

CARBON NANOTUBES

A bright future for defects

Covalently bonding groups to the walls of carbon nanotubes has been previously observed to quench their photoluminescence. Now, it has been shown that, if you get the chemistry just right, their photoluminescence can in fact be significantly brightened by introducing defects through functionalization.

Qing Hua Wang and Michael S. Strano

In crystalline materials such as metals and semiconductors, it is the defects rather than the perfect lattice structure that lead to the most interesting and useful properties. For example, line dislocations in metals allow them to be malleable by moving and sliding under mechanical stress; adding impurities to them can result in alloys with superior strength and corrosion resistance; and substituting lattice atoms with dopants in semiconductors allows the Fermi level to be precisely tuned for making transistors. In all of these examples, the careful incorporation of defects imparts very useful properties to crystalline materials¹. It now turns out that adding a controlled concentration of defects can also have benefits for carbon nanotubes, which are cylindrical lattices of carbon atoms. Writing in *Nature Chemistry*, Wang and co-workers² describe an unexpected new effect by which defects in carbon nanotubes dramatically increase the intensity of their photoluminescence.

Single-walled carbon nanotubes (SWCNTs) are nanoscale cylinders of carbon — graphene sheets rolled up into narrow tubes. The direction of this rolling is called the chiral vector (n,m), where the integers n and m indicate the number of unit cells along the unit vectors of the graphene lattice. Depending on its chiral vector, a SWCNT can be semiconducting or metallic. When a photon is absorbed by a SWCNT, an electron is excited from the valence band to the conduction band, and a bound electron–hole pair, called an exciton, is formed. In metallic nanotubes, the excited electron is immediately replaced by another electron, but in those that are semiconducting the exciton can either travel along the nanotube, relax to a ‘bright’ state and emit another photon of lower energy, or relax to a ‘dark’ state where the energy is lost as heat without the emission of light (hence the name). This photoluminescence emission from the bright state has been the key to a diverse set of optical applications such as *in vivo* bioimaging³, molecular sensing⁴ and optoelectronics⁵.

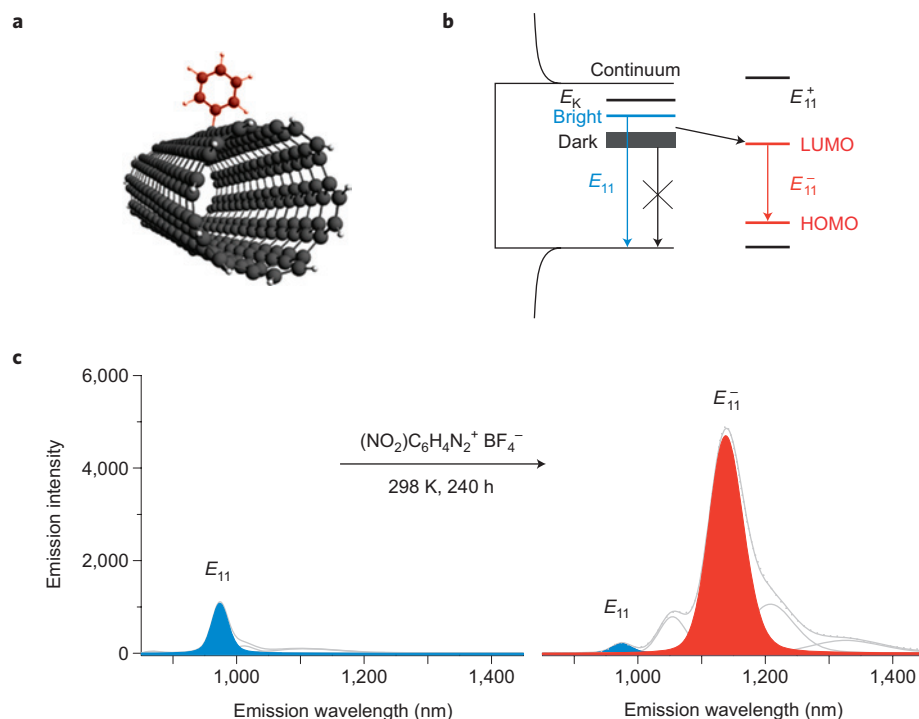


Figure 1 | Photoluminescence brightening of single-walled carbon nanotubes by covalent defect formation². **a**, Schematic of single-walled carbon nanotube with a single covalent defect from an attached aryl group. **b**, Energy levels of a pristine carbon nanotube (left), showing the photoluminescence corresponding to the E_{11} bright exciton. Dark states lying below the E_{11} level do not allow light emission. After covalent modification, the breaking of symmetry causes energy levels to split at the frontier orbitals, creating new energy levels (right) from which excitons can optically emit at the E_{11}^- energy. **c**, Light-emission spectra for pristine (6,5) carbon nanotubes (left) and 4-nitrobenzenediazonium-functionalized (6,5) carbon nanotubes (right). The E_{11} photoluminescence peak diminishes after covalent functionalization, but the brighter and red-shifted E_{11}^- peak appears.

