Watching Solution Growth of Nanoparticles in Graphene Cells

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MATERIALS SCIENCE

Watching Solution Growth of Nanoparticles in Graphene Cells

The growth and coalescence of platinum nanocrystals held in a pocket created by graphene sheets is followed at atomic resolution in an electron microscope.

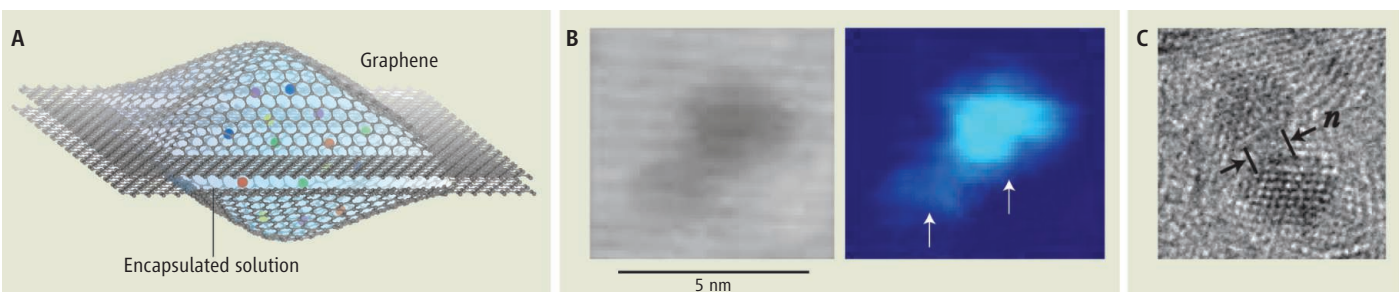
Christian Colliex

The characterization of grown nanoscale objects can now be realized at an unprecedented level of spatial resolution with transmission electron microscopes (TEMs). Crystalline structures can typically be resolved to better than 0.1 nm (*1*), chemical identification can be achieved at the level of single atoms or single atomic columns (*2*), and optical properties can be mapped at the nanometer scale (*3*). However, these frozen snapshots at defined stages after the growth process do not reveal the real-time dynamics of crystal nucleation and growth. To improve our understanding of the atomistic processes involved during these chemical reactions, sequences of high-resolution EM images of the specimen in the solution need to be recorded. On page 61 of this issue, Yuk *et al*. (*4*) report atomic-resolution images obtained with the Transmission Electron Aberration-Corrected Microscope I (TEAM I) (*5*) of colloidal platinum (Pt) nanocrystals growing inside liquid-containing cells bounded by graphene sheets that reveal unexpected insights into the growth mechanism.

In a recent review article, de Jonge and Ross (*6*) noted that electron microscopy of specimens in liquids has a long history [for example, see Ruska (*7*)]. Nonetheless, to solve the intrinsic difficulty of observing a liquid sample under the vacuum environment of the electron microscope column, unconventional designs of specimen holders have to be developed. The open environmental chamber generally used for monitoring gas and liquid reactions (in which gas or vapor is rapidly pumped away) is not compatible with situations requiring a thin and stable liquid layer. The recent and rapid progress in microfabrication technologies, and in microfluidics in particular, has allowed the realization of hermetically sealed cells. In most studies reported (*8*, *9*), these "liquid cells" are generally made of 100-nm-thick silicon nitride (Si_3N_4) layers separated by a silicon oxide buffer of typically 0.5 to 1 μm thick. The dynamics of the diffusion and growth of nanoparticles during chemical reactions or electrodeposition processes can be monitored by the incident TEM electron beam through the viewing windows. However, for several reasons—in particular, the limited transparency of the cell and the possible interaction between the particles in suspension and the window surfaces—the spatial resolution for imaging or analysis (or both) has remained on the order of 1 nm.

