

vaccinated mice from an otherwise lethal dose of the flu virus.

At first sight, these results may not be too impressive, as the synthetic particles and alum induced similar vaccination effects. Yet more interestingly, the authors demonstrated that in addition to eliciting an immune response, the particles have the capacity to modulate it. In reality, immune responses have immense plasticity: they can respond with minute changes to the environmental conditions present during vaccination. By changing the encapsulated cytokine — in their case from TNF to interleukin IL-12 — St John and colleagues showed that the immune response could be steered towards a so-called Th1 phenotype, a response involving T cells that is most effective at fighting intracellular pathogens and can also mediate an effective attack against cancer cells. Indeed, whereas stimulating an immune reaction through TNF led to large amounts of antibodies that were protective against the viral

flu challenge, stimulation mediated by IL-12 directed the response towards the massive production of interferon-gamma by Th1 lymphocytes (Fig. 1b). Hence, the production of mast-cell-like particles with a defined composition in terms of immobilized cytokines or other well known immunostimulatory and immunomodulatory substances is a proof of concept that may pave the way from the rather undefined alum to tailor-made adjuvants with highly specific and predictable functions.

Further work is needed to investigate the mechanisms by which the encapsulated cytokines mediate the observed immune responses. The authors suggest that the synthetic mast-cell particles may modulate the function of dendritic cells — potent immunostimulatory cells that behave as natural adjuvants⁶. Furthermore, other cytokines and the highly immunogenic pathogen-associated molecular patterns (PAMPs; small molecular motifs of

microorganisms recognized by immune cells) will have to be encapsulated and tested as immune stimulants. In light of the importance of dendritic cells and the receptors for PAMPs in innate and adaptive immunity, as demonstrated by the 2011 Nobel prize in Physiology or Medicine, synthetic adjuvants such as those reported by St John and collaborators might play an important role in the design of effective vaccines against potent infections such as HIV or malaria. □

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References

1. Dudeck, A. *et al.* *Immunity* **34**, 973–984 (2011).
2. Kunder, C. A. *et al.* *J. Exp. Med.* **206**, 2455–2467 (2009).
3. St John, A. L. *et al.* *Nature Mater.* **11**, 250–257 (2012).
4. Kool, M. *et al.* *J. Exp. Med.* **205**, 869–882 (2008).
5. Janeway, C. A. Jr *Cold Spring Harb. Symp. Quant. Biol.* **54**, 1–13 (1989).
6. Schuler, G. & Steinman, R. M. *J. Exp. Med.* **186**, 1183–1187 (1997).

WETTING

Unobtrusive graphene coatings

The contact angle of water drops on substrates for which the wettability is dominated by van der Waals forces remains unchanged when the substrates are coated with a monolayer of graphene. Such 'wetting transparency' could lead to superior conducting and hydrophobic graphene-coated surfaces with tunable electronic properties.

Frieder Mugele

Wetting behaviour is determined by the intermolecular interactions between the wetting liquid and the substrate it rests on. When the attractive interactions among the molecules in the liquid outweigh those between the liquid and the solid, a macroscopic drop at equilibrium displays an almost spherical shape with a large contact angle. Conversely, the more strongly the liquid is attracted by the atoms in the substrate, the more spread the drop is, and the smaller its contact angle. The wetting behaviour is thus determined by the few molecules within the nanometric range of interaction at the liquid/substrate, liquid/gas and solid/gas interfaces. Therefore, the interactions and thus the water–substrate contact angle can in principle be altered by any thin surface coating. For instance, coatings of self-assembled monolayers of a silane allow the contact angle of water on clean silicon to be tuned from zero to ~115° (ref. 1). Still, not all coating materials need to completely

disrupt the water/substrate interactions at the interface. Writing in *Nature Materials*, Rafiee and colleagues report that a graphene monolayer barely perturbs the contact angle of water on graphene-coated copper (Fig. 1a), gold and silicon — but it does so on graphene-coated glass². Using theory and computer simulations, the authors demonstrate that such 'wetting transparency' for the metal substrates is a consequence of the van der Waals forces between the liquid and the substrate being able to 'see through' the graphene layer. However, when the wettability is dominated by interactions of shorter range — such as the hydrogen bonds formed between water and glass — graphene's wetting transparency is lost.

What makes graphene so interesting for wetting? Most of the excitement about the material is related to its extraordinary electronic, mechanical and optical properties. With high-quality graphene becoming available as a large-area coating,

other aspects such as its macroscopic stability and its interaction with fluids become increasingly interesting. For example, how does the contact angle on graphene coatings evolve with the number of coated layers, and how many layers does it take to reach the contact angle for bulk graphite? Rafiee and co-authors addressed both questions by depositing graphene onto various substrates with intrinsic water contact angles ranging from approximately 20° to 85°. For 4–6 graphene layers, all drops displayed the typical contact angle of bulk graphite, approximately 90°, a result that the authors confirmed with molecular dynamics simulations.

