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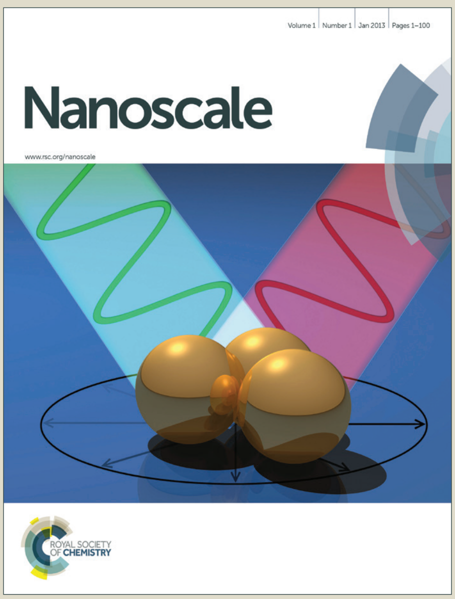

Visible Diffraction from Quasi-crystalline Arrays of Carbon Nanotubes

By *Timothy P. Butler*[1], *Haider Butt*[2], *Timothy D. Wilkinson*[1] *and Gehan A. J. Amaratunga*[1]*

[1]Centre for Advanced Photonics and Electronics, Electrical Engineering Division,
Engineering Department, University of Cambridge, Cambridge CB3 0FA , U.K.
[2]School of Mechanical Engineering, University of Birmingham,, Birmingham, UK

[*] E-mail: gaja1@cam.ac.uk

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Abstract

Large area arrays of vertically-aligned carbon nanotubes (VACNTs) are patterned in a quasi-crystalline Penrose tile arrangement through electron beam lithography definition of Ni catalyst dots and subsequent nanotube growth by plasma-enhanced chemical vapour deposition. When illuminated with a 532nm laser beam high-quality and remarkable diffraction patterns are seen. The diffraction is well matched to theoretical calculations which assume apertures to be present at the location of the VACNTs for transmitted light. The results show that VACNTs act as diffractive elements in reflection and can be used as spatially phased arrays for producing tailored diffraction patterns.

Multiwall carbon nanotubes can be taken as analogues for graphitic rods with nanometre scale diameter. As such they exhibit semi-metallic dielectric and electrical properties close to those of graphite [1]. The catalytic growth of large-area arrays of vertically-aligned multiwall carbon nanotubes (VACNTs) at predetermined spatial locations with controlled diameters and heights through electron beam lithography and plasma-enhanced chemical vapour deposition (PECVD), originally developed for field emission sources in vacuum electronics [2], is now a standard 'turn-key' technology. VACNTs also provide a route to exploring electromagnetic phenomena at optical wavelengths as their dimensions can be made compatible with those required for strong interaction. The first examination of the optical properties of arrays of VACNTs was by Kempa *et al*, [3]. They focused on the photonic band gap properties of a nanotube array. A further study by the same group made use of the metallic properties of multiwall carbon nanotubes to consider a random array of VACNTs as an array of simple dipole antennas operating at optical wavelengths [4]. Here we report the utilisation of vertically aligned carbon nanotubes in the reflection field of coherent laser light to obtain visible diffraction. With the VACNTs placed in locations which correspond to a two dimensional Penrose tiled quasi-crystal over a large area, strong and clear diffraction patterns are observed. The diffraction patterns correspond to those expected from light transmitted through apertures placed in the same pattern.

Diffraction patterns from a 2-D Penrose tiled quasicrystal structure formed by etching air cylinders into a quartz substrate have previously been reported [5]. In that work, HeNe laser light at 633nm was transmitted through the dielectric quasi-crystal formed by the air cylinders in quartz and relatively weak diffraction spots observed. The air cavities were 3μm in diameter, 700nm in depth and placed 10μm apart on a tile side (the pattern area was 0.013mm^2). In this work we use a finer 'inverse' structure of quasi-periodic pentagonal arrays of VACNTs on a Si substrate. They are fabricated through the deposition of catalyst dots from which a single VACNT grows [6, 7] in controlled locations patterned by electron-beam lithography (EBL). The VACNT diameter, related to patterned catalyst diameter, is 80 - 120nm, and length 700nm. The spacing between VACNTs on a tile side is 1400nm and the pattern area is 2.5 mm^2. In contrast to the previous work, here we in effect employ an array of metallic nanometre scale rods to act as a hologram for reflected light. This allows the reversibility of the optical EM waves from the light source through reflection to be exploited to get a 'beaming' effect, similar to that obtained from RF EM waves emanating from a phased array antenna. Since the VACNTs are placed in a 2-D quasi-crystalline array (i.e. having periodic breaking of symmetries), a rich diffraction pattern, or many 'beamlets' are seen. We also report and compare the 'beaming' through diffraction observed from periodic 2-D crystalline arrays of VACNTs.

The VACNT arrays are excited with 532nm laser light and the results are compared with theoretical predictions of diffraction for crystals with tenfold symmetry. The flexibility and accuracy of the EBL system used allows the production of array patterns over large areas on wafers up to 8" diameter, so that the exciting beam of laser light falls entirely on the array without the need for complicated alignment procedures.

