Giant Raman scattering from J-aggregated dyes inside carbon nanotubes for multispectral imaging

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Raman spectroscopy uses visible light to acquire vibrational fingerprints of molecules, thus making it a powerful tool for chemical analysis in a wide range of media. However, its potential for optical imaging at high resolution is severely limited by the fact that the Raman effect is weak. Here, we report the discovery of a giant Raman scattering effect from encapsulated and aggregated dye molecules inside single-walled carbon nanotubes. Measurements performed on rod-like dyes such as \(\alpha\)-sexithiophene and \(\beta\)-carotene, assembled inside single-walled carbon nanotubes as highly polarizable J-aggregates, indicate a resonant Raman cross-section of \((3 \pm 2) \times 10^{-22} \text{ cm}^2 \text{ sr}^{-1}\), which is well above the cross-section required for detecting individual aggregates at the highest optical resolution. Free from fluorescence background and photobleaching, this giant Raman effect allows the realization of a library of functionalized nanoprobe labels for Raman imaging with robust detection using multispectral analysis.

Although Raman spectra display narrow bands containing powerful information for chemical analysis and detection, its use for high-resolution optical imaging remains marginal due to its inherent lack of sensitivity. The Raman cross-section, which relates the scattered intensity of a molecule to the incident power density of the light, is typically \(1 \times 10^{-24} \text{ to } 1 \times 10^{-30} \text{ cm}^2 \) per molecule, which is too low for imaging and detecting individual objects at high resolution. This disadvantage is further compounded by the strong fluorescence background and photodegradation of chromophores that can accompany Raman spectroscopy.

Two main enhancement strategies—resonant Raman spectroscopy (RRS) and surface-enhanced Raman spectroscopy (SERS)—have been pursued in the past to solve at least the sensitivity issue and to derive Raman nanoprobe labels (also called tags) for imaging applications\(^1\)\(^2\). However, each has shown significant limitations. With RRS, optical resonances in dye molecules such as Rhodamine 6G, which are conveniently located in the visible spectrum, can boost the cross-section to \(\sim 1 \times 10^{-18} \text{ cm}^2 \) per molecule. However, making Raman dye labels is barely practical due to stability issues, especially as a consequence of photobleaching and the presence of a strong fluorescence background\(^2\)\(^3\). Approaches based on SERS can further increase the cross-section by coupling with plasmonic resonances in metallic nanostructures, leading to an immense but local enhancement of the electromagnetic field\(^1\)\(^2\)\(^4\)\(^5\). The success of this approach is demonstrated by the fact that the SERS cross-section of resonant dyes can reach up to \(\sim 1 \times 10^{-18} \text{ cm}^2 \) per molecule, a value that is close to the cross-section of fluorescence. The SERS effect has been successfully implemented in the design of Raman nanoprobes, but the specific requirements in terms of size, shape (enabling hot spots by interparticle geometry) and composition (typically Ag, Au) of the SERS antennas add stringent design constraints and stability issues. Furthermore, the occurrence of hot spots in SERS leads to inhomogeneous enhancements that greatly complicate quantitative analysis.

Here, we report the discovery of giant resonant Raman effects from J-aggregated dyes encapsulated inside single-walled carbon nanotubes (SWNTs). The scattering intensities of the dyes combined with the suppression of background fluorescence and photobleaching provide robust spatial and multispectral detection of a single assembly in the limits of optical resolution. We elucidate the origin of this Raman effect and demonstrate its use in the design of a new library of stable, yet chemically tuneable, Raman nanoprobes for experiments in Raman imaging and labelling. Multispectral Raman imaging demonstrations of dyes encapsulated in SWNT (dyes–SWNT) nanoprobes deposited on surfaces, attached onto yeast cells and functionalized with biotin to detect surface patterns of streptavidin are also presented.

For our study, well-known organic dyes such as \(\alpha\)-sexithiophene (6T) and \(\beta\)-carotene (\(\beta\)car) were encapsulated inside SWNTs with diameters of \(\sim 1.3 \pm 0.2 \text{ nm} \) (ref. 6). As schematized in Fig. 1, a three-step procedure was followed to fabricate the dyes@SWNT in solution: (1) purification (oxidation) and cutting of SWNTs; (2) encapsulation of the dyes inside the SWNT (giving 6T@SWNT); and (3) covalent functionalization (labelled 6T@f-SWNT). Only a detailed Raman study on 6T encapsulated in SWNTs (6T@SWNTs) is presented below, but the same conclusions can be drawn for \(\beta\)car@SWNTs and other dyes tested so far. The detailed characterization of the dye@SWNT systems prepared by our method is consistent with results from other groups on 6T@SWNTs\(^7\)\(^8\)\(^9\)\(^10\) and \(\beta\)car@SWNTs\(^1\)\(^2\)\(^3\)\(^10\)\(^11\) in bulk form and clearly indicates that the dyes have been encapsulated (see Supplementary Figs 1, 3 and 5 for details.)

