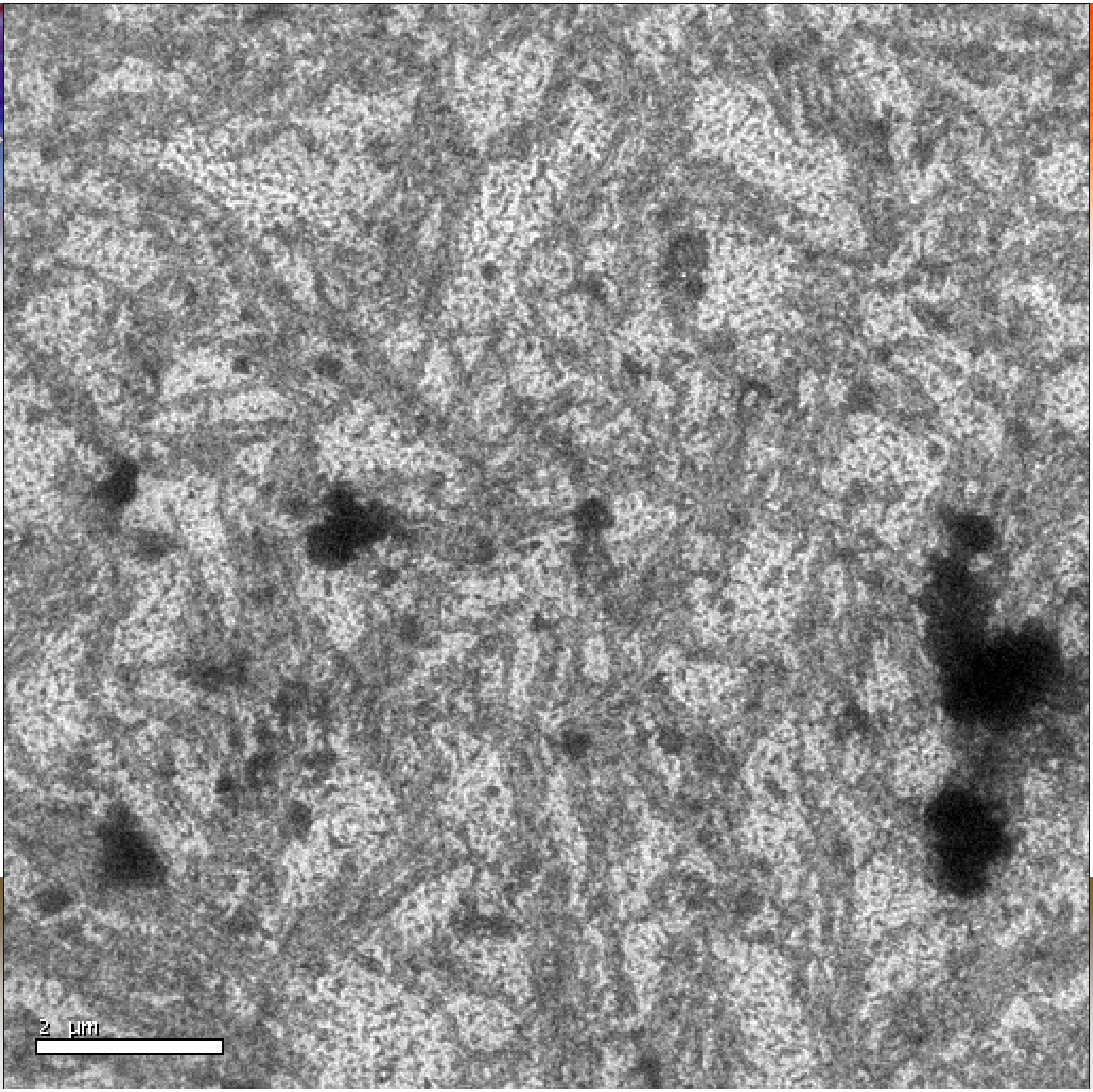
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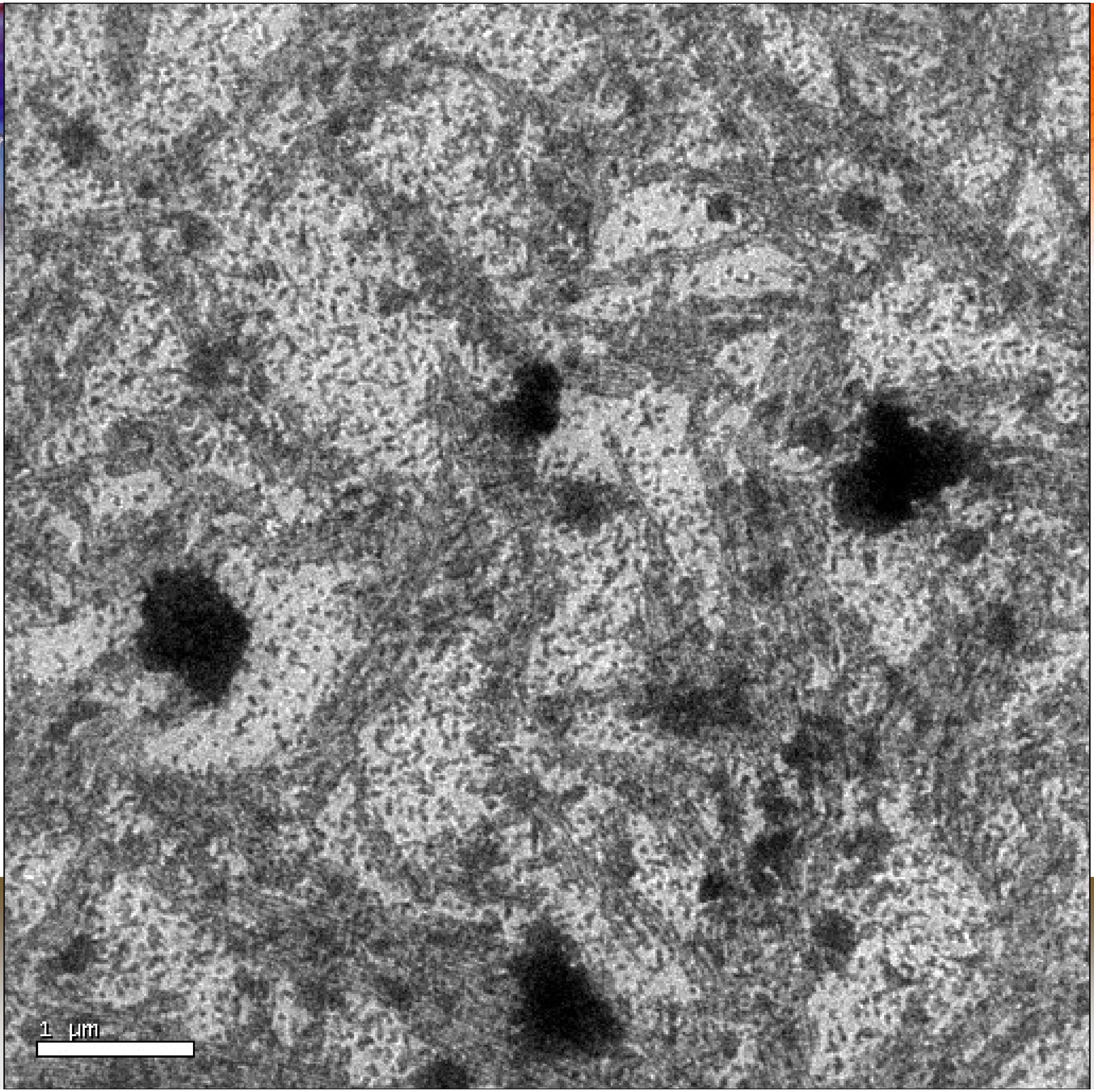
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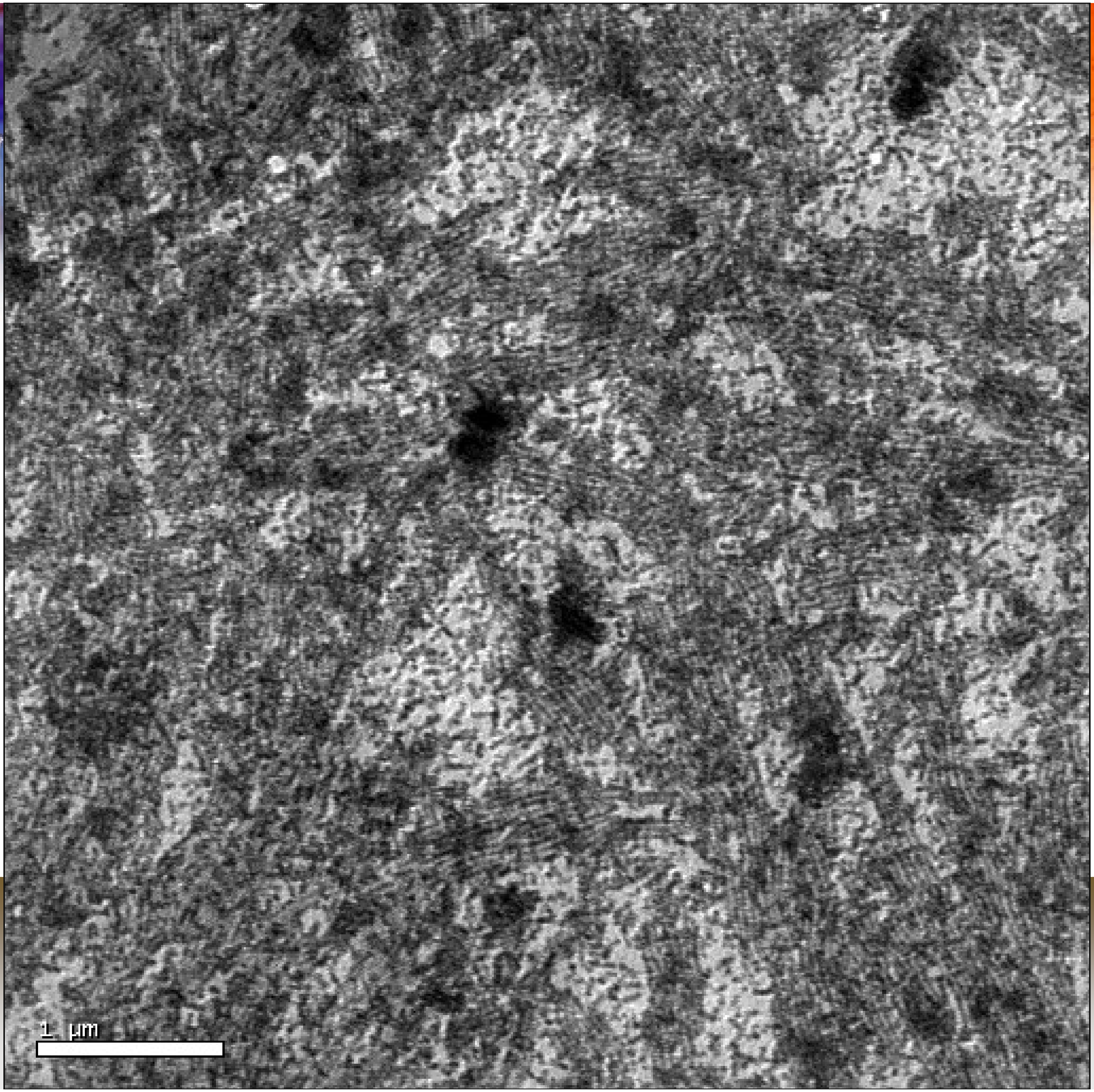
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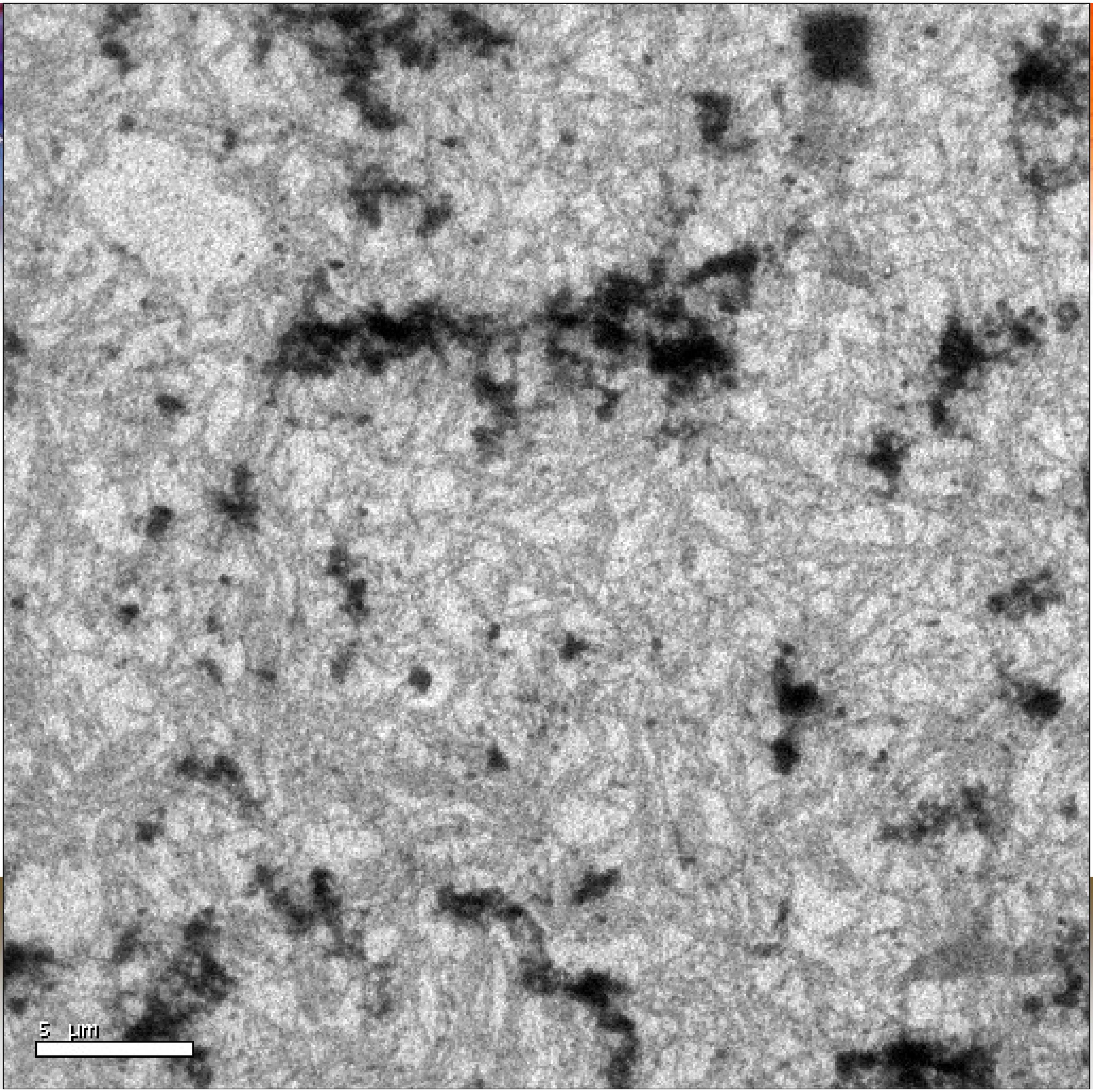
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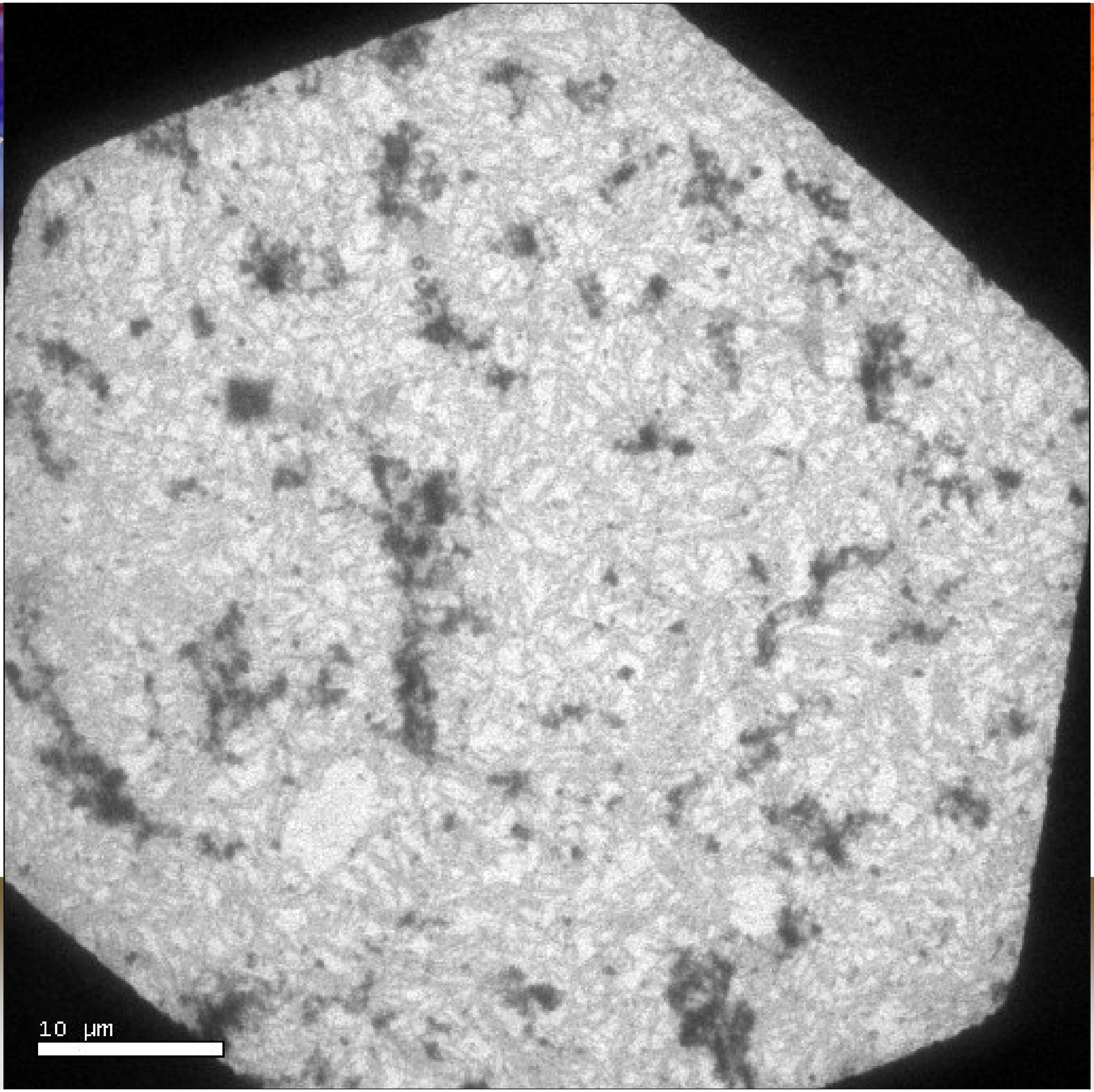