The "trick" responsible for the success of Yuk *et al*. in achieving atomic resolution is their use of graphene layers as sealing windows for liquid cells. These subnanometer-thick suspended membranes offer very weak intrinsic contrast—they act like clear windows—because carbon has a low atomic number so that it only weakly scatters the electron beam. Graphene also exhibits high mechanical strength and impermeability, and its surface is chemically nonreactive. This approach scales up what has been done with single-walled carbon nanotubes, which have been used in the electron microscope to isolate and preserve individual molecules (carbon peapods and coronene) for ultrahigh resolution imaging or analysis (*10*, *11*). Yuk *et al*. had previously reported the synthesis of stacked graphene layers (or other two-dimensional sheets) as sandwiches or veils to encapsulate various guest nano-objects (*12*). The use of such graphene liquid cells (GLCs) to trap minute volumes of a solution in a pocket, typically from 6 to 100 nm thick, or a blister, is a natural extension of these methods (see the figure, panel A). The authors report a success rate >90% for producing viable GLCs.

This performance of GLCs can be compared with the same authors' silicon-based microchip (*13*); panels B and C of the figure display micrographs recorded by the same group on the growth of colloidal Pt nanocrystals at similar stages. In the earlier study, the coalescence of particles was inferred from changes in shape and in diffraction contrast based on the observation of polycrystalline assemblies. With the use of GLCs, such changes are fully revealed with the atomic structure. Many measurements were performed that defined the crystallographic orientation changes during nanocrystal attachment. The variation in neck diameter as particles coalesced was monitored, along with the total changes in diameter and length. Frame-by-frame inspection of the recorded sequences of micrographs (with ~30-ms time resolution) allowed the dance of nanocrystals along their diffusion trajectories and the rearrangement of the crystalline structure to be followed. This level of spatial resolution



Growth inside the microscope. (**A**) A schematic is shown of a GLC developed by Yuk *et al*. that locally encapsulates the growth solution of Pt nanocrystals for structural studies in a TEM. (**B**) Micrographs of the coalescence process between two particles shown in (*13*) with a silicon liquid cell. (**C**) Micrograph of the coalescence process between two Pt nanocrystals using the GLC in TEAM I, at a stage near that shown in (B). The neck distance *n* is ~1.2 nm.

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(below 1 Å) in TEAM I, which is equipped with spherical and chromatic aberration correctors, was achieved with primary electrons of 80 keV, which are much less damaging to samples than the 300-keV electrons used in (*13*). The use of correctors that can tolerate objective lenses with larger gaps between the pole pieces also enhances the free space available for the specimen holders.

With the new level of performance demonstrated in this work, Yuk *et al*. have studied in detail various (and unexpected) stages of the colloidal growth of Pt nanoparticles. Open questions remain, such as the role of the ligand molecules attached to the metallic species or how the first burst of electrons acts as the seed of the nucleation process. The properties of nanoparticles are highly dependent on their size, shape, and environment, and such studies should provide insights that may allow the design of homogeneous assemblies of nanoparticles of defined sizes, morphology, and connectivity. Their approach opens new domains of research in the physics and chemistry in the fluid phase in general. How this new generation of liquid cells will be useful for biochemical and biological problems, where the use of microchip-based liquid cells has not been fully exploited, in spite of the spectacular advances recently shown for imaging of whole biological cells in liquids (*14*) is to be further explored.

References

1. R. Erni, M. D. Rossell, C. Kisielowski, U. Dahmen, *Phys. Rev. Lett.* **102**, 096101 (2009).
2. D. A. Muller *et al*., *Science* **319**, 1073 (2008).
3. L. F. Zagonel *et al*., *Nano Lett.* **11**, 568 (2011).
4. J. M. Yuk *et al*., *Science* **336**, 61 (2012).
5. See http://ncem.lbl.gov/team/TEAMpage/TEAMpage.html.
6. N. de Jonge, F. M. Ross, *Nat. Nanotechnol.* **6**, 695 (2011).
7. E. Ruska, *Kolloid Z* **100**, 212 (1942).
8. J. M. Grogan, L. Rotkina, H. H. Bau, *Phys. Rev. E Stat. Nonlin. Soft Matter Phys.* **83**, 061405 (2011).
9. A. Radisic *et al*., *Nano Lett.* **6**, 238 (2006).
10. K. Suenaga *et al*., *Science* **290**, 2280 (2000).
11. T. Okazaki *et al*., *Angew. Chem. Int. Ed.* **50**, 4853 (2011).
12. J. M. Yuk *et al*., *Nano Lett.* **11**, 3290 (2011).
13. H. Zheng *et al*., *Science* **324**, 1309 (2009).
14. N. de Jonge, D. B. Peckys, G. J. Kremers, D. W. Piston, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 2159 (2009).