The presence of optical resonances was established by the acquisition of absorption spectra for bulk SWNTs, 6T@SWNTs and 6T@f-SWNTs dispersed in mineral oil (Fig. 2a). Absorption of the 6T dyes in the 6T@SWNT spectrum is clearly seen as an intense and structured band in the wavelength range between 350 and 700 nm. Additional weak SWNT absorption bands are observed, overlapping in part with the 6T band.

To avoid averaging effects and other optical phenomena such as energy transfer between adjacent 6T@SWNTs, Raman measurements at \(\lambda = 532 \text{ nm} \) wavelength excitation were taken on isolated SWNTs deposited on a 100-nm-thick oxide grown on a silicon dioxide layer on a silicon wafer. The 6T@SWNTs were synthesized using a single-step chemical vapour deposition (CVD) method, followed by a purification step using ozone, as described in the Methods section. The Raman spectra were obtained using a Confoscan3 microscope (Jobin-Yvon, France) equipped with a 532 nm laser (20 mW, 50× objective).
6T@SWNTs and 6T@f-SWNTs dispersed in mineral oil at room temperature. Dotted lines correspond to Raman laser lines stretching mode vibrating along the main axis of the 6T molecules.

For clarity, the Raman spectra are shifted vertically (by steps of 1). Peaks indicated by * are unambiguously ascribed to the C=C stretching mode at 1,450 cm⁻¹ observed from other 6T aggregates on the oxide surface. Significantly, only minimal fluorescence at λ = 532 nm was detected. Both results are consistent with previous work on bulk 6T@SWNTs in solution, although some fluorescence was detected but at shorter excitation wavelengths. Other studies on different dyes inside SWNTs reported efficient fluorescence quenching by the SWNTs, and this effect, seen in weakly bonded chromophore–SWNT complexes, was explored recently in the context of light harvesting applications.

A rough estimate of the Raman cross-section of encapsulated 6T aggregates can be inferred using the SWNT signal as an internal standard, with (Supplementary Figs 6, 7 and Supplementary Table 1). We therefore conclude that the Raman signal from the 6T@SWNT is strongly enhanced and arises from an encapsulated 6T J-aggregate, and not from other 6T aggregates on the oxide surface. Significantly, only minimal fluorescence at λ = 532 nm was detected. Both results are consistent with previous work on bulk 6T@SWNTs in solution, although some fluorescence was detected but at shorter excitation wavelengths.

Additional polarization experiments at 532 nm were carried out on the same individual 6T@SWNT (Fig. 3c), where the polarization angle Ω is defined by the polarization vector of the incident light and the orientation of the nanotube axis. Superposition of a cos²Ω dependency over the polarization-dependent intensity of the 6T mode at 1,450 cm⁻¹ and the SWNT mode at 1,590 cm⁻¹ demonstrates that the transition dipole moments of the molecules are aligned. Thus, a 6T aggregate is clearly formed with polarizability tensors α_j perfectly oriented along the nanotube axis. This result is consistent with the structure of 6T@SWNT illustrated in Fig. 1, which was previously deduced from transmission electron microscopy images and calculations: the 6T molecules are stacked in pairs and aligned head-to-tail, thus forming J-type aggregates inside the nanotube.