However, the quantum yield — the ratio of output to input photons — of semiconducting SWCNTs is usually about 1%, far lower than would be expected for a direct-bandgap semiconductor. The luminescence can be enhanced by various chemical treatments to remove external quenching routes, but the most significant of these is via the ‘dark’ states lying just a few millielectronvolts below the ‘bright’ exciton states⁷.

Wang and co-workers have now discovered² a new and surprising

mechanism for enhancing the photoluminescence of SWCNTs using covalent chemistry. Covalent functionalization of the sidewall of SWCNTs has been previously well known to quench photoluminescence⁸; therefore, it is quite remarkable to find that when a low concentration of sidewall defects are introduced, the normal ‘bright’ emission from the ‘ E_{11} ’ transition drastically decreases and is replaced by a new, far brighter and red-shifted peak. Wang and colleagues observe a maximum brightening

in photoluminescence intensity of about 28-fold.

They introduce the defects by functionalizing the SWCNTs using aryl diazonium salts. This covalently attaches aryl groups to the nanotubes (Fig. 1a), creating defect sites on their sidewalls at which the orbital hybridization of the associated carbon atoms changes from sp^2 to sp^3 . These defect sites break the symmetry of the lattice, altering the nanotubes' electronic structure by splitting the degenerate frontier orbital energy levels (this was examined and confirmed using density functional theory calculations²). The energy-level splitting (Fig. 1b) results in two new optically allowed transitions, E_{11}^- and E_{11}^+ (Fig. 1c). The energy level responsible for the E_{11}^- emission lies just below the level responsible for the E_{11} emission and allows excitons to decay radiatively rather than via the non-radiative 'dark' states, as in the pristine SWCNTs. It is this E_{11}^- transition that is responsible for the new, bright photoluminescence.

The enhanced E_{11}^- peak is seen to build steadily in intensity with reaction time, but the chemistry has to be just right because this phenomenon only occurs within a narrow window of reaction conditions, explaining why it has not been detected before. The critical reaction parameter is the reagent concentration, which directly influences the density of functional groups introduced to the surface. At the optimal

defect density, there is approximately one functional group per 20 nm of nanotube length, which is about five times shorter than the exciton diffusion length. At higher densities, the photoluminescence from both E_{11}^- and E_{11} are quickly quenched.

The defect-enhanced photoluminescence emission can also be chemically tuned by changing the chemical substituents on the aryl group. Introducing various electron-withdrawing or -donating functional groups shifts the LUMO or HOMO levels, respectively, of the defect site. The energy shift of the brightened E_{11}^- peak can be tuned over a range of 35 meV just by changing the chemical substituent. The degree of red-shifting of the E_{11}^- peak also depends on the diameter of the nanotube and its (n,m) vector.

Interestingly, a recent Article in *Nature Photonics* by Miyauchi and colleagues⁹ described a mechanism of the brightening of excitonic photoluminescence in SWCNTs by oxygen dopants, first observed by Ghosh and co-workers in 2010¹⁰. In the case of oxygen dopants in SWCNTs, the original E_{11} peak is slightly diminished, but a new E_{11}^* peak arises. The presence of covalent oxygen dopants can also cause energy-level splitting and local trapping of excitons, which can then emit radiatively. The oxygen-induced brightening has many similarities to the diazonium-induced brightening, but the degree of enhancement is lower, and the energy and intensity

of the enhanced photoluminescence are not chemically tunable as in the system described by Wang².

The surprising and fascinating photoluminescence brightening observed by Wang and colleagues enriches not only our understanding of carbon nanotube photophysics, but also our ability to chemically control their quantum states and harvest excitonic energy more efficiently as light. We now have yet another example where defects in materials play a crucial role in imparting interesting and useful properties. □

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CARBENE CATALYSIS

An internal affair

Preparing powerful reactive intermediates such as enolates and homoenolates for C–C bond formation used to require strong bases and stoichiometric reagents. They can now be catalytically generated from α -functionalized aldehydes or even from saturated esters under mild conditions using N-heterocyclic carbene catalysts.

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Students of organic chemistry are encouraged to studiously master 'functional group transformations', the interconversion of each carbon-based functional group to the others, taking careful account of the oxidation state and choosing, as necessary, an appropriate oxidizing or reducing agent. More recently, chemists have taken a more holistic view of functional groups and oxidation states within an organic molecule and recognized that isohypsic or 'redox neutral' transformations can be achieved by concomitant transformation of functional

group arrays. This sophisticated approach to rearrangements and the generation of uniquely reactive intermediates is most evident in the field of N-heterocyclic carbene (NHC) catalysis, which has quickly risen from near obscurity to one of the most active and powerful classes of catalysis.

The new era of NHC-catalysed reactions began in 2004 with the recognition that these molecules can mediate the conversion of α -functionalized aldehydes into activated carboxylic acids, allowing ester and amide formation without the need

for stoichiometric coupling reagents and the formation of associated byproducts^{1,2}. Similarly, α,β -unsaturated aldehydes could be converted to the saturated esters by simultaneous reduction of the olefin and oxidation of the aldehyde, and also — by the choice of reaction conditions and catalysts — be used to catalytically generate species that react as homoenolates^{3,4} and enolates⁵. The generation and bond-forming reactions of each of these intermediates could even be sequenced together in a single catalytic cycle, leading to the formation of complex, multicyclic products under simple reaction