Supporting Information

Synthesis of pyramidal and prismatic hexagonal MoO_3 nanorods using Thiourea

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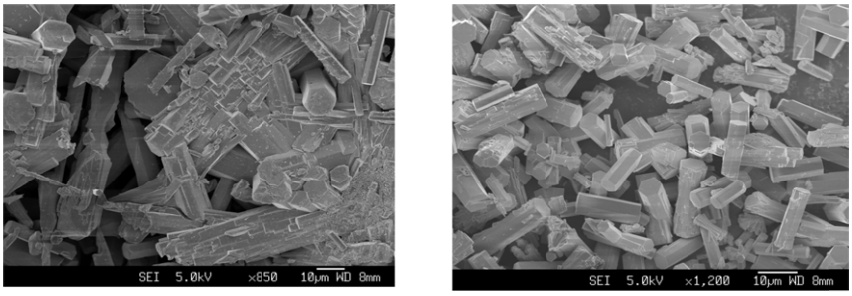
1. Optimization of the reaction parameters to synthesize pyramidal and prismatic morphology of hexagonal MoO_3 nanorods

1.1 Effect of the amount of source material (Mo powder)-

Here we have shown the effect of the concentration of the source material on the morphology on the nanostructure and found that the uniform prismatic morphology with a smaller diameter is possible when the concentration of the source material was 0.75 gm/ 5ml of H_2O_2, keeping all the remaining reaction parameters same.



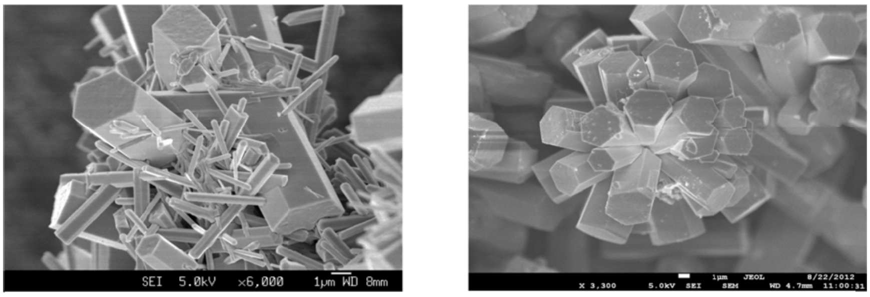
0.25 gm Mo

0.5 gm Mo

Figure S1: Effect of the source material on the morphology of the product

1.2 Effect of the concentration of ammonium ions (amount of thiourea)-

The role of thiourea is found vital in our study because hexagonal frame work can only be realized if ammonium ions are found to be in the reaction. In the main paper we have discussed about the samples synthesized with 0.22 M, 0.44 M and 0.88 M thiourea. Here we addressed the effect of the excessive amount of ammonium ions on the morphology of the hexagonal MoO_3 while all the remaining parameters were fixed.



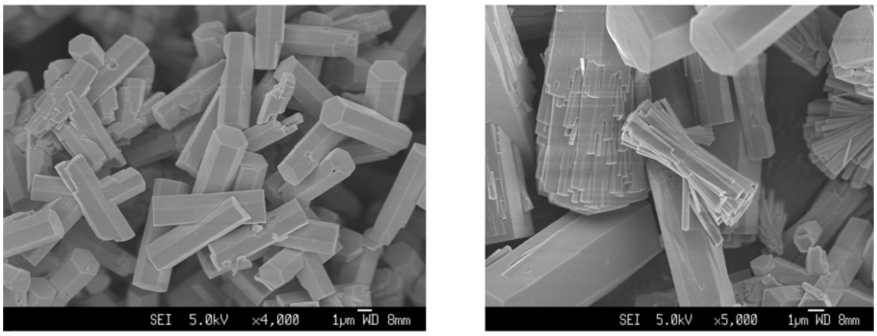
1.5 M Tu

2.5 M Tu

Figure S2: Morphology evolution at higher concentration of thiourea crystals

1.3 Effect of the concentration of ammonium ions (concentration of KOH solution)-

In order to evaluate the effect of the concentration of potassium hydroxide we performed experiment with 0.1 M and 0.3 M of KOH solution as the solvent to make ammonium ions solution using 0.88 M thiourea.



0.1 M KOH

0.3 M KOH

Figure S3: Morphology evolution with two different concentration of KOH solution

2. Reaction of Thiourea with peroxomolybdaic acid solution

No addition Mo^{+6}

Upon addition

Mo^{+5} and Mo^{+6}

After addition Mo^{+5}

Figure S4: Transformation of the peroxomolybdaic acid solution during the addition of the ammonium ions solution.