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ECOLOGY

How Bacterial Lineages Emerge

Bacterial speciation is driven by interplay between natural selection, genetic linkage, and lateral gene transfer.

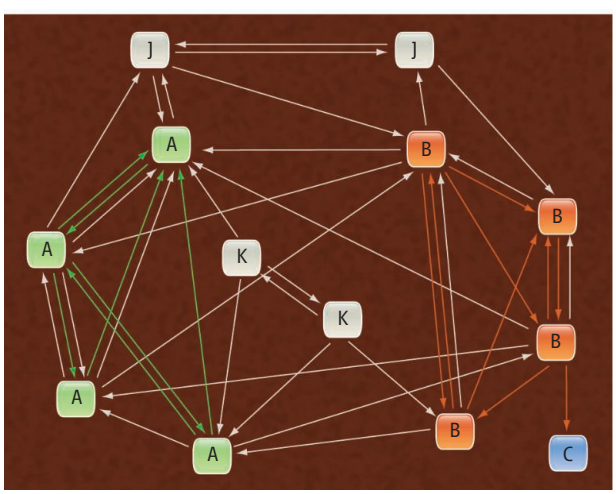
R. Thane Papke and J. Peter Gogarten

Most people today recognize bacterial names like *Escherichia coli* and *Neisseria meningitidis*. Yet, from an evolutionary viewpoint, the clarity of species labels for bacteria is blurred by rampant horizontal gene transfer between bacteria (*1*). The forces driving speciation in bacteria include niche adaptation, selective sweeps, genetic drift, recombination of genetic material, and geographic isolation. How do those forces maintain species homogeneity or bring about lineages, when gene swapping is apparently so rife?

On page 48 of this issue, Shapiro *et al*. (*2*) address these questions by providing a high-resolution snapshot of early lineage divergence in marine bacteria. They find clues to the dynamics of prokaryotic genomes, such as with whom the organisms frequently exchange genes, how lineages originate, and, ultimately, what is (or is not) in a name.

Most theoretical and observational insights into what species are and how they came to be are derived from studies of sexually reproducing eukaryotes (*3*), in which reproduction and recombination are necessarily connected. Asexual lineages in both prokaryotes and eukaryotes have often been described in terms of selection and genome-wide genetic linkage, which resets to zero the genetic diversity at every locus (*4*). However, even though Bacteria and Archaea reproduce asexually, many prokaryotic populations evolve in ways that resemble randomly mating, sexually reproducing eukaryotes: Alleles in these bacterial populations are randomly assorted among individual cells (strains), and diversity at single loci can be purged independently of the other chromosomal loci.

The only mechanism that can explain these observations is a high rate of horizontal gene flow compared to the rates of clonal expansion or reproduction. The main difference from eukaryotes is that prokaryotic reproduction is independent of DNA acquisition and recombination. Instead, DNA is obtained from fragmented chromosomes obtained via parasexual means (that is, without reproduction). These mechanisms of DNA exchange are not restricted to gene exchange within species, and therefore traits can and do come from highly divergent organisms. For example, imagine that acacia trees could exchange DNA with lions and that the resulting new tree developed "limbs" that allowed them to attack grazing giraffes. This is in a sense what prokaryotes do all the time. Very different pathways for bacterial speciation have been described (*5*, *6*); often the data reveal frequent gene flow within multiple exchange groups.



A structured exchange community. Members of two distinct niches are shown as green and orange squares; gray squares are relatives occupying different niches. Genes that adapt their hosts to these niches are mostly exchanged or recombined between members of the same niche (green and orange arrows), but they might also be shared with recent niche invaders (blue square), accelerating their adaptation to a new habitat. Other genes are freely exchanged between members of different niches (gray arrows). Shapiro *et al*. show that semi-stable adaptations to specific niches can emerge in the presence of high rates of gene flow within and between lineages.

Horizontal gene flow is thus both a homogenizing and a diversifying force. It typically involves groups of organisms that preferentially exchange genetic material. Mathematical models of gene flow independent of selection and based on sequence similarity alone

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