

Preferential Growth of Metallic SWNTs Achieved

One obstacle to the implementation of single-walled carbon nanotubes (SWNTs) in electronic devices is that their synthesis results in a mixture of conducting and semiconducting species. Progress has been made in separating SWNTs based on their conductivities, which is determined by chirality. Some progress has been made in controlling SWNT structure during growth (e.g., semiconducting SWNTs are produced preferentially by plasma-enhanced chemical vapor deposition), demonstrating that somewhat different mechanisms lead to different chiralities. Recently, A.R. Harutyunyan and co-researchers at the Honda Research Institute, Columbus, Ohio, in collaboration with T.M. Paronyan of the University of Louisville, S.M. Kim of Purdue University, and their colleagues, were able to increase the fraction of CNTs with metallic conductivity grown from Fe nanocatalysts from 33% to a maximum of 91% by varying the conditions under which the catalyst was annealed.

As reported in the October 2 issue of *Science* (DOI: 10.1126/science.1177599;

p. 116), Harutyunyan and co-researchers annealed *in situ* Fe nanocatalysts deposited onto a flat SiO₂/Si support, using an ambient atmosphere of He or Ar, and varying ratios of H₂ and H₂O. Using methane as the carbon source, SWNT synthesis was performed at 860°C. The researchers observed with scanning electron microscopy that increasing the concentration of reductive species (Ar:H₂ was increased from 9:1 to 8:2 at 840 Torr with ~3.5 mTorr H₂O) during catalyst conditioning resulted in higher densities of SWNTs on the substrate. This led them to perform a systematic study of SWNT growth on catalysts annealed *in situ* under varying ambient conditions. The ratio of metallic to semiconducting tubes was obtained by measuring the SWNT's Raman breathing modes, specifically, $R = I_{\text{met}}/I_{\text{sem}}$ where I_{met} and I_{sem} are the integrated intensities of the metallic and semiconducting SWNTs, respectively. The researchers observed an increase in R by (1) replacing Ar with He; (2) increasing the H₂ content in the Ar-H₂ atmosphere; and (3) increasing the annealing time from 1 minute to 10 minutes. A very high R value of 20.2, which corresponds to over 90% metallic SWNTs, was

obtained with a He:H₂ ratio of 8:2 and an annealing duration of 10 minutes.

The researchers verified their Raman spectra analysis by measuring field-effect transistor performance for 47 individual SWNTs and characterizing them according to their source-drain current. Another set of experiments demonstrated that the catalyst annealed in the presence of H₂O in the ambient atmosphere together with He promotes the growth of metallic tubes whereas semiconducting tubes are favored by catalysts annealed with an ambient atmosphere of H₂O and Ar. The researchers also investigated the mechanism of tube formation with *in situ* transmission electron microscopy of the Fe nanocatalysts under varying gaseous environments in analogy with the SWNT-synthesis conditions. Differences in both morphology and coarsening behavior of the nanocatalyst were observed.

The researchers said that "these catalyst rearrangements demonstrate that there are correlations between catalyst morphology and resulting nanotube electronic structure and indicate that chiral-selective growth may be possible."

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Quasicrystalline Order Revealed in Nanoparticle Superlattices

Quasicrystals are a class of materials that show sharp diffraction peaks despite presenting forbidden symmetry operations in classical crystallography. D.V. Talapin and M.I. Bodnarchuk from the University of Chicago; E.V. Shevchenko from Argonne National Laboratory; and X. Ye, J. Chen, and C.B. Murray from the University of Pennsylvania, have reported in the October 15 issue of *Nature* (DOI: 10.1038/nature08439; p. 964) that different binary nanoparticle colloidal systems can self-assemble into 12-fold rotational quasicrystalline order. According to the researchers, the compositional flexibility demonstrated that quasicrystal ordering could be a relatively common phenomenon in nanocrystal solids, with suitable size ratios between particles.

The researchers obtained the quasicrystalline nanoparticle assemblies by evaporating relatively concentrated colloidal solutions of 13.4-nm Fe₂O₃ and 5.0-nm Au monodisperse nanoparticles capped with oleic acid and dodecanethiol molecules, respectively, in tetrachloroethylene at 50°C under reduced pressure (~3.2 kPa) on a carbon-coated transmission electron microscopy grid or a silicon nitride membrane tilted by 60° or 70°. The researchers used the surfactant molecules to introduce short-range steric repulsion that counterbalanced the van der Waals forces and prevented uncontrollable aggregation of nanocrystals in the colloidal solution. They observed that during this process the nanocrystals self-assembled in AlB₂- and CaB₆-type phases, and on the (3².4.3.4) Archimedean tiling structure, depending on the Fe₂O₃-to-Au nanoparticle ratio. This structure is formed by five planar polygons (three triangles and two squares) sharing a common vertex in such a way that they fill the plane with no overlaps and no gaps, depending on the Fe. The nomenclature of these structures lists in order the polygons that meet at each vertex using integers that correspond to the numbers of sides of the polygons. So, the (3².4.3.4) structure consists of two triangles sharing a common edge, surrounded by two squares at each side of the triangles, and filling the empty space by another triangle, all of them

sharing a common vertex. In proximity to the (3².4.3.4) phase in the binary phase diagram of these nanoparticles, the researchers observed reproducible formation of a type of binary superstructure without translational symmetry. They observed that these structures showed sharp electron diffraction patterns revealing dodecagonal rotational symmetry, a symmetry operation forbidden in periodic structures. The researchers identified these self-assembled nanoparticle superstructures as dodecagonal quasicrystals (DDQC), a phase that formed also from colloidal solutions containing 12.6-nm Fe₃O₄ and 4.7-nm Au nanocrystals, and 9-nm PbS and 3-nm Pd nanocrystals, with size ratios between particles of ~0.43.

The researchers said that the space-filling factor had a significant effect on the relative stabilities of binary nanoparticle phases, and the quasi-periodicity could be a result of maximizing the entropy of arrangement of square and triangular "tiles." They consider that the discontinuity in the entropy density corresponding to the DDQC state might provide a mechanism for locking the quasicrystalline state over a range of nanocrystal concentration ratios. The researchers think that these studies will provide insight into the formation of the quasicrystal phase in atomic systems, and can be used as a convenient platform for detailed investigation of quasicrystal properties.

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Addendum

David N. Seidman and Krystyna Stiller, Guest Editors of the theme "A Renaissance in Atom-Probe Tomography" (*MRS Bulletin*, October 2009), note that in 1973, J.A. Panitz invented the 10-cm atom probe (discussed on p. 745)—now called the imaging atom probe—which is the progenitor of all atom-probe tomographs, citing the following references: J.A. Panitz, *Rev. Sci. Instrum.* **44**, 1034 (1973) and J.A. Panitz, "Field Desorption Spectrometer," U.S. Patent 3868507 (1975).