The detection of a Raman signal from the encapsulated 6T molecules in an isolated SWNT is unexpected, because only a few hundred molecules (545 at maximum filling) are present within the 600 nm focus spot of our Raman instrument. Indeed, surfactant molecules and even large polymers (Supplementary Fig. 14) attached to the nanotube sidewalls are generally not detected in Raman microspectrometry. For further comparison, 6T aggregates (diameter, 40 nm) located on SiO₂/Si but far away from the SWNTs were probed using Raman spectroscopy and AFM. As expected, submicrometre aggregates and even a 50-nm-thick film of 6T gave much weaker signals and strong fluorescence backgrounds. Therefore, the detection of a Raman signal from the 6T@SWNT is strongly enhanced and arises from an encapsulated 6T J-aggregate, and not from other 6T aggregates on the oxide surface. Significantly, only minimal fluorescence at λ = 532 nm was detected. Both results are consistent with previous work on bulk 6T@SWNTs in solution, although some fluorescence was detected but at shorter excitation wavelengths. Other studies on different dyes inside SWNTs reported efficient fluorescence quenching by the SWNTs, and this effect, seen in weakly bonded chromophore–SWNT complexes, was explored recently in the context of light harvesting applications.

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standard. Using laser excitation at $\lambda = 532$ nm (an RRS condition for both 6T and SWNTs) and the highest spatial resolution ($\sim 600$ nm) of our microscope, the Raman bands of the 6T at 1,450 cm$^{-1}$ and of the SWNT at $\sim 1,590$ cm$^{-1}$ exhibited nearly the same integrated peak intensity ($A_{6T}/A_{SWNT} = 0.7$). Considering that the RRS cross-section of the G-band of an individual SWNT is $\sim 1 \times 10^{-21}$ cm$^2$ sr$^{-1}$ (refs 19–21), we estimated the cross-section of the 6T J-aggregate to be roughly the same. (Note that a cross-section between $1 \times 10^{-22}$ and $4 \times 10^{-22}$ cm$^2$ sr$^{-1}$ is reported for the radial breathing mode (RBM), but the G-band is about ten times more intense.)

To confirm this estimate, a separate experiment based on the substitutional method described in refs 19 and 22 (for details see Supplementary page 21) was devised. Using spectra from a large ensemble of individualized 6T@SWNT and graphene as an internal standard deposited in the same area of the SiO$_2$/Si substrate. Using the literature values for the Raman efficiency of graphene ($\sim 200 \times 10^{-22}$ cm$^2$ sr$^{-1}$) and 6T@SWNT with an average length of 0.6 $\pm$ 0.1 $\mu$m. This value of the cross-section assumes that the signal ratio is $A_{6T}/A_{SWNT} = 0.7$ when the filling of 6T inside nanotube is at a maximum. Complete filling with the 6T J-aggregate is, however, unlikely, given the liquid-phase procedure used for the encapsulation in this study. This Raman cross-section value is thus only a lower bound (note that the cross-section of incoherent Raman scattering scales linearly with the number of molecules) and clearly demonstrates a giant Raman scattering effect from the 6T J-aggregate inside the SWNT. Using the RRS data mentioned above on amorphous aggregates and on thin films of 6T molecules on SiO$_2$/Si, the normalized signal of the 6T@SWNT compared to other similarly close-packed 6T aggregates is $\sim 1 \times 10^4$ times more intense (Supplementary Table 1).

To understand the origin of the enhancement of the Raman cross-section, we investigated the influence of the SWNT resonances on the Raman scattering from the dyes and tested the hypothesis that strong optical resonances in the SWNT can produce an optical antenna effect similar to a SERS mechanism. That is, the scattering efficiency can be reduced or enhanced by the optical near-field at the interior of the SWNT. The strength of this effect was estimated by modelling the SWNT as a hollow cylinder with an infinitesimal wall characterized by an optical frequency conductance $g$ (ref. 23). By applying Mie theory (see Supplementary page 14 for details; Supplementary Fig. 10), it can be shown that $E_{int}/E_0$, the ratio of the optical electric field in the interior of the SWNT to the illuminating plane wave, is given by

$$E_{int}/E_0 = \left(1 - \frac{igZ \cdot H_{10}^{(1)}(ka) \cdot J_0(ka)}{H_{10}^{(1)}(ka) \cdot J_0(ka) - H_{10}^{(1)}(ka) \cdot J_0(ka)}\right)^{-1},$$

where $k = 2\pi/\lambda$, $a$ is the SWNT radius, $Z$ is the impedance of free space, and the usual cylindrical Bessel function notation is used. With a tube of radius $a = 0.6$ nm and a peak optical conductance $g = 8e^2/\hbar$ (that is, in resonance), the field at the interior of the SWNT at an incident wavelength $\lambda = 633$ nm is $E_{int}/E_0 = 0.999$, corresponding to a negligible screening of the optical near-field. This estimate shows that the small SWNT diameter, as compared to the optical wavelength, renders optical enhancement or screening ineffective in the visible spectrum.