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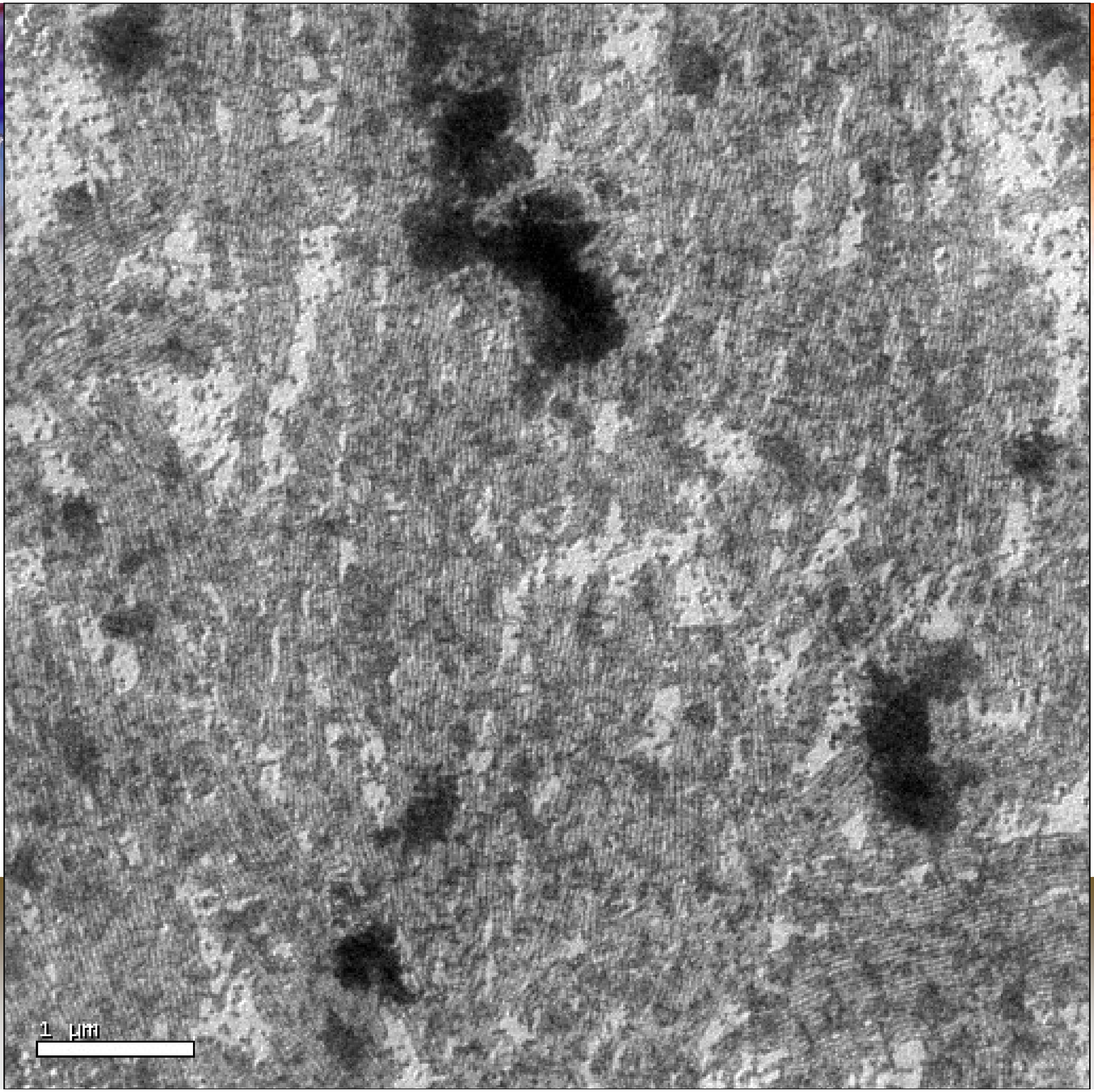
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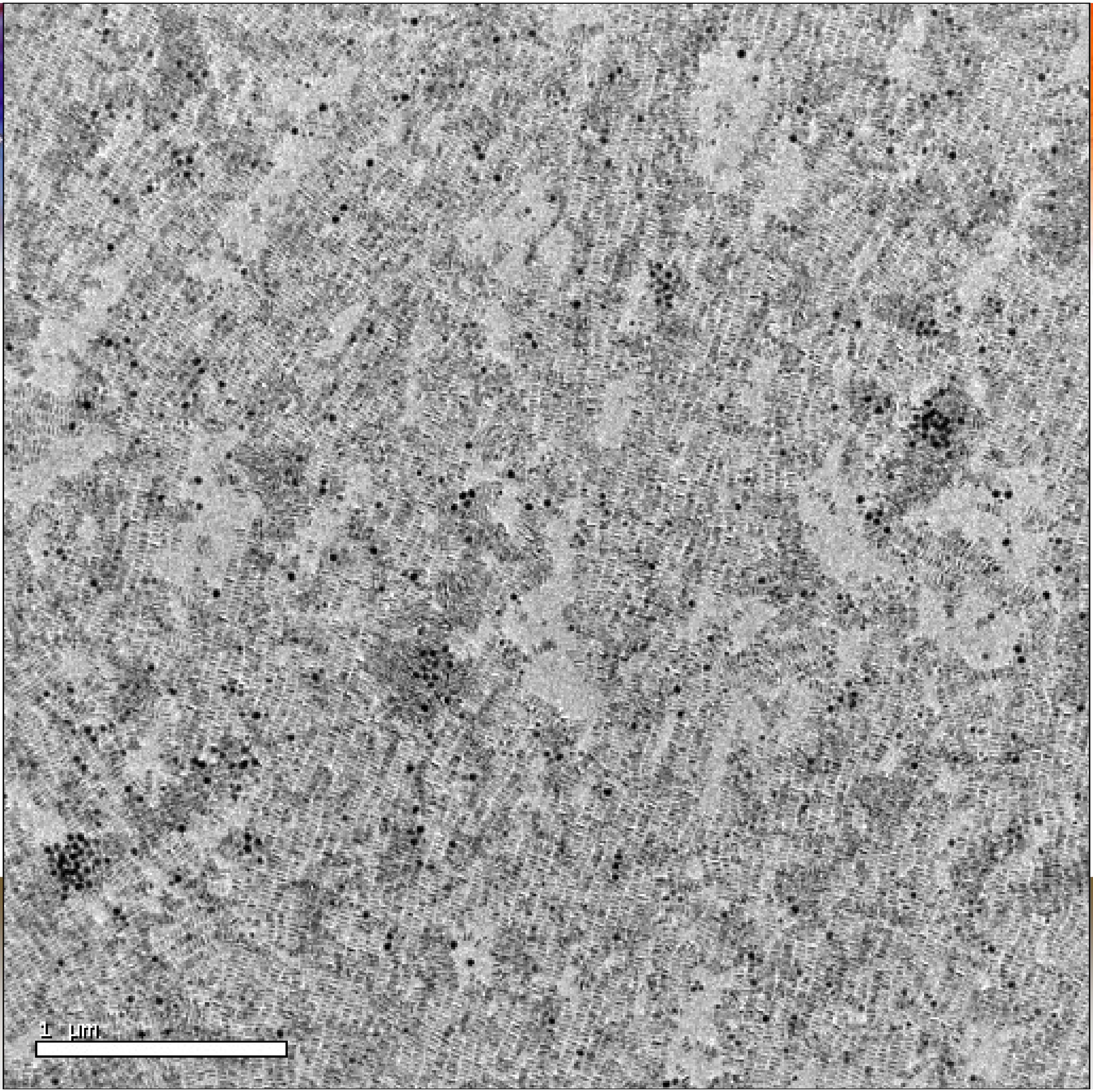
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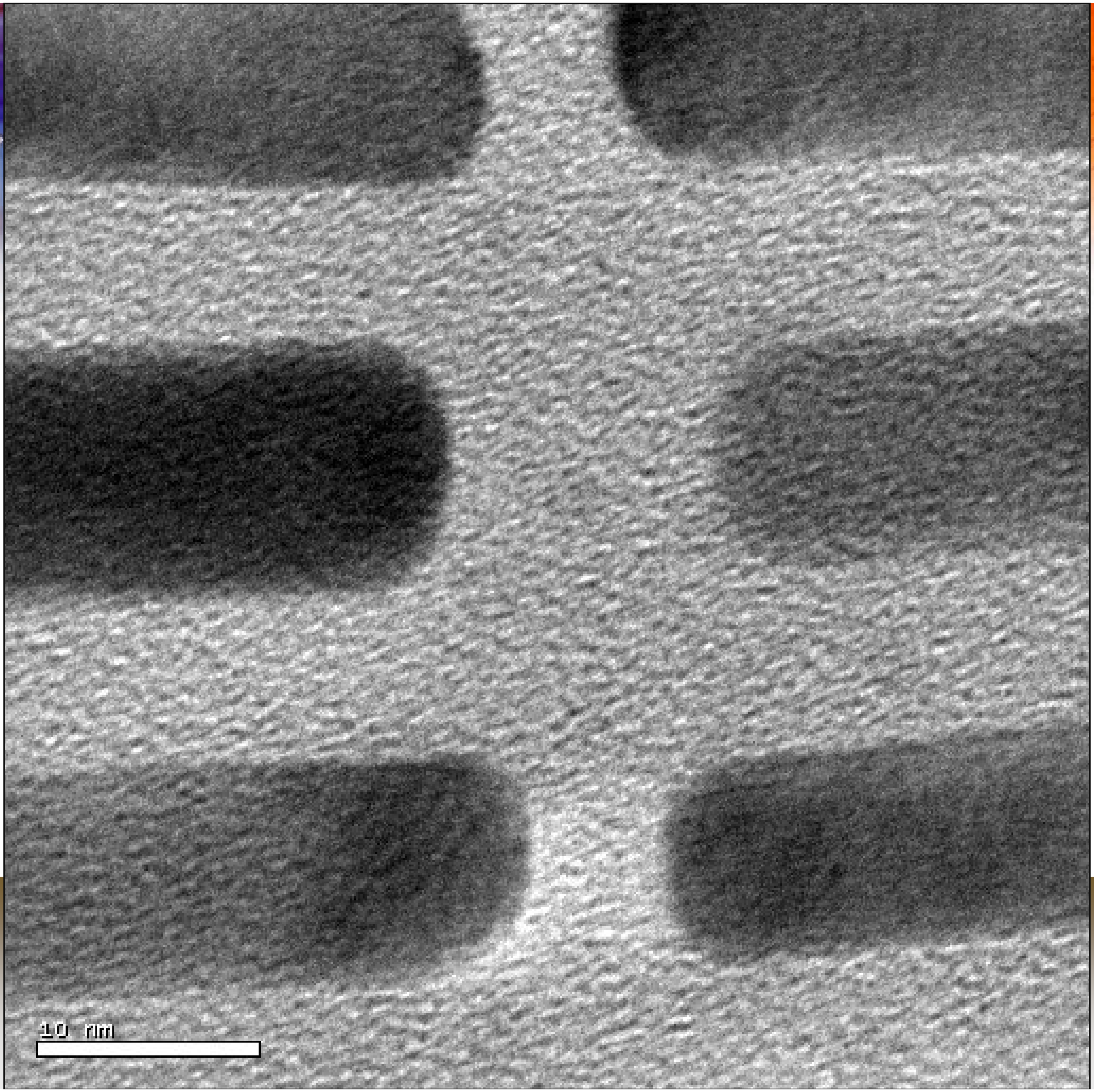
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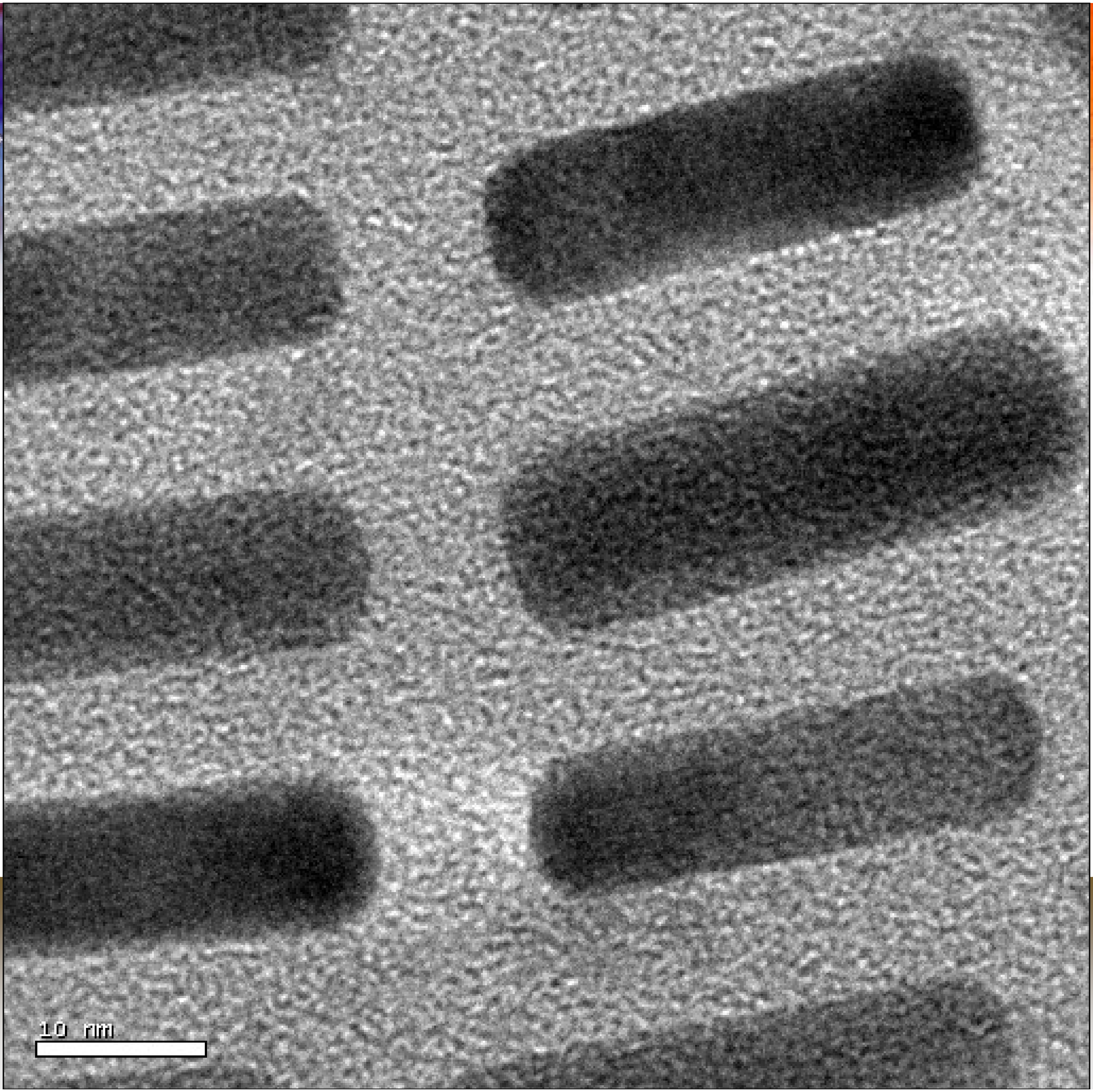
