Condensed-matter physics

Magnetism found in zigzag graphene nanoribbons

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The inclusion of nitrogen atoms stabilizes the zigzag edges of carbon-based nanoribbons, enabling the ribbons to be decoupled from a substrate and providing a probe for their unconventional magnetism. **See p.647**

Graphene is a single layer of carbon atoms arranged in a honeycomb lattice. Thin, flexible, transparent and metallic, it therefore forms an ideal material for many applications, especially for a type of electronics known as spintronics. In spintronic devices, the magnetic moment (spin) of an electron can be just as useful as its charge for storing information and performing logic operations. It has been predicted that when graphene is shaped into nanoribbons, with zigzag edges that are stabilized by carbon–hydrogen bonds, it should exhibit magnetic states that show particular promise for carbon-based electronics[1]. However, a clear experimental demonstration of this magnetism in nanoribbons that are long enough to be technologically relevant has not been possible. On page 647, Blackwell *et al.*[2] overcome this hurdle — reporting the synthesis and characterization of zigzag graphene nanoribbons in which carbon atoms spaced at regular intervals along the edges have been replaced by nitrogen atoms.

The unconventional magnetism of zigzag graphene nanoribbons arises because the topological properties of graphene induce electronic states that are spatially localized along the ribbon's edges. Calculations predict that the electrons in these states have spins that tend to align parallel with each other if they are on the same edge, and show antiparallel alignment if they are on opposite edges[3]. Although there is some evidence of the resulting magnetic moments and their complex interactions in graphene nanostructures with short zigzag edges[4–7], this magnetism has so far eluded direct experimental verification in longer nanoribbons.

Blackwell and colleagues synthesized nanoribbons in which one out of every six carbon atoms along the edges had been replaced by nitrogen. This substitution had a small effect on the electronic structure of the ribbon and, in particular, on the edge states responsible for the magnetism. However, the nitrogen stabilized the otherwise highly reactive zigzag edges, anchoring the ribbon to the underlying surface, which — in this case — was made of gold. This reduced the interaction of the edge states with the metal, preserving their magnetism and allowing them to be visualized with scanning tunnelling microscopy.

Technological applications require graphene nanoribbons to be made reproducibly, with atomic precision. Synthesizing the ribbons on a surface provides a viable route for doing so. Using this technique, carefully designed molecules are deposited on a heated surface (usually gold or silver) that is capable of catalysing a reaction to create long chains of molecules. At a higher temperature, the surface then catalyses another reaction that generates the desired nanoribbon structure[8]. Although many different types of graphene nanoribbon have been produced using this technique in the past decade, the synthesis of structures exhibiting long zigzag edges proved to be particularly challenging, which is probably related to the high reactivity of the zigzag edges.

"The edge states can be clearly visualized, even when the nanoribbons are adsorbed on gold."

A successful strategy for synthesizing a six-atom-wide graphene nanoribbon on a gold surface was proposed and tested in 2016 (ref. 9). However, the magnetic edge states were not found using this set-up, because the nanoribbon coupled strongly to the metal substrate. By placing the nanoribbons on top of a monolayer of salt, the researchers were able to detect spectroscopic signatures of the presence of edge states, but found no clear evidence of magnetism[9].

Blackwell and co-workers modified the synthesis protocol used previously to incorporate nitrogen atoms at the edges of the six-atom-wide nanoribbons (Fig. 1). These ribbons were also strongly coupled to the gold substrate, and the authors found no signature of the edge states in spectroscopic data obtained with scanning tunnelling microscopy, in which a sharp metallic tip measures the spatial distribution and energy of the electronic states in the sample. When they applied a sufficiently large voltage to the graphene with the tip, however, the ribbons underwent an irreversible structural transformation that decoupled them from the surface. This response had not been seen before in graphene nanoribbons and, although the exact mechanism has yet to be established, the presence of regularly

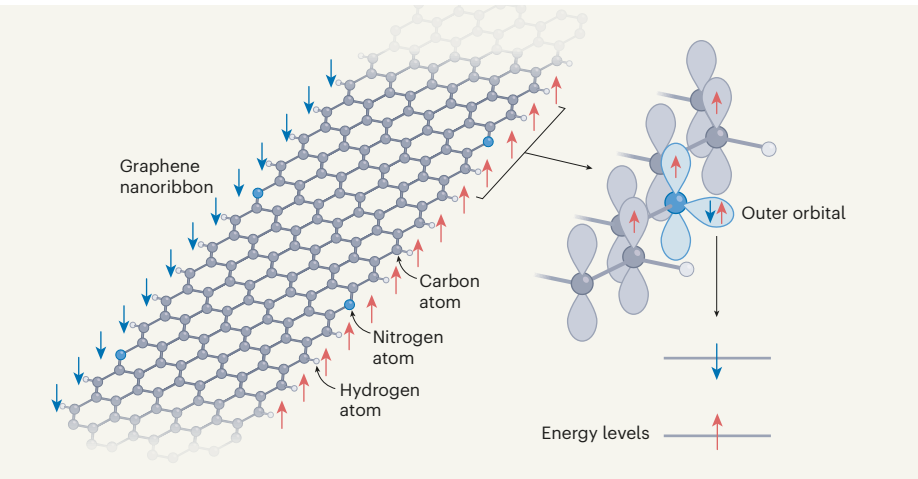

Figure 1 | Magnetism in zigzag graphene nanoribbons with nitrogen substitutions. Blackwell *et al.*[2] studied graphene nanoribbons comprising a single layer of carbon atoms, six atoms wide, stabilized by hydrogen atoms along the zigzag edges. The authors replaced every sixth edge atom with a nitrogen atom. Red and blue arrows show the alignment of magnetic moments (spins) of the electrons in the edge states, leading to magnetism at the ribbon edges. This well-defined spin orientation affects other electronic states. The grey lobes represent orbitals of the carbon atoms, and the blue lobes are those of the nitrogen atoms. There is an energy difference between spin orientations in the outer orbital of the nitrogen atom, which can be detected and used as a probe for the magnetism at the edges of the nanoribbon.

spaced nitrogen atoms at the edges seems to be crucial for this phenomenon to occur.

