Exploring nanodiamonds that can be activated as photocatalysts with sunlight

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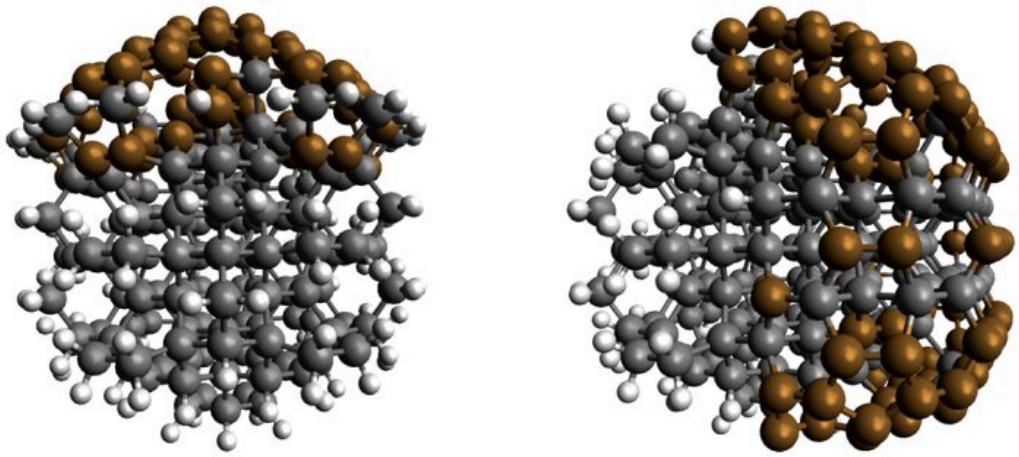

The illustration shows two variants of nanodiamond materials with different surfaces: $C_{230}H_{106}$ on the left, $C_{286}H_{68}$ on the right. Sp3 C atoms (diamond) black, sp3x C atoms (fullerene-like) brown, H atoms: Light grey. When the surface is partially covered by hydrogen atoms, nanodiamonds can absorb light in the visible range and emit electrons into solution. Credit: T. Kirschbaum / HZB

Nanodiamond materials have great potential as catalysts. Inexpensive nanoparticles made of carbon provide very large surfaces compared to their volume. However, to catalytically accelerate chemical reactions in an aqueous medium, electrons from the catalyst need to go into solvation and in pure diamond materials this requires high-energy UV light for excitation. On the other hand, the extremely small sizes of the nanoparticles allow new molecular states on the surfaces of nanodiamonds that also absorb visible light.

As part of the DIACAT project, a team at HZB has now investigated different variants of nanodiamond materials during excitation with light and analyzed the processes with extremely high time resolution. Nanodiamond samples with different surface chemistries were produced by the group of Dr. Jean-Charles Arnault, CEA, France and Prof. Anke Krueger, now at the University of Stuttgart. The nanoparticles differed in their surfaces, which contained different amounts of hydrogen or oxygen atoms.

"The hydrogen on the surfaces makes electron emission much easier," explains Dr. Tristan Petit, nanodiamond expert at HZB. "Among the many variants, we discovered that a certain combination of hydrogen as well as fullerene-like carbon on the surfaces of the nanoparticles is ideal," he says.

In the Laserlab at HZB they studied aqueous nanodiamond dispersions with different surface terminations such as hydrogen, -OH or -COOH after exciting them with ultrafast laser pulses. "We were able to experimentally measure exactly how the absorption profile behaves with different excitation wavelengths in the UV range at 225 nm and with blue light in the visible range at 400 nm," explains Dr. Christoph Merschjann, HZB.

"We wanted to find out what happens in the first crucial picoseconds

after excitation with light, because that is the time when an electron leaves the surface and goes into the water," says Merschjann. The theory team led by Dr. Annika Bande contributed modeling with density functional theory to interpret the spectra. The data showed, as expected, that UV light brings electrons into solution in all samples, but for those samples that had fullerene-like carbon on their surfaces, this was also achieved with visible light.

"In this work we show—to the best of our knowledge for the first time—that the emission of solvated electrons from nanodiamonds in water is possible with visible light," Petit says.

This is a decisive step towards opening up nanodiamond materials as photocatalysts. These inexpensive and metal-free materials could be a key to further processing CO_2 into valuable hydrocarbons with sunlight in the future, or even to convert N_2 into ammonia.

The research is published in the journal *Nanoscale*.

More information: Franziska Buchner et al, Early dynamics of the emission of solvated electrons from nanodiamonds in water, *Nanoscale* (2022). DOI: 10.1039/D2NR03919B

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