The calculation of the diffraction pattern for a periodic system revolves around the construction of the reciprocal lattice and subsequent placement of the first Brillouin zone; however, in this case the aperiodicity of the pentagonal array requires a different approach due to the lack of translational symmetry. The reciprocal lattice of such an array is densely filled with reciprocal lattice vectors, with the consequence that the wave vector of a transmitted/reflected light beam encounters many diffraction paths. The base set of reciprocal lattice vectors for the pentagonal array, which has tenfold symmetry, may be constructed by rotating a unit vector ten times through an angle of $\pi/5$ [5]. This base set is then summed through all possible combinations to produce the reciprocal lattice vectors for the pentagonal array; the greater the order of summation the more complete the set. The diffraction pattern may alternatively be predicted by utilising concepts of Fourier optics [8]. The quasi-periodic array of nanotubes act like a hologram (an array of apertures) for the reflected electromagnetic waves, producing a replay field described by the process of Fraunhofer diffraction. The resultant replay fields can be accurately calculated by taking the Fourier transform of the holograms.

To perform the 2D fast Fourier transform (FFT) of the quasi-crystalline nanotube array, a normal scanning electron micrograph was taken, as shown in Figure 2. A square section is cut from the micrograph, thresholded to produce a binary image then blended at the edges to alleviate the effects of the square periodicity inherent in the FFT algorithm before performing the transformation.

The Si wafer bearing the pentagonal array was mounted onto a post with a flat screen set above it. The plane of the screen is parallel to the plane of the sample and the screen has a small aperture in its centre, as shown in figure 3 inset. A 532nm (green) laser was mounted above the screen, arranged so that the beam was normally incident at the sample. The reflected diffraction pattern produced when the sample was illuminated was captured by a camera and corrected for distortion due to the off-axis camera position.

The observed diffraction pattern is in very good agreement with the calculated results. A comparison of the two is presented in figures 4(a) and 4(b). The pattern order also shows good agreement when compared with the Penrose reciprocal lattice calculated using the five lattice vectors, Figure 4(c). The diffraction pattern in Fig. 4(b) shows bright outer spots which correspond to the superposition of two pentagrams rotated by angle $\pi/5$ with respect to each other. The Penrose tiling as seen in the SEM image of Fig 1(a) is generated from "fat" and "skinny" rhombi (P3 group), whose base angle is $\pi/5$. Detailed diffraction patterns from quasi-crystals, such as those in Figures 3, 4 and 5, have not been observed to date at the optical frequencies.

The remarkable 'richness' and intricacy of the optical replay field emanating from the quasi-crystalline VACNT array is best seen in the spherical diffraction pattern shown in Fig. 5. The results clearly show that the quasiperiodic array of nanotube antennae act as diffractive elements (apertures) for the reflected light, producing remarkable and striking diffraction patterns (replay fields).

In some complimentary work we have shown that patterned VACNT arrays which form a regular 2-D crystal can also be used to obtain meta-material properties associated with nanoscale metal wires [9]. In this mode the reduced plasma frequency in the VACNT due to induced current flow in the axial direction and the resulting circumferential magnetic field is exploited to obtain a negative permittivity in the optical frequencies [10]. The wavelength of the plasma oscillations for a regular VACNT array is given by

$$\lambda_p \cong a\sqrt{2\pi \ln(a/r)}$$

where a is the 2-D lattice constant and r is the VACNT diameter. In the quasi-periodic array used here r is nominally 100nm and the spacing a between them is 1400nm. Given that the permittivity function as a function of plasma frequency is given as

$$\varepsilon(\omega) \equiv 1 - \frac{\omega_p^2}{\omega^2}$$

the negative permittivity regime, when no light can be transmitted into the array, will only result at wavelengths larger than $\lambda_p \cong 5700\,\text{nm}$. The optical wavelengths at which the diffraction is measured are well below this. Hence light transmission into the VACNT array is not prohibited. On the other hand the orientation of the axes of the VACNTs are normal to the plane of incidence of the EM wave in the diffraction pattern measured in Fig. 3. This makes both the electric and magnetic field components normal to the VACNT axis. For capture of the spherical diffraction pattern shown in Figure 5, the laser was incident at an angle of 50 deg from the normal. In this case there is a component of the electric filed in the incident EM wave along the VACNT axis.

In figure 3 diffraction patterns from square and hexagonal 2D crystals and a pentagonal quasi-crystal are compared. The spherical far field diffraction patterns are captured from a smaller dome and hence truncated compared to that in Fig. 5. Here the diffraction pattern seen when white light is used as the incident source can be compared with that seen when the monochromatic 532nm laser source is used. The expected spectral splitting of the white light diffraction spots is clearly evident. The rightmost column of Fig. 3 shows the diffraction patterns captured when the VACNT array axis is normal to the plane of incident light. The characteristic square and hexagonal diffraction patterns are seen from the corresponding arrays. The spots can then be considered as beams formed through VACNTs acting as diffractive elements in reflection mode.

Micro-scaled patterns of light resulting from the quasi-periodic VACNT arrays as shown here are difficult to replicate/forge. A ready application for them would therefore be for security purposes such as to validate the originality of brands, passports, cheques, important documents etc. They can also be used, in either periodic or quasi-periodic form, for directing a single beam of coherent light to many spatial locations simultaneously. There could of course be many other