However, the evolution of the contact angle with the number of graphene layers is in line with predictions from classical wetting theory³, in which the effective interface potential that describes the wetting properties is decomposed into additive contributions from short-range chemical interactions, and the longer-

range van der Waals and electrostatic interactions. Yet so far it has been difficult in experiments to disentangle the effects of chemical interactions from those of the van der Waals and electrostatic forces. But graphene overcomes this limitation. Because of the extreme thinness of graphene, the layer closest to the substrate fixes the short-range forces, and any additional layer affects only the long-range interactions. The authors describe the transition in contact angle from graphene to graphite on copper by using a simple pairwise-additive model for the van der Waals interactions. For a single coating of a layer of graphene, van der Waals forces are unperturbed by the layer and the interaction range remains barely unchanged (Fig. 1b). As additional layers are added, the interaction range shifts away from the substrate and the water molecules interact with an increasing number of carbon atoms. The transition is gradual because the spacing between adjacent graphene layers is merely 0.34 nm.

From a fundamental perspective, there may be more to the wetting transparency of very thin layers. Given the electronic properties of graphene, one might expect that the Hamaker constant associated with the van der Waals interaction varies strongly with a decreasing number of graphene layers⁴. But such effects may be too subtle to be picked up by macroscopic contact-angle measurements. However, atomic force microscopy imaging of nanometre-sized drops on graphene sheets of variable thickness might be able to do so. Also, the wettability of nanodrops on suspended graphene sheets should deviate

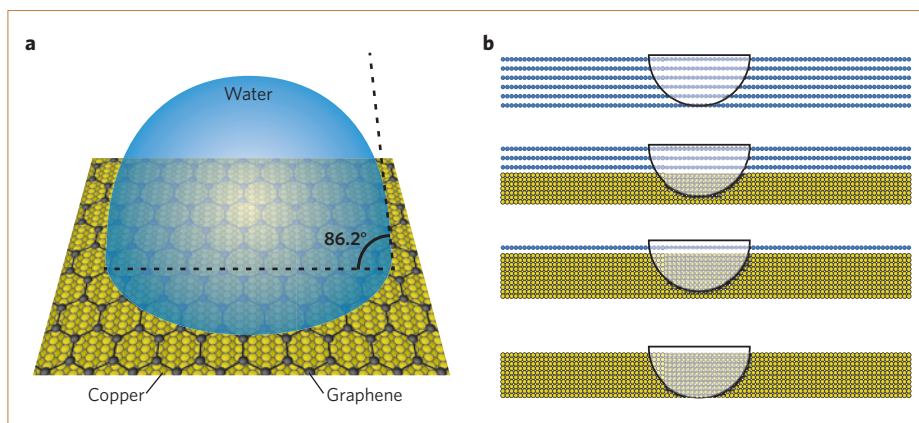


Figure 1 | Graphene's wetting transparency. **a**, The contact angle of a water drop on a graphene-coated copper substrate (86.2°) hardly changes from that on bare copper (85.9°). **b**, Schematic² of the interaction volume between a water drop and a substrate (yellow) coated with graphene layers (blue). As the number of graphene layers increases, the interaction volume shifts away from the substrate and includes a higher proportion of carbon atoms than substrate atoms.

strongly from the extrapolated behaviour for bulk graphite⁵.

The wetting transparency of conformal graphene coatings may enable applications in which electronic and wetting properties can be independently controlled. For example, by making use of graphene's fairly inert electrochemical properties, the active control of electrowetting on graphene-coated surfaces should be possible. Also, coatings of chemically perfect graphene layers of laterally varying thickness may enable ways of guiding liquids by means of long-range forces. Furthermore, Rafiee and colleagues took advantage of the unobtrusive wetting of graphene coatings and their conformability and surface passivation — that is,

prevention of oxidation — to demonstrate that the condensation heat transfer from a copper substrate can be enhanced by 30–40%. Certainly, irrespective of how unobtrusive graphene may be, in wetting it will not keep a low profile. □

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References

1. Ulman, A. *Introduction to Ultrathin Organic Films* (Academic, 1991).
2. Rafiee, J. *et al. Nature Mater.* **11**, 217–222 (2012).
3. De Gennes, P. G. *Rev. Mod. Phys.* **57**, 827–863 (1985).
4. Rajter, R. F., French, R. H., Ching, W. Y., Carter, W. C. & Chiang, Y. M. *J. Appl. Phys.* **101**, 054303 (2007).
5. Bao, W. *et al. Nature Nanotech.* **4**, 562–566 (2009).

DISSOLUTION PROCESSES

Stuffed structures

Understanding oxide dissolution processes on the molecular scale remains a challenge. A study on nanoscale oxides suggests a mechanism for dissolution that proceeds through the formation of oxygen-stuffed metastable structures.

Paul Fenter

Dissolution is pervasive in the natural and industrial world, from the weathering of rocks, which provides nutrients for the ecosystem and feedback to regulate global climate¹, to metal-oxide corrosion, which is critical for many technologies². Despite the importance

for disciplines as diverse as geochemistry and materials science, understanding how such solids dissolve remains a challenge. A study of oxygen-exchange reactions at the surface of nanoscale oxide materials known as polyoxometallates (POMs), reported by James Rustad and William Casey in

Nature Materials, suggests a new molecular-scale mechanism that controls the dissolution rate of oxides³.

It is well understood that dissolution proceeds by the solvation of lattice cations. This solvation requires the disruption of multiple metal–oxygen bonds, typically