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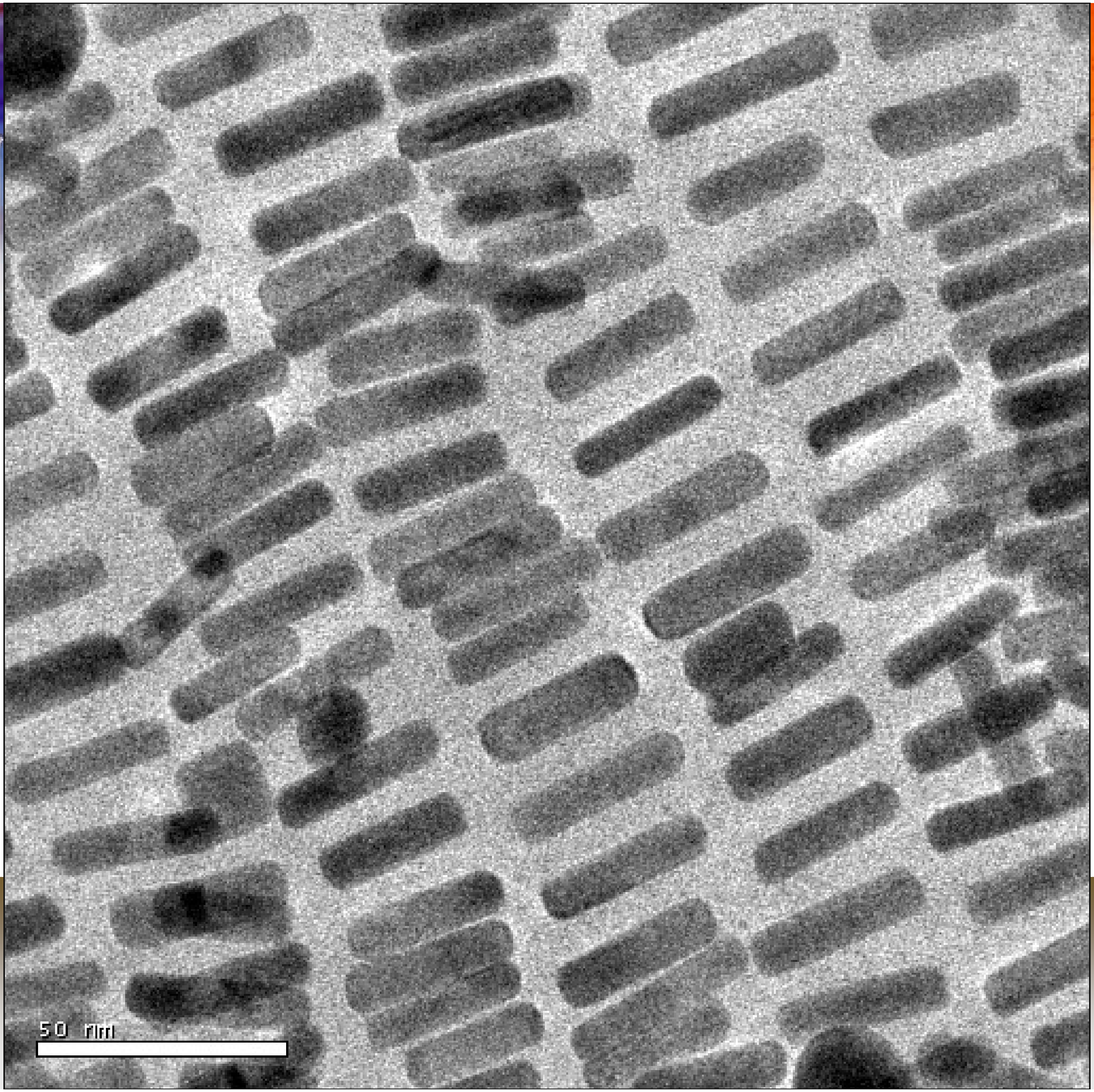
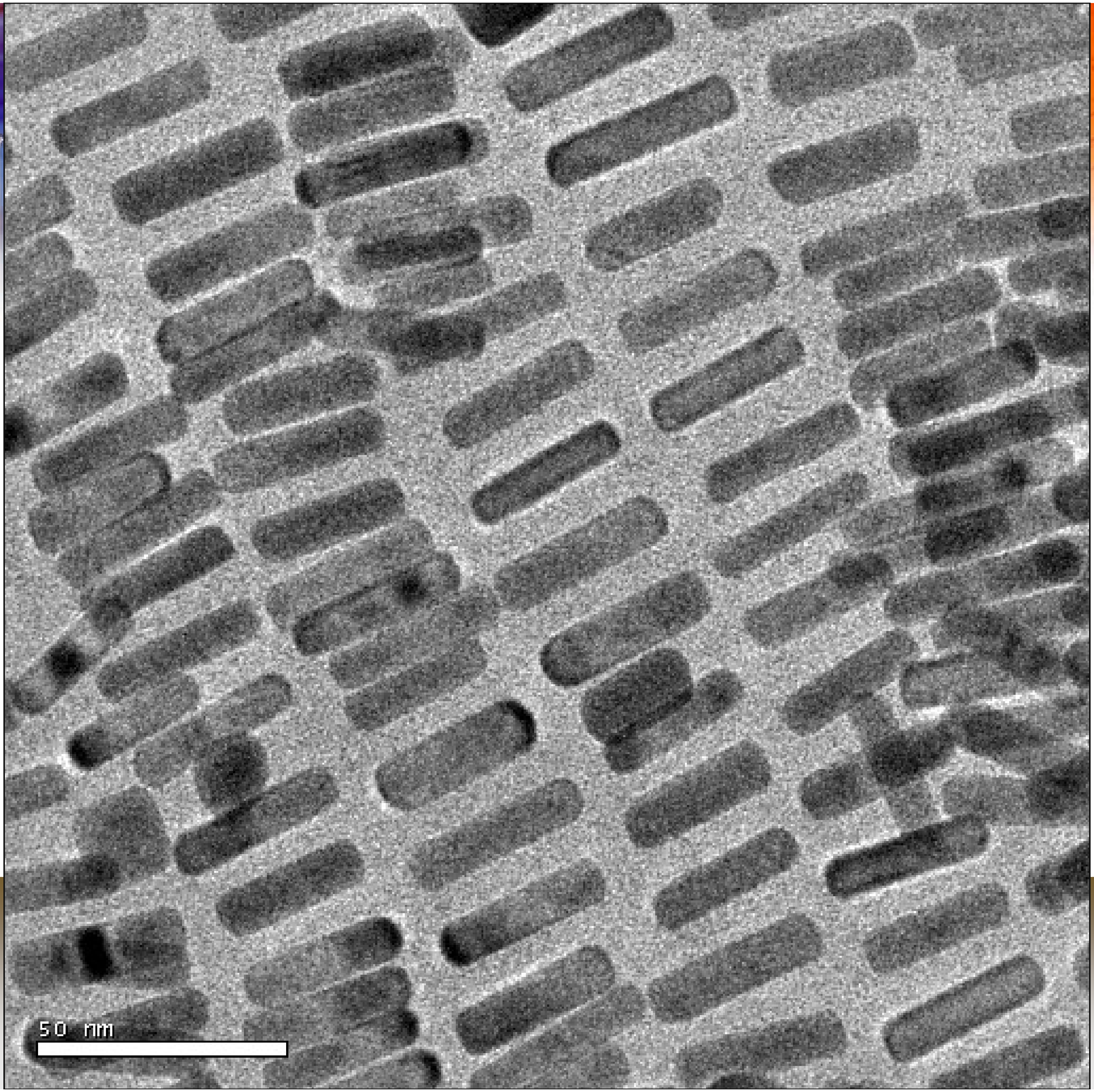

50 nm


50 nm

(i) and (ii) are the consistent mechanisms for GNRs with ARs of 3 and 16, respectively,

if (iii) is the driving force behind the assembly, citrate adsorbed ends and CTAB adsorbed sides of GNRs should attract each