

Surfactant Mediated Reductive Pathways for High yield Synthesis of 1D Rh Nanostructures from MW Heating and Their Shape Transformation

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Introduction

The synthesis of noble metal nanoparticles (NPs) has a great importance because of all the possible applications in the emerging field of nanotechnology, and for the improvement of catalytic properties.¹ Shape control synthesis of a thermodynamically unstable 1D nanocrystal is a real challenge. Morphology control during NP synthesis is now a hot topic because small morphology changes bring spectacular effects. Here CTAB upon decomposition produced ammonia which in turn acted as a reducing agent² and the undecomposed CTAB stabilized the nanostructures. The present work is one of the very few in the area of shape transformation under judicious control of pH. Interesting shape transformation from nanorods and nanowires to octahedral or spherical particles has been examined categorically deploying a redox reaction. However, octahedral particles are obtained exclusively from pentagonal faceted nanorods.

Experimental

Synthesis of 1D nanostructure: To an acidic aliquot of RhCl_3 , water was added and heated in a water bath for 2 hours keeping the volume constant with water and then neutralized with dilute ammonia solution for nanorod synthesis. Finally aqueous solution of CTAB was added and the mixture was heated for ~90 seconds in an ordinary microwave oven. Nanonetwork structure was obtained in an acidic condition devoid of ammonia. In situ generated NH_4Cl driven acidic condition produced cylindrical rods with high aspect ratio.

Results and Discussion

The product shows a permanent double hump absorption curve for the 1D nanoarchitecture (Curve D, Figure 1) with surface plasmon peaks at 234 nm and 312 nm reported for the first time for the 1D nanostructures.

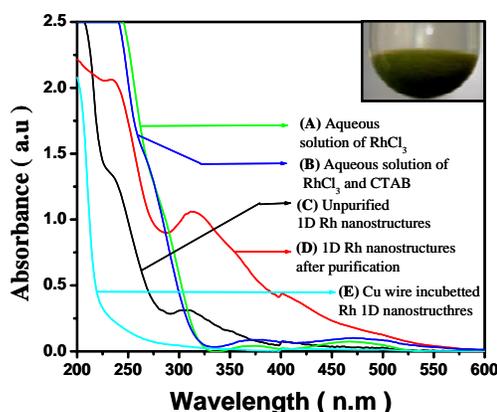


Figure 1: UV-vis absorption spectra indicating Rh NP synthesis from aqueous RhCl_3 solution.

We have presented the effect of CTAB, pH and impurity for the change in aspect ratio and sharpness of the edges of Rh nanorods (Figure 2).

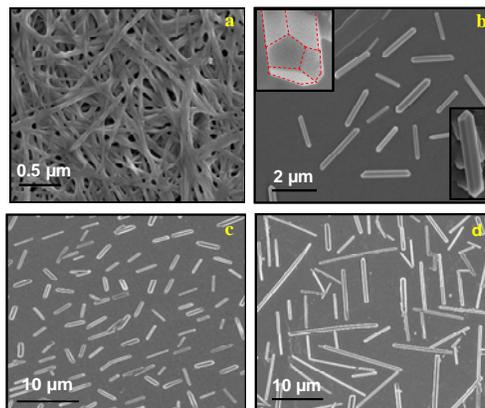


Figure 2: FESEM images of nanonetwork structure (a) and nanorod having different shape and aspect ratio, (b) Pentagonal faceted nanorod of 1-2 μm length (c) Cylindrical nanorod of 5-10 μm length (d) Cylindrical nanorod of 10-20 μm length.

Interesting shape transformations from nanorods and nanowires to octahedra or spherical particles have been examined categorically deploying a redox reaction on copper. However, octahedral particles are obtained exclusively from pentagonal faceted nanorods (Figure 3). During the synthesis, due to the incomplete reduction there remains some unreacted Rh(III) ions associated with the Rh nanocrystals. This incomplete reduction and the Rh(III) ion mediated shape transformation has become a definitive pathway while dealing with the rods and wires.

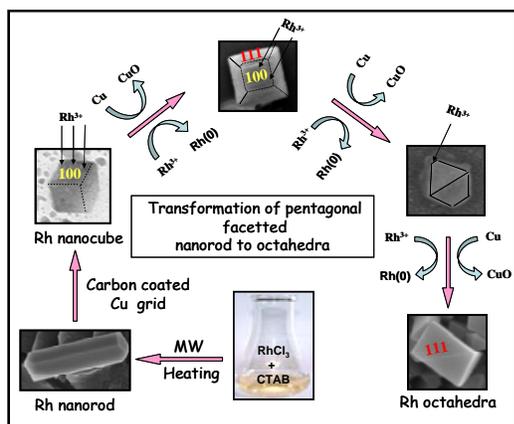


Figure 3: Mechanistic pathway showing the ex situ transformation of pentagonal faceted nanorod to octahedra.

We presume that unreacted Rh(III) get adsorbed on (100) facets of the nanocubes and is reduced during the oxidation of metallic copper. So copper is oxidized by Rh(III) ions. As prepared pentagonal faceted rhodium nanorod solution on TEM grid oxidize Cu to CuO nanowire (Figure 4).

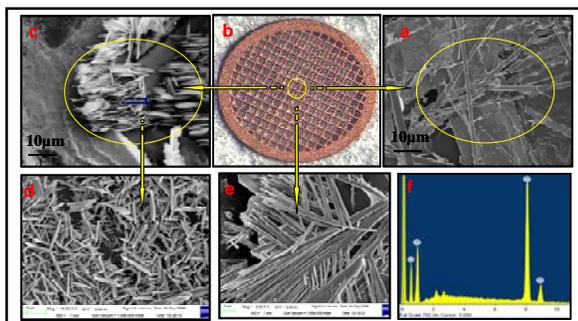


Figure 4: The sample for FESEM analysis was prepared by placing a drop of the solution containing Rh nanostructure onto a carbon-coated Cu grid (TEM grid) followed by slow evaporation of the solvent at ambient condition. (a): FESEM images of CuO nanowire formed

when the solution of cylindrical Rh nanorod was dispensed onto the Cu grid. (b): Digital image of a TEM grid. (c) & (d): FESEM images of CuO nanoplates, and (e) nanowires respectively formed when pentagonal faceted nanorod solution was dispensed onto the Cu grid. (f): EDX spectra of the evolved CuO nanostructures.

Conclusion

A new CTAB mediated bottom up process of reduction of Rh(III) ions from boiling aqueous solution has been presented. It has been demonstrated that microwave heating, pH as well as impurity well account the size and shape selective synthesis of rhodium NPs. The unique and stable double hump curve as the electronic spectral profile for the one dimensional structure is presented. Ex situ shape transformation of rhodium NPs has also been demonstrated in selectively chosen redox environment in the presence of CTAB and Rh(III) ions. Pentagonal faceted rods from neutral solution on Cu grids selectively produced octahedral Rh(0) particles. Thus Cu surface, pH, CTAB and Rh(III) co-jointly influence the shape transformation. It would be possible now to study the shape selective catalysis involving Rh NPs because of the availability of plentiful supply of Rh nanorods and nanowires from the reported simple synthetic procedures.

Acknowledgement: DST, New Delhi for financial assistance and Indian Institute of Technology, Kharagpur for research facilities.

References:

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