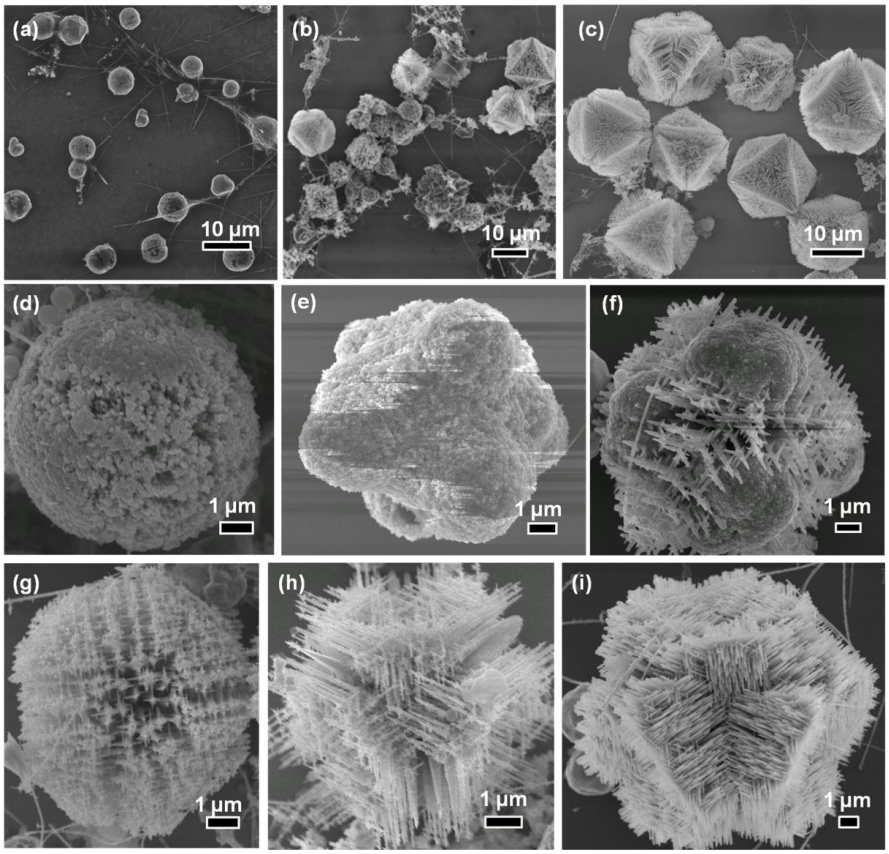
Unique Process Directing Role of Graphene Oxide in the Formation of Metal Oxide Mesocrystals

Mesocrystal, an intriguing structure made up of non-spherical nanomaterials as building blocks and grown by non-classical crystallization process, is of great interest to the scientific community in recent years. Its formation and growth mechanisms have greatly advanced our knowledge of naturally-occurring biominerals, in which the knowledge gained has been aptly applied to the synthesis of novel functional materials capable of displaying unprecedented properties.

Conventionally, the fabrication of Cu_2O nanomaterials routinely resulted in simple morphology such as nanowires. The formation of Cu_2O mesocrystals has not been demonstrated yet, possibly due to the intrinsic limitation of ionic precursors-based routes. Therefore, we ask a vital question: is there an appropriate modifier which can promote the formation of a polymeric matrix which is essential for the aggregation of amorphous nanoparticles at the early stage? To achieve this, we would need a two-dimensional nanomaterial with ample functional groups and graphene oxide (GO) sheets fit this criteria seamlessly. Graphene based sheets can be viewed as graphitic soft materials such as polymer, surfactant, colloid, membrane and liquid crystals. The quasi-two dimensional structure of GO tethered with abundant oxygen functional groups impart dual molecule-colloid properties which can elicit multivalent interaction with Cu^{2+} as well as the polymer additive, both of which induce and stabilize the aggregation for subsequent particle-mediated crystallization.

In this research highlight, we draw attention to our recent discovery of an alternative crystallization pathway mediated by graphene oxide stabilized clusters prior to nucleation (Suzi Deng *et al*, J. Am. Chem. Soc., 2012, 134 (10), pp 4905–4917, coverpage for NanoToday). This collaborative project is led by Dr Deng Suzi and it involves Dr Fan Hai Ming from Northwest University, Dr Sayle from Cranfield University and Prof Subodh Mhaisalkar from Nanyang Technological University. We reported the hydrothermal synthesis of reduced graphene oxide (rGO)-conjugated Cu_2O nanowire mesocrystals by non-classical crystallization in the presence of GO and *o*-anisidine. We elucidate the synthetic pathways and demonstrate a practical application for a novel composite where reduced GO (rGO) sheets are conjugated extensively with Cu_2O mesocrystals. The resultant composite is uniquely different from conventional crystals because it possesses distinct octahedral crystal faces and highly anisotropic interpenetrating nanowire building blocks which represent a new class of mesocrystal termed “nanowire mesocrystals”. This is only made possible by the presence of GO and poly(*o*-anisidine), which act as mediators for the non-classical crystallization of the Cu_2O nanowire mesocrystal via an economical and convenient one-pot hydrothermal approach.



