

positive sample bias, the COFs depolymerized, restoring the supramolecular assemblies. The ability to selectively drive either the polymerization or the depolymerization to completion at room temperature is unprecedented for COF-forming reactions, and clearly indicates the power of the non-thermal activation mechanism. Both reactions proceeded slowly enough for their kinetics to be monitored by normal STM imaging, with the depolymerization reaction being about ten times faster than the polymerization.

The processes that produce highly ordered covalent materials such as COFs require dynamic covalent chemistry⁴ — reactions in which covalent bonds form reversibly, thereby allowing self-healing of defects in the nascent COF, and hence the formation of crystalline materials that have ‘long-range order’. The reversible condensation of boronic acids aids the formation both of bulk COFs³ and of single-layer COFs synthesized on surfaces^{5,6}. In both cases, however, the polymerization required temperatures of around 100 °C; it was inconceivable that such COF formation could occur at room temperature.

Cai and colleagues’ work is therefore a stunning example of an underexplored phenomenon: how exceptional environmental conditions can alter the progress of chemical reactions. The authors accredit their astonishing finding to the influence of the strong, oriented electric field beneath the STM tip. Although the applied voltages in STMs are modest (just a few volts, at most), the close proximity of tip to the sample (less than 1 nanometre away) gives rise to strong, static electric fields of the order of 10⁹ volts per metre, which are otherwise difficult to reach.

STMs have demonstrated a striking ability to induce individual molecules to undergo a variety of processes⁷, such as changing conformation, dissociation and chemical reactions. These processes could, in principle, be driven by the electric field. But the STM tip can also act as a powerful oxidizing or reducing agent, depending on the voltage between it and the surface that it scans across. Moreover, at liquid–solid interfaces, scanning of the STM tip causes ‘nano-stirring’ of the liquid. All of these tip effects could promote chemical reactions individually or in combination with each other, but the intimate connections between them make it difficult to separate out the effects that are at play in experiments.

So does the electric field definitely drive Cai and colleagues’ reactions, or could another mechanism be involved? Boronic acids act as Lewis acids (electron-pair acceptors), and so an alternative explanation is that electron-transfer processes are responsible. This possibility should now be explored.

Carrying out STM experiments at liquid–solid interfaces is relatively straightforward, facilitating future studies of the reported reactions. However, the reaction system itself is highly complex. For example, crucial factors

that could affect the surface reactions include the solvent, the surrounding solute molecules (boronic acids that are still in solution, rather than on the graphite surface) and even dissolved impurities; none of these are easy to visualize using STMs, which can image only surface-bound molecules. The main challenge now, therefore, is to devise experiments or computational simulations that provide further clues about the mechanism. Cai *et al.* have taken the first step in this direction by studying the solvent dependence of the reactions. Future studies could also shed light on the role of water molecules, which are essential for the depolymerization reaction.

Since their development in 1981, STMs have enhanced our understanding of fundamental atomic processes on surfaces, and are still the sole analytical tool for tackling various ongoing research problems in surface science. Stunning experiments have also shown that STMs can be used to assemble atoms or molecules into precise nanostructures (see refs 8 and 9, for example), and to manipulate the chemical state of those structures¹⁰. But scaling up such experiments to make practically useful quantities of materials has been impossible, because the processes involved are inherently serial operations and atomic in scale.

Cai and colleagues’ work provides an

intriguing test case for whether STM-induced processes can be translated to more-macroscopic scales. This would require comparably strong electric fields to be produced at least on the micrometre scale — which seems feasible, but challenging. If achieved, this would not only verify the proposed mechanism, but also constitute a milestone in bringing such unconventional chemistry closer to our macroscopic world. ■

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MARINE CONSERVATION

Fishing boats leave few safe havens for sharks

Global satellite tracking of the oceans has revealed a high degree of spatial overlap between where sharks and industrial fishing vessels are found. This finding underscores the need for shark–conservation efforts. [SEE ARTICLE P.461](#)

JULIA K. BAUM

Oceans cover 70% of our planet, extending for hundreds of millions of kilometres. Despite their vastness, oceans have not escaped the effects of human activity, and evidence has steadily accumulated in recent decades that disturbances such as overexploitation¹, plastic pollution² and climate change³ have had major negative consequences for marine life. Queiroz *et al.*⁴ add another dimension to this story on page 461, by showing that vessels fishing on the high seas (the regions of oceans beyond national boundaries) overlap substantially with areas of the ocean that are frequented by sharks, leaving these wide-ranging animals with scant refuge from fishing pressure.

As some of the oceans’ fiercest predators, sharks were once presumed to be safe from overfishing⁵. Yet when shark-targeted

commercial fisheries were developed in the mid-twentieth century, this presumption was soon proved incorrect. Most of these fisheries underwent a swift cycle of boom and bust, lasting only a decade or so before shark populations plummeted and the fisheries collapsed⁶.

