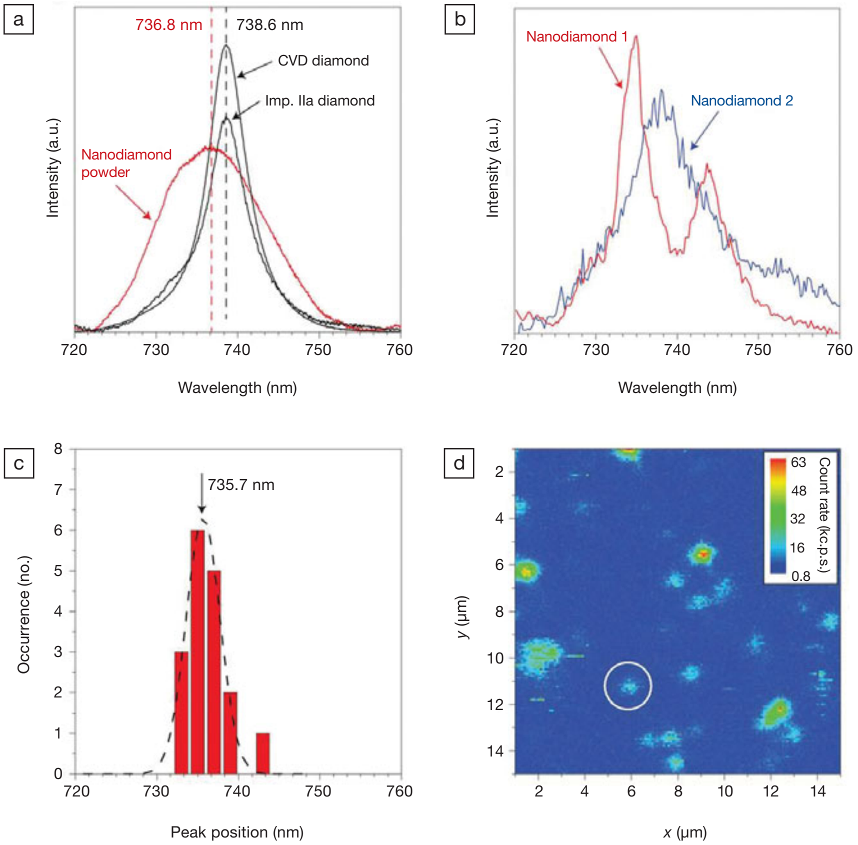
Nano Focus

Molecular-sized fluorescent probes achieved with nanodiamonds

Nanometer-sized fluorescent species are of great value in many applications ranging from materials science to medicine. In an article published in the December 8, 2013 online edition of *Nature Nanotechnology* (DOI: 10.1038/NNANO.2013.255), an international team of researchers from 10 different institutions, led by Jörg Wrachtrup of the University of Stuttgart, Germany, has now succeeded in investigating the fluorescent properties of nanodiamonds with sizes less than 2 nm, which contain stable photoluminescent color centers, termed silicon vacancies (SiV).

The researchers relied on theoretical predictions to guide their experimental work. Using first-principle density functional theory, they modeled a SiV defect with a silicon atom located between two vacant sites in the diamond lattice. Their calculation of the formation energies for SiV defects in 1.1–1.8 nm nanoparticles suggested that SiV defects are stable even in very small nanodiamonds. Excitation-state energies were also determined using time-dependent density functional theory, which showed a quantum confinement effect on the bandgap of nanodiamonds.

To test the theoretical predictions, nanodiamonds were extracted from the meteor Efremovka CV3 chondrite. A narrow zero-phonon line characterized defect luminescence near 738 nm (1.68 eV) in the photoluminescence spectrum. A blueshift in the SiV peak was also observed in nanodiamonds as compared with their bulk counterparts (see Figure). Further analysis of nanodiamonds from colloidal solution and dispersed on a silica slide using confocal microscopy showed stable fluorescence for at least 5 min, which was sufficient to acquire high-quality photoluminescence spectra. Nanodiamonds typically show one or two resolved emission peaks, and significant shifts were observed between different nanoparticles. The variations in the SiV emission band position (see b and c in the Figure) can be explained by the existence of strong lattice stress in diamond nanoparticles, where the shift provides evidence for the quantum confinement effect predicted by the researchers' theoretical calculations.



(a) Background-subtracted SiV photoluminescence spectra measured with 488 nm laser excitation at room temperature for meteoritic nanodiamond powder, chemical vapor deposition (CVD) laboratory-grown diamond single crystal, and Si^{+}-implanted type IIa (Imp. IIa) diamond. The position of the SiV peak maximum is 736.8 nm for the meteoric nanodiamond powder, and 738.6 nm for CVD and natural diamonds. (b) Photoluminescence spectra of two exemplary nanodiamonds dispersed on a silica slide. Nanodiamond 1 is marked in the confocal scan image (d) by a white circle and its photon statistics. (c) Peak positions of all analyzed spectra. The average of all peak maxima is 735.7 nm. (d) Confocal fluorescence scan image of the dispersed nanodiamond sample using a red laser and 9 mW excitation power. Reproduced with permission from *Nature Nanotech*. (2013), DOI: 10.1038/NNANO.2013.255.

A more accurate size of the fluorescent nanodiamonds was obtained by fluorescence correlation spectroscopy (FSC). FCS provides a highly sensitive quantitative statistical analysis of fluorescence fluctuations, which can be used to determine the hydrodynamic radius of the fluorescent diamond nanoparticles. The photon statistics of the SiV fluorescence were also determined, revealing three emitters within the fluorescent spot and showing that the fluorescent emissions from SiV in these small nanodiamonds are stable and bright enough for application.

These small nanodiamonds, which have dimensions comparable to dye molecules, are therefore promising as, for example, fluorescent markers in cell biology where having sizes smaller than typical proteins is highly advantageous. In addition, the SiV in diamond exhibits its narrow-band near-infrared emission, which is another important criterion for life science applications.

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