

Self-Assembled Graphene Nanosacks

Yantao Chen, Fei Guo, Ashish Jachak, Sang-Pil Kim, Dibakar Datta, Jingyu Liu, Indrek Kulaots, Charles Vaslet, Hee Dong Jang, Jiaying Huang, Agnes Kane, Vivek B. Shenoy, **Robert H. Hurt**

Brown University, Providence, Rhode Island, USA

Northwestern University, Evanston, Illinois, USA

Robert.Hurt@brown.edu

Graphene oxide (GO) is a promising giant molecular precursor for the creation of new carbon materials, because it can be aligned, stacked, folded, or otherwise assembled in the colloidal state into complex two- or three-dimensional structures [1-6] and then reduced to carbon. Here we show that monolayer graphene oxide can be co-suspended with a variety of second components in dilute aqueous phases and ultrasonically nebulized and dried/heated to produce electron transparent graphene “sacks” that encapsulate an internal cargo.

Graphene oxide was prepared by a modified Hummers method and purified by a two-step acid-acetone wash [7]. Suspensions were ultrasonically aerosolized to produce a mist of microdroplets suspended in a gas flow, which were dried in situ by heating (70-600 C). When graphene oxide is the only component in suspension, the products are crumpled graphene nanoparticles similar to those reported recently [5,8]. In the presence of a second component, however, the products are “filled graphene nanosacks” (Fig. 1). At low filler concentrations, the crumpled nanoparticle structure is preserved but the second component is found *inside* a thin graphene shroud (Fig. 1a). At higher filler concentrations, we still see a graphene shroud (Fig. 2b), but the graphene has fewer creases and the structure resembles a sack with a cluster of filler (Ag nanoparticles) as contents or “cargo”. The filler appears to act as a scaffold that mechanically supports the graphene sack and prevents complete collapse to crumpled graphene. We have also fabricated filled graphene nanosacks using cargos that include hydrophilic, aryl-sulfonated carbon black nanoparticles (Fig. 1f), fluorescein-sodium dye, and salmon sperm DNA. If the chosen filler has a high atomic number, it can be directly visualized inside the sack by SEM (Fig. 1a, b). Organic or carbon-based fillers are not easily observable, but their presence is reflected in the swollen sack structure (Fig.1f), and can be seen by TEM.

We propose that the filled graphene nanosacks are a self-assembled structure that occurs by spontaneous segregation of the sack and filler into a core-shell symmetry. There is a thermodynamic driving force for GO to adsorb at the liquid-vapor interface, and previous studies have reported the formation of GO surface films on drying droplets [3]. In addition, GO has a large hydrodynamic radius (750 nm) and low diffusion coefficient, and as a result is overtaken and scavenged by the receding water-air interface during droplet drying. To better understand formation mechanisms, we carried out molecular dynamics (MD) simulations of droplet drying in the presence of monolayer graphene (Fig. 2a) and graphene oxide (Figure 2b). For graphene there is a noticeable gap at the water interface, and the droplet appears to template or guide the graphene into a scroll structure during drying. We believe that weak van der Waals forces in the water/graphene system [9] allow graphene to slide on the droplet surface, which enables this “guide and glide” assembly mode. Graphene oxide in contrast clings to the droplet surface through hydrogen bond interactions and is dragged inward as the droplet volume is reduced by drying (“cling and drag” mechanism). These simulations together with calculations of diffusion rates for the sacks and fillers lead to the conceptual model shown in Fig. 3 for the formation of filled graphene nanosacks.

We currently envision a broad set of technological uses for filled graphene nanosacks. Many potential applications derive from the ability of sacks to isolate nanoparticle cargos from biological tissue or the natural environment where particle release is undesirable due to human or ecological toxicity. Inside the sacks, nanoparticle cargos can be isolated from biological target molecules associated with toxicity, while still exhibiting useful photonic, magnetic, or radiological functions.