During addition of thiourea solution into the peroxomolybdaic acid solution we found the change in the color of the solution, due to the reduction of the peroxomolybdaic acid solution.

3. Thermal Analysis of the samples (DSC/TGA):

Figure S5: DSC/TGA plot of the h-MoO_3 nanorods (A-1, A-2, A-3 and No Thiourea)

Figure S5, shows the DSC/TGA behavior of the as synthesized samples at a fixed heating rate of 10 K/min. A slight weight loss (< 4%) after 20 min (~200 °C) was observed in all the samples. This is probably caused by the absorbed water molecules; a slight endothermic peak in the DSC characteristic signifies the effect. All the samples (A-1, A-2 and A-3) synthesized using thiourea begin to show a weight loss (< 3%) at 40 min (~400 °C) in the TGA curves where an endothermic peak in DSC curves is observed. The maximum weight loss of the samples occurs after 75 min (~750 °C) attributable to the sublimation of the MoO_3, an endothermic peak in the DSC curves reflects this behavior.

4. An appended experiment with Urea:

Precursor solution was prepared with urea instead of thiourea, using the process as explained in the experimental section of manuscript. In brief, 5 ml of H_2O_2 (30%) was mixed into 0.75 gm Mo powder in an ice bath and left for stirring for 15 min. followed by addition of 100 µl HNO_3. A clear yellow solution was formed (peroxomolybdic solution). In order to prepare solution of urea, 0.88 M of urea was mixed into a 0.5 M KOH solution (pH ~ 13.1). The solution of urea dropwise added into peroxomolybdic solution (pH ~ 1.7). This resultant solution was stirred for 1 hour and then transferred to an oven in a vial for reaction at 100 °C for 18 hours.

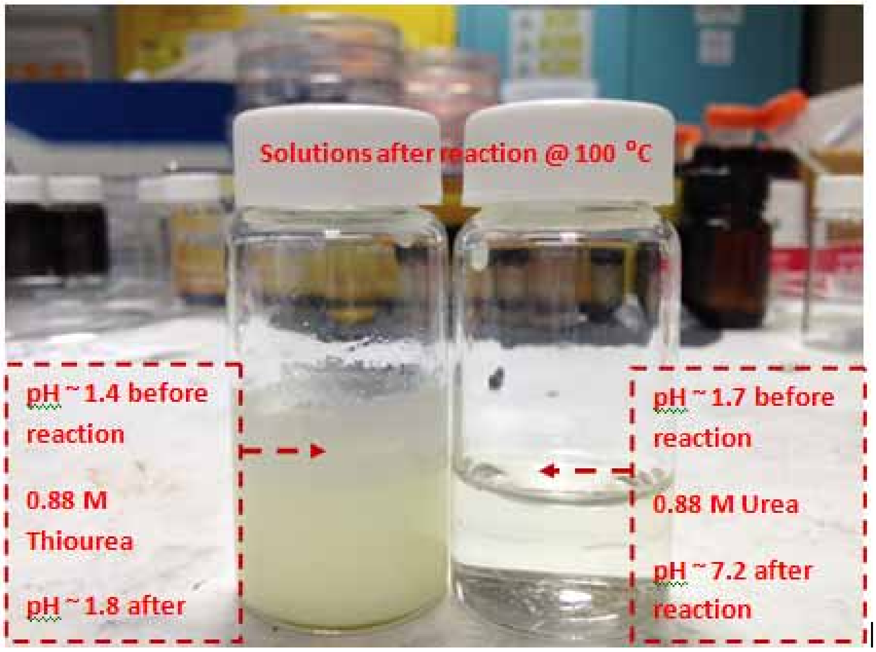


Figure S6: Precursor solution with thiourea (left side vial) and urea (right side vial) after reaction at 100 °C.

After completion of the reaction a clear solution was obtained (right side vial) while at same conditions a yellowish solution was achieved when thiourea was used (left side vial) instead of urea. We also found a pH =7.2 and pH =1.8 of the resultant solutions (after reaction) prepared with urea and thiourea respectively. The change in pH values of two solutions suggests the degree of oxidation of urea and thiourea in peroxomolybdic solution.

In both the cases partial oxidation of the solutions gives ammonium ions. The solution prepared with urea has an initial pH ~ 1.7 (pH ~ 1.4 for thiourea) before the reaction while after reaction pH ~ 7.2 (pH ~ 1.8 for thiourea) was found. Drastic change in pH of the solution prepared with urea suggests an increase in pH of the solution during course of reaction which triggers the generation of ammonia molecules according to reaction

$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

As the course of reaction passes concentration of ammonia molecules increases which leads to the dissolution of MoO_3 molecules in the solution (a clear solution signifies this effect).