Our experiments support this calculation and rule out the antenna effect from the SWNT being the cause of the giant Raman effect from the dye J-aggregate. In our samples, two different families of nanotubes—semitubing (s-SWNT) and metallic (m-SWNT) species—are present. The optical resonances can be excited with laser lines at $\lambda = 633$ nm for the m-SWNTs and at $\lambda = 532$ nm and 488 nm for the s-SWNTs. Using AFM, two individual SWNT specimens were selected and subsequently probed in situ using Raman microspectrometry before and after encapsulation. In Fig. 3, RRS spectra taken at $\lambda = 633$ nm, 532 nm and 488 nm for the two 6T@SWNTs confirmed that one nanotube is metallic (Fig. 3a) and the other is semiconducting (Fig. 3b). In other words, the semiconducting nanotubes present two sharp and distinct G-peaks, and the metallic nanotube features a broad and downshifted G-band, which is due to a Kohn anomaly in the nanotube bandstructure. At $\lambda = 532$ nm and 488 nm, the individual 6T@m-SWNT spectrum showed an intense peak from the 6T molecules at 1,460 cm$^{-1}$ and almost no signal from the m-SWNT. Using AFM image of the SWNT and a description of the polarization angle.
is observed: the signal is weak for the 6T molecules and strong for the m-SWNT. The Raman scatterings of the m-SWNT and 6T are therefore uncorrelated and simply follow their respective resonance profiles. For the individual 6T@-SWNT (Fig. 3b), the Raman signatures from both constituents are seen at $\lambda = 488$ nm and 532 nm, but not at $\lambda = 633$ nm, indicating that the 6T scattering intensity is only correlated to the resonance of the 6T aggregates. Whether the SWNT is metallic or semiconducting, in resonance or not, has no observable influence on the scattering of the encapsulated 6T. This finding indicates that the reported giant cross-section is a robust phenomenon that depends mainly on the optical properties of the confined dye aggregates. As discussed below, this is a key feature enabling a whole new set of applications with functionalized dyes@SWNT nanoprobes for multispectral Raman labelling and imaging.

All our experiments point towards an enhancement mechanism that is driven by RRS and J-type aggregation induced by confinement. The Raman signal of the dyes was also found to be stable against photobleaching, even at high laser fluence, and free from fluorescence. By considering that 545 molecules of 6T is the maximum number that can fit inside a 600-nm-long SWNT (that is, the diameter of our laser spot) and assuming incoherent scattering, a RRS cross-section of $\sim6 \times 10^{-24}$ cm$^2$ sr$^{-1}$ per 6T molecule can be deduced. Literature data for 6T were not found, but this value is similar to the RRS cross-section of other dyes such as Rhodamine 6G$^3$ and $\beta$-carotene$^{24,25}$ in solution and to the cross-section of Rhodamine 6G physisorbed on a graphene layer where fluorescence is also quenched$^{26}$. However, the cooperative effect of many molecules aligned as a J-aggregate inside SWNT boosts the total cross-section to $\sim1 \times 10^{-21}$ cm$^2$ sr$^{-1}$ per dye@SWNT assembly in the laser focal point or, more conveniently, to a value of $\sim1 \times 10^{-24}$ to $1 \times 10^{-22}$ cm$^2$ sr$^{-1}$ for each nanometre of filled SWNT depending on the resonant dye. This remarkably large cross-section has important implications for Raman imaging because a shorter segment of the dye aggregate, at least shorter than the optical resolution limit of our instrument (<600 nm), can be readily detected using conventional Raman microspectrometry.

Another main requirement in the elaboration of a competitive nanoprobe for imaging is its covalent functionalization. We probed the influence of chemical functionalization of 6T@SWNTs using a radical reaction that covalently attaches bromophenyl moieties to the nanotube sidewall. This is an important step towards achieving the dispersion, chemical functionality or selectivity and biocompatibility of the 6T@SWNT nanoprobes. In Fig. 2a, the bulk 6T@f-SWNT products in mineral oil exhibit an absorption spectrum that is similar to that of 6T@SWNT, except for a significant weakening of the SWNT absorption bands. The Raman spectrum taken after functionalization of the individual semiconducting 6T@SWNT of Fig. 2b is shown at the bottom. After functionalization, the G-band of the SWNT at $\sim1,590$ cm$^{-1}$ decreases in intensity, which is related to disorder induced into the carbon lattice by covalent bonding of the bromophenyl grafts$^{27}$. The fluorescence quenching ability of the f-SWNT is preserved, as no fluorescence is observed in the spectra. More
importantly, the Raman intensity of the 6T modes remains constant, which indicates that the SWNT sidewall acts as a barrier that protects the dyes\(^1\)\(^2\) and their giant scattering cross-section. That is, the toughness of the Raman signal of the dyes to functionalization reactions, photobleaching (see Supplementary page 26) and even to harsh treatment in a Piranha solution, a strong oxidizing reagent composed of 1:3 \(\text{H}_2\text{O}_2\) and \(\text{H}_2\text{SO}_4\), are further proof that the toughness of the Raman signal of the dyes to functionalization.