References

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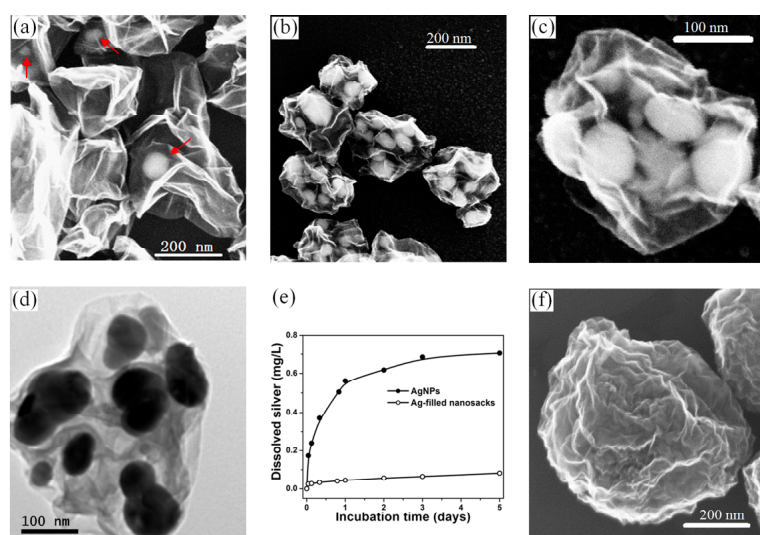


Figure 1. Filled graphene nanosacks from drying binary microdroplet suspensions. (a) SEM of Ag-nanoparticle-filled sacks at low loading (Ag:GO mass ratio 0.06); (b,c,d) SEM/TEMs of silver nanoparticles at higher loading (Ag:GO mass ratio 2); (e) Time-resolved release of Ag^+ in 5 mM pH 4 acetate buffer from gradual oxidation of encapsulated nano-silver particles, vs. free Ag nanoparticle control to show the inhibiting effect of encapsulation, (f) hydrophilic, aryl-sulfonated carbon black (CB) nanoparticles at high loading (CB:GO ratio 2).

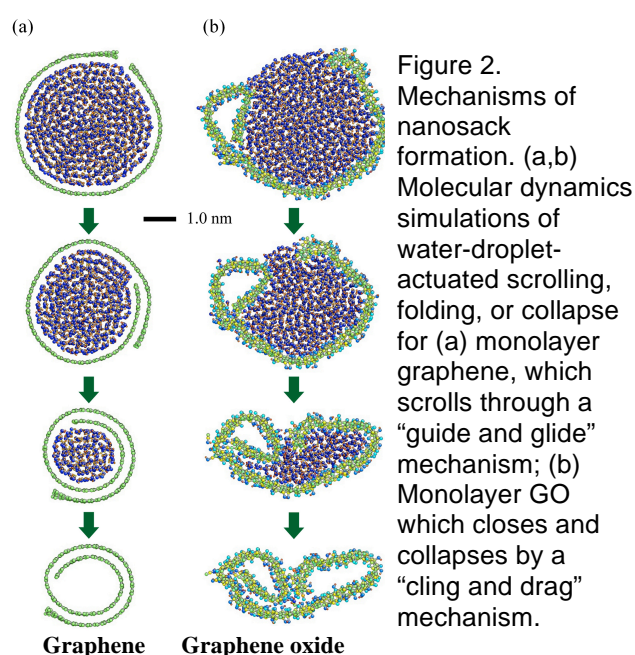


Figure 2. Mechanisms of nanosack formation. (a,b) Molecular dynamics simulations of water-droplet-actuated scrolling, folding, or collapse for (a) monolayer graphene, which scrolls through a "guide and glide" mechanism; (b) Monolayer GO which closes and collapses by a "cling and drag" mechanism.

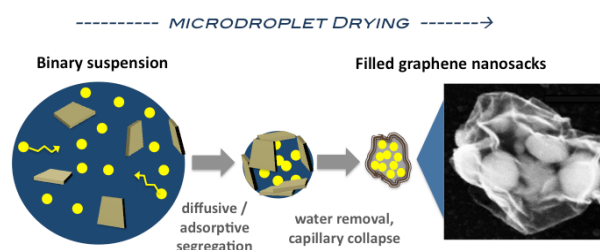


Figure 3. Conceptual model for the colloidal self-assembly of filled graphene nanosacks. Microdroplet drying leads to graphene oxide adsorption and scavenging at the receding gas-water interface, while the second component diffuses away from the interface becomes incorporated in the final nanoparticle core. Colloidal segregation is followed by sack closure and collapse by capillary forces. High filler loading acts as a scaffold to prevent complete sack collapse.