other, resulting in an endto-side assembly; if (iv) is the driving force, GNRs with an AR of 3 should be separated by adding enough CTAB (e.g., 0.5 mL of 40 mM CTAB) to cover whole surface of the GNRs
because the citrate anions are easily replaced by CTAB due to the strong affinity of CTAB to gold surface.

Also in the case of GNRs with an AR of 16, the concentration of citrate anions is simply too low to connect so many GNRs (The estimated concentration of citrate anions in the solution is <10 nM.); the addition of 0.5 mL of 40 mM CTAB to the end-to-end connected GNR solution (AR) 16) results in the singly dispersed GNRs in the solution, therefore, the GNRs are not aggregated (i), but connected by the interdigitated CTAB at the gap where the CTAB-covering rate is comparatively low (ii). In contrast, the
GNRs with an AR of 3 are aggregated at the end positions so that the GNRs are not separated by adding CTAB to the solution.

0.020 g of NaBH4 was dissolved in 50 mL of 0.025 M ice-cold sodium citrate solution, 0.6 mL of which was added to a mixture of 0.2 mL of 0.025 M sodium citrate solution and 19.8 mL of 0.25 mM HAuCl4 solution. This solution was used as a seed solution. Separately, a growth solution was prepared by adding 350 μL of 0.1 M ascorbic acid solution to a mixture of 2.319 g of CTAB and 63 mL of 0.25 mM HAuCl4 solution. 9, 9, and 45 mL of the growth solution were transferred into three beakers named A, B, and C, respectively. 800 μL of the seed-solution was added to beaker A while stirring for 5 s. 800 μL of the solution in beaker A was added to beaker B while stirring for 10 s. Then, 4 mL of the solution in beaker B was added to beaker C and stirred for 10 s, followed by aging for 1 day to finalize the growth reaction of GNRs. After discarding whole solution in beaker C, the residual precipitated on the bottom of the beaker was dispersed with 10 mL of Milli-Q water by sonication.