Experiments on a variety of rod-like dyes indicate that the giant cross-section observed in the 6T@f-SWNT system is common to a large family of chromophores. For instances, methylene violet B, 3,3′-dimethylthiadicarbocyanine iodide (DTDCI) and oligothiophene derivatives such as 3,6-bis-[2,2′]bithiophenyl-5-yl-2,5-di-noc-tylpyrrolo[3,4-c]pyrrole-1,4-dione (DPP2) encapsulated inside SWNTs gave similar RRS responses but at a longer wavelength of \(\lambda = 633\ \text{nm}\) (Fig. 4d). These general properties of dye@SWNT nanoassemblies thus make them well adapted for constructing Raman nanoprobes for imaging and tagging experiments. For the purpose of demonstrating the applicability of the Raman effect, we tested various nanoprobes in different imaging configurations. A submonolayer of 6T@SWNTs deposited on a SiO\(_2\)/Si substrate was first patterned and then imaged using scanning electron microscopy (SEM; Fig. 4a) and micro-Raman mapping (Fig. 4b). The Raman acquisition time at 300 \(\mu\text{W}\ \mu\text{m}^{-2}\) laser power density was only 5 s per pixel. The Raman 6T signal correlates with the varying density of nanoprobes observed using SEM (Fig. 4c), indicating that the signal is probably proportional to the density of nanoprobes. In another experiment, shown in Fig. 5a, a mixture of isolated \(\beta\text{car}@\text{SWNT}\) and 6T@SWNT nanoprobes was deposited on SiO\(_2\)/Si and subsequently analysed by hyperspectral Raman imaging at \(\lambda = 532\ \text{nm}\) excitation. Thanks to the sharp and specific vibrational signatures of each nanoprobe, the 6T@SWNTs (red) and \(\beta\text{car}@\text{SWNTs}\) (green) fingerprints were readily and unambiguously detected and selectively localized on the surface without interference from each other. The presence of a third dye@SWNT in Fig. 5b, arising from phenazine molecules (Ph@SWNTs in blue, Supplementary Fig. 9), was also detected, further illustrating the powerful application of multispectral bands in identifying nanoprobes, even when they are overlapping at the same location.

It is important to mention here that SWNTs are already known as giant Raman scattering objects exhibiting RRS cross-sections between \(1 \times 10^{-22}\) and \(1 \times 10^{-23}\ \text{cm}^2\ \text{sr}^{-1}\) depending on the bands\(^{19-21}\). They also produce no fluorescence in the visible spectrum, which is a key feature enabling Raman applications. In effect, Dai and co-workers have shown that functionalized SWNTs can be used as Raman labels for protein detection\(^{28}\) and biological imaging of cancer cells\(^{39}\). As Raman nanoprobes, SWNTs are therefore interesting, but they provide a small number of Raman-active bands, which is clearly limiting in the context of imaging and multiplexing. Furthermore, SWNTs with different chiralities operate at different RRS energies, which implies that SWNT labels require fastidious sorting on the basis of their resonance energies. Adding chemical functions onto the SWNT sidewalls...
by covalent reaction (to aid dispersion in liquids and biocompatibil-
ity) drastically reduces their Raman cross-section. In this context, the
giant Raman cross-section reported here on J-aggregated dyes inside SWNTs is an important step forward that circumvents the
hurdles of using the SWNT signal only for detection. Finally, multi-
plexing of the Raman signals as shown above is similar to that of Raman labels made with functionalized SWNTs with different con-
tents of 13C/12C isotopes28,29. However, the number of combinations that can be derived with dye@f-SWNT is by far greater due to the large number of dyes and their narrow bandwidths in the Raman spectra.

