Physicists Find Light-sensitive Molecule Can Heal Itself in the Dark

April 10 2007

Sometimes all an overworked molecule needs is a good night's rest. According to a study by physicist Mark Kuzyk and colleagues at Washington State University, a molecule that loses its ability to fluoresce when struck by a laser beam regains that ability if it's allowed to 'rest' in the dark. Recovery begins within 30 minutes and is nearly complete after 8 hours of rest, the study found.

"It's almost as if you have a piece of paper that's yellowed over time, and you put it in a dark room for a day, and it comes back brand-new," said Kuzyk.

The research team of Kuzyk and students Ye Zhu and Juefei Zhou discovered the "self-healing" property in AF455, a dye compound that was designed to excel at two-photon absorption. That's a process in which the absorption of light energy from a laser causes a change in the molecule that can be harnessed for various purposes. Many molecules also glow, or fluoresce, during two-photon absorption, which allows researchers to monitor the process.

Among the most prominent uses of two-photon absorption are optical data storage and photolithography, a technique using lasers to assemble parts for microscopic motors and nano-sized robots. Two-photon absorption can also be a nuisance, causing degradation of lasers and optical switches that route signals around the internet.

The report is published in the April 15 issue of the journal *Optics Letters*.

Any material exposed to high-intensity light will degrade over time, said Kuzyk. White paper turns yellow, dyes bleach and fade and molecules that fluoresce when struck by a laser—as the chemical in the present study does—stop fluorescing. Until recently, that degradation in response was thought to be irreversible.

Most previous experiments showing recovery of function in laser dyes were conducted with the dye in liquid solution, where movement of molecules resulted in replacement of spent molecules with fresh ones, said Kuzyk. In the new study, the dye was embedded in a methacrylate polymer. Each molecule was held in place, so a laser focused on the same spot in the polymer would strike the same molecules throughout the course of the experiment.

“That’s one of the first questions people ask when they see this,” said Kuzyk. “They say, ‘isn’t this just the liquid replenishing the stuff that was damaged?’ Nope, this is in a polymer. So you know that it’s the same molecule that’s sitting at that point, as you had before.

“The molecule itself is actually recovering.”

The researchers found that with constant irradiation by the laser, with the most intense dose (4.5 microjoules per pulse), within 200 minutes the response had dropped to about 60 percent of the starting level. The laser was then turned off and the sample allowed to ‘rest’ in the dark. After that it was briefly irradiated at 30-minute intervals, to measure its fluorescent response. Just half an hour after being put in the dark, AF455 had already begun to recover. It continued to improve throughout the 8-hour dark period.

The more intense the laser used, the faster the material lost its ability to respond. In all cases, regardless of the intensity of light used to exhaust the material, recovery proceeded with the same time constant. That indicates the mode of recovery does not depend on the severity or means of the decline, Kuzyk said.

So far, the self-healing property does not appear to be a general phenomenon of fluorescing materials. Partial recovery is known to occur in one other molecule, while full recovery has only been observed in AF455 and in DO11, another compound studied by Kuzyk's group.

Kuzyk said his lab is working to understand the mechanism behind recovery—what in the molecules' structure makes them self-healing—in hopes of finding ways to endow other molecules with the same ability. In DO11 the decline in function seems to involve two molecules coming close enough together to form a dimer. In that case, he said, recovery occurs when the two molecules forming the dimer separate again. His group found that process is entropic, meaning that the molecules can recover on their own, but they recover faster if they are heated. Whether that also occurs in AF455 has not yet been determined.

While the mechanism of recovery in AF455 is still unknown, Kuzyk said the observation itself is significant.

"The fact that it is happening is very interesting, because it means that when you make devices out of this kind of material, as long as you let them rest once in a while, they appear to be able to work for much longer" than materials that lack the self-healing ability, he said.

At a certain point during the experiments with low-intensity lasers, Kuzyk said, the sample reached equilibrium: its recovery rate matched the decay rate, and the sample did not change further over time. Kuzyk said that raises the possibility that in applications that only need a low intensity of stimulus and a modest level of response, such as the creation of glowing display screens, AF455 might need no rest at all.

The report is available online at
www.opticsinfobase.org/abstract.cfm?msid=78687

Source: Washington State University