The expansion of industrial fishing across the high seas in the latter half of the twentieth century subjected sharks to another threat. Most of those fisheries target tuna and billfish (such as swordfish). These fast-moving fishes have high population growth rates, which allow them to withstand greater fishing pressures than the sharks that are taken alongside them as by-catch (species caught unintentionally) or as secondary targets. Despite the risk of overfishing sharks, regional fisheries-management organizations have been reluctant to develop management plans or catch limits for sharks, and have little incentive to collect data that



Figure 1 | A blue shark (*Prionace glauca*). Queiroz *et al.*⁴ have generated global maps showing the degree of spatial overlap in the oceans between commercial fishing vessels and shark species, which included *P. glauca*.

could be used to demonstrate the negative effects that fishing is having on these species.

However, assessments of available regional data have reinforced concerns about sharks, painting a stark picture of populations that have declined precipitously^{7,8}. Sharks, along with their relatives, are now thought to be one of the most threatened groups of marine species, with one-third of them assessed as being at risk of extinction⁹. Nevertheless, the patchy availability of fisheries-dependent data has meant that the full extent to which sharks interact with fishing fleets on the high seas — and the impacts of these fisheries on them — has remained unknown.

Scientists are increasingly using satellite-derived data to fill in such knowledge gaps about the human ‘footprint’ in the world’s oceans. For example, the automatic identification system (AIS) — a locator system used by many boats as a safety feature to prevent collisions — provides data that enable boat movements to be monitored globally. Analyses of AIS data have revealed that fishing-vessel tracks are found across much of the oceans¹⁰.

Queiroz and colleagues paired AIS data with satellite-tracked movements of 1,681 tagged sharks to provide a global estimate of the extent to which areas of the ocean frequented by sharks overlap with active zones of industrial fishing. Focusing on vessels using fishing gear called pelagic longlines, which are responsible for the majority of catches of oceanic sharks globally¹¹, the authors report that almost one-quarter of the average space that individual sharks move through monthly overlaps with the footprint of these fleets.

White sharks (*Carcharodon carcharias*) and

porbeagles (*Lamna nasus*) are listed as being at risk of extinction on the International Union for Conservation of Nature’s Red List of Threatened Species. Worryingly, of the shark species studied by the authors, these two had some of the greatest overlap between the areas they prefer and those targeted by the longline fleets. Spatial overlap between the locations of fishing vessels and sharks was also high for commercially valuable shortfin mako (*Isurus oxyrinchus*) and blue (*Prionace glauca*) sharks (Fig. 1).

Underlying the high degree of spatial overlap between sharks and industrial fishing vessels is the mutual targeting of areas of the oceans that attract fish because of their favourable productivity and temperature profiles. Unsurprisingly, congregating in such areas enables both the fishing vessels and the sharks to enhance their catch rates.

More work remains to be done to determine the full extent to which fishing vessels intercept sharks on the high seas. Queiroz and colleagues’ study rests almost entirely on data for just 11 shark species, which were tagged and released from a limited number of locations, and it is estimated that AIS transmitters are fitted on only 50–75% of large fishing vessels. Even with these limitations, the study is a testament to the capacity of modern ecology to provide insights about human impacts on the natural world through the power of collaborative science and big data — more

than 150 researchers contributed to collecting or analysing the data from the tagged sharks. Other scientists working in fields facing conservation crises would do well to adopt this type of collaborative approach.

Queiroz and colleagues’ study underscores the urgent need for conservation measures to protect large ocean-dwelling sharks. With little to no management measures in place for most of these species, the authors suggest that large-scale marine reserves could help to limit shark exploitation on the high seas.

The idea is a timely one^{12,13}. At a United Nations meeting this spring, there were calls to designate 30% of the high seas as marine protected areas, and groups are actively working on site-selection proposals (see go.nature.com/2ohnluq). Nations are in the process of negotiating the first high-seas conservation treaty¹⁴, which will include provisions for establishing protected areas outside the limit of national territories. Such protected areas could provide huge benefits to sharks, especially if the information from Queiroz and colleagues’ study is taken into account. However, improvements in fisheries-management measures, including a rise in onboard observers and enforced shark-catch limits, would also be needed to ensure that fishing pressure on sharks outside protected areas is not excessive.

Moving forward, the challenge will be to use the results of this new study to spur effective shark-conservation measures. By illuminating the frequency with which these wide-ranging fishing fleets overlap with sharks, and the hotspots of these interactions, Queiroz *et al.* have provided a much-needed blueprint for conservation actions that could be used to provide sharks with safe havens in our increasingly crowded oceans. ■

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This article was published online on 6 August 2019.