Finally, we present preliminary results for the use of dyes@f-
SWNT as contrast agents for living cells and for biomarker types of application. βcar@SWNTs were functionalized using poly(ethy-
lene glycol) bis-(3-aminopropyl) (PEG) to allow their solubility in physiological saline solution and mixed with a culture of a yeast
called Candida albicans (see Methods and Supplementary page 6 for
details). Figure 5c (top) presents an optical image of aggregates of Candida albicans cells mounted on a glass slide after tagging with βcar@PEG–SWNTs and rinsing with saline solution. The Raman hyperspectral image taken at the same place (Fig. 5c, bottom) shows that the tagged yeasts scatter strongly at the characteristic Raman frequency of the βcar@PEG–SWNT nanoprobes. The uniform contrast across the cells indicates also that the βcar@PEG–SWNT nanoprobes have bonded to the cell membranes and some may have penetrated into the yeasts. Importantly, the tagged yeasts lived more than three weeks after their incubation with βcar@PEG–SWNTs, which is a good but preliminary indica-
tion of the low toxicity of the dyes@f-SWNTs. The dyes@f-
SWNT can also be used as probes for protein recognition. As a
proof of concept, streptavidin was patterned onto a surface using
microcontact printing (see Supplementary page 7, Supplementary
Fig. 15), and its detection was carried out using the probe βcar@f-SWNT functionalized with PEG–biotin (βcar@PEG-
Biot–SWNT). Using Raman hyperspectral imaging of the peak
centered at 1,520 cm−1, it was possible to determine whether the streptavidin was present either in the dots of the pattern, or sur-
rounding the dots (Fig. 5d and inset).

In summary, the dye@f-SWNT nanocomposites access to a
giant resonant Raman scattering effect that is powerful for multi-
plex Raman imaging experiments. Our study shows that the
SWNT is in essence a capsule that not only quenches fluorescence,
but acts also as a template for J-aggregation as well as a protection for the dye molecules from the environment. By adding chemical
functions to the SWNT sidewalls and by expanding the variety of
capsulated dyes exhibiting such giant Raman scattering, out-
standing opportunities can be created with the dyes@f-SWNT nanocomposites for experiments requiring a large library of robust
and nanometre-sized Raman tags.

Methods
The SWNTs used in this work were produced by laser ablation30 and had a diameter distribution of 1.3±0.2 nm. The SWNTs were first purified in concentrated nitric acid, washed with water, dried and then dispersed in dimethylformamide (DMF). Encapsulation of these imaging experiments. Our study shows that the
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The yeasts were finally mounted on a glass slide for imaging. Raman imaging was performed using an inverted Raman microscope from Photon etc. In

The streptavidin patterns were created by microcontact printing of albumin from bovine serum using a polydimethylsiloxane stamp. Experimental procedures and materials are described in detail in the Supplementary pages 1–8.

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Author contributions

Data were collected and analysed by E.G., N.Y.-Wa.T., F.L., J.C., M.-A.N. and R.M. The experiments were conceived by E.G., N.Y.-Wa.T., J.C., F.L., M.-A.N. and R.M. Calculations were carried out by E.G., T.S. and R.M. Samples were prepared by N.Y.-Wa.T., E.G., N.C., F.L., F.R., J.C. and M.-A.N. All authors contributed to writing the manuscript.

Competing financial interests

The authors declare no competing financial interests.

ERRATUM

Carrier-envelope phase effects on the strong-field photoemission of electrons from metallic nanostructures

Björn Piglosiewicz et al.

Nature Photonics http://dx.doi.org/10.1038/nphoton.2013.288 (2013); published online 10 November 2013; corrected online 19 November 2013.

In the version of this Letter originally published online, one beam was missing in the interferometer section depicted in the schematic shown in Fig. 1a. This error has now been corrected in both the HTML and PDF versions of this Letter.

CORRIGENDUM

Hyperbolic metamaterials

Alexander Poddubny, Ivan Iorsh, Pavel Belov & Yuri Kivshar

Nature Photon. 7, 948–957 (2013); published online 28 November 2013; corrected after print 28 November 2013.

In the version of this Review published in print, “Si/Ge (ref. 23)” was listed on the eight line of the second column on the second page (page 949). This should have read “Ag/Ge (ref. 23)” This error has been corrected in both the HTML and PDF versions of the Review.