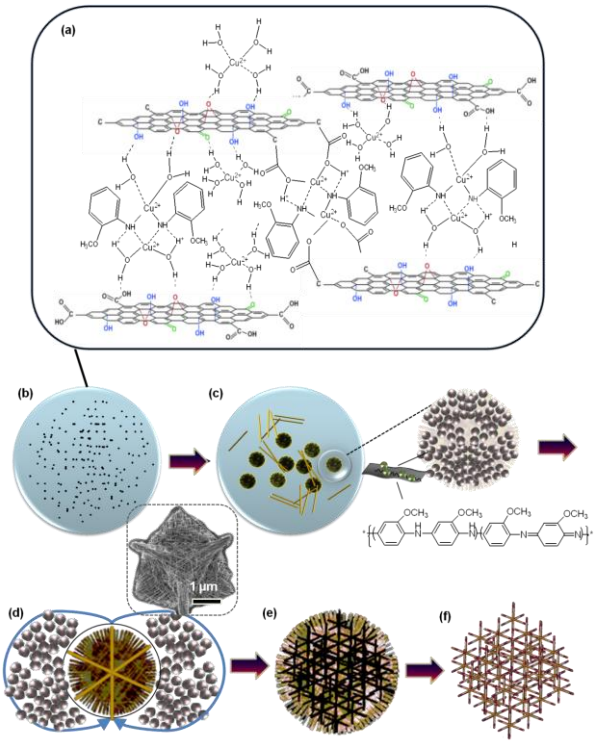
Morphology evolution of the precursors to the Cu2O nanowire mesocrystals, as indicated by SEM images of the intermediates and products grown for reaction times of (a) 3h (b) 9h (c) 15h. (d-i) Representative SEM images illustrating the mesoscale transformation from (d-f) spherulite to (g) hierarchical nanowire structure, and finally (h, i) octahedral nanowire mesocrystal.

Significant findings in this work:

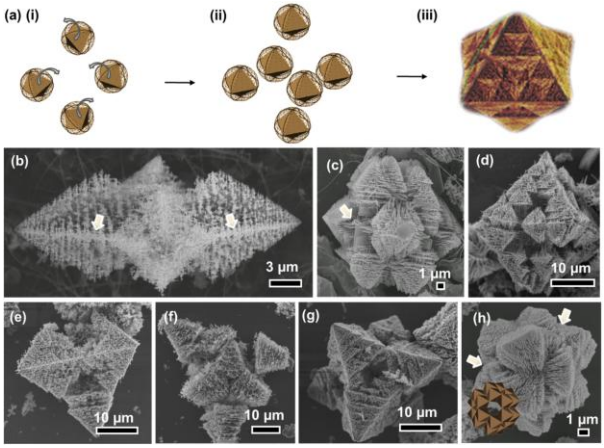
1) We provided a unifying crystallization mechanism and model system of controlled Cu_2O aggregation and crystallization for the three-dimensional self-organization of highly anisotropic 1D functional nanowire building blocks into mesocrystals. Detailed insights into a non-classical crystallization strategy (i.e. particle-mediated aggregation under diffusion-limited conditions) and elucidation of the formation mechanism of the nanowire mesocrystals, by time-dependent characterization, isolation of various mesocrystal intermediates and molecular dynamics simulations. GO sheets play an eminent role in the transition of growth mechanism from conventional ion-by-ion growth to non-classical particle-mediated aggregation by complexing with poly(*o*-anisidine) to serve as unconventional polymeric matrices for Cu_2O nuclei seeding, promotes the formation of amorphous microsphere, and mesoscale transformation to the final mesocrystal.

2) Identification of a higher-tier growth, on top of the peculiar particle-mediated morphogenesis of the octahedral nanowire mesocrystals. Individual octahedral mesocrystals undergo oriented attachment to create complex voided Sierpinski polyhedrons, and structures with defects.

3) Demonstration of the rGO-Cu_2O mesocrystals composites as superior NO_2 sensors with enhanced sensitivity over the constituent counterparts at room temperature. This is attributed to the synergistic combination of the mesoporous structure of the unique nanowire mesocrystal and enhanced conductivity of interconnecting rGO networks. To summarize, our work is an important step towards designing mesocrystal-based nanodevices for practical applications, such as ultrasensitive environmental sensors.



Schematic illustration of the Cu2O crystallization process assisted by o-anisidine and GO.



Second tier growth via oriented attachment.

Reference:

"Reduced Graphene Oxide Conjugated Cu2O Nanowire Mesocrystals for High Performance NO2 Gas Sensor" Suzi Deng,[1] Verawati Tjoa,[2,7] Hai Ming Fan,*[3,6] Hui Ru Tan,[4] Dean C. Sayle,[5] Malini Olivo,[6] Subodh Mhaisalkar,[2] Wei Jun,[7] Chorng Haur Sow*[,1],
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