Simulations that Blackwell *et al.* performed to complement their experiments suggest that the nitrogen atoms at the edges of the nanoribbons form strong bonds with the substrate. The most stable configuration of the ribbons seems to be one with substantial corrugation, with the nitrogen atoms sitting at the lowest positions. As a result, the edge states, which tend to localize in the carbon segments, are decoupled from the surface. These edge states can thus be clearly visualized, even when the nanoribbons are adsorbed on gold.

Although the edges of graphene nanoribbons have previously been altered to decouple them from the substrate[9], the technique of substituting the carbon atoms with nitrogen ones has the advantage of leaving the electronic and magnetic properties of the nanoribbon almost unmodified. And it has another benefit: nitrogen atoms can be used to probe the magnetism of the edge states. The spins of the electrons are all aligned along the edges of the nanoribbon, including those at the nitrogen sites. This affects other electron states, particularly those of the outer orbitals of the nitrogen atoms (Fig. 1), which do not participate in binding to the carbon structure. The spin directions of the two electrons in these outer orbitals have different energies – one is higher than the other. This difference can be detected with the scanning tunnelling microscope and represents direct evidence of the magnetism of the long zigzag edges in these graphene nanoribbons.

The work by Blackwell and colleagues offers exciting opportunities to study the magnetic properties of graphene nanostructures grown on metal surfaces. Future research will determine whether the observed surface-decoupling mechanism also applies to other structures and substrates. Similarly, the use of nitrogen as a local probe will probably inspire a search for other substitutions that could offer spectroscopic signatures of magnetism, while preserving the electronic structure of the zigzag edge.

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Sociology

What surveys really say

Frauke Kreuter

Increasing the sample size of a survey is often thought to increase the accuracy of the results. However, an analysis of big surveys on the uptake of COVID-19 vaccines shows that larger sample sizes do not protect against bias. **See p.695**

The accuracy of survey results is often thought to increase with sample size. However, Bradley *et al.*[1] show on page 695 that this is not always the case. Although 'big' surveys can, under certain conditions, be useful for tracking changes in a population measure over time and across space, their estimates of population variables can be considerably biased.

Early in the COVID-19 pandemic, many nations lacked essential epidemiological data – even those with well-developed public-health monitoring infrastructures. There was a scarcity of timely information on regional increases in SARS-CoV-2 infections, on adherence to physical-distancing measures and on the social and economic effects of the pandemic. The state-sponsored data collections that existed at the time were often too slow to meet the demands generated by the pandemic.

As a result, some private companies jumped in to offer data; for example, Google, in Mountain View, California, provided anonymized, aggregated data on people's mobility (go.nature.com/3htjccv), and Facebook in Menlo Park, California, presented anonymized and aggregated data about the development of connections between different geographical regions (go.nature.com/3lwknax). The London-based lifestyle company ZOE built the ZOE COVID Study app in collaboration with academic partners (go.nature.com/3i7ypxj). The app surveyed participants who downloaded it, to identify infection hotspots and track the effect of mitigation measures. And when vaccination programmes were rolled out, it was used to record COVID-19 vaccine side effects. In addition, various private-sector surveys – many of which were archived by the US-based Societal Experts Action Network (go.nature.com/3rcmkwh) – produced data on changes in the public's response to the pandemic.

"These findings are a reminder to researchers that statistical precision does not equate to unbiased population estimates."

The US Census Bureau, in partnership with various federal agencies, and the Delphi group at Carnegie Mellon University, based in Pittsburgh, Pennsylvania, in partnership with Facebook, designed and performed massive surveys to forecast the spread of COVID-19 and measure its effects; questions about vaccination were added in early 2021. With more than 3 million and 25 million responses collected, respectively (as of November 2021; see go.nature.com/3dg0qvy and go.nature.com/3y2r1bk), these are now probably the largest US surveys relating to the pandemic. However, using a subset of responses, Bradley and colleagues demonstrate that the US Census Bureau–federal agencies survey (dubbed the Census Household Pulse survey) and the Delphi–Facebook survey overestimated the vaccination uptake compared with the benchmark data from the US Centers for Disease Control and Prevention (CDC) (Fig. 1).

The authors conclude that having more data does not necessarily lead to better estimates. They discuss how design choices in survey-data collection can lead to error – in this case, the overestimation of vaccination uptake. Their findings are a reminder to researchers that statistical precision does not equate to unbiased population estimates.

Bradley and co-workers focus on three elements that can contribute to the size of the error – that is, the difference between estimates from big surveys and actual population values. These elements are data quantity (the fraction of a population that is captured in the sample), problem difficulty (how much variation in the outcome of interest there is in the population) and data quality. The quality is very difficult to assess, because there is usually no independently verified 'ground truth' or 'gold standard' with which to compare survey data. In this case, the CDC's reports of the numbers of vaccines administered provide benchmark data with which the estimates reported in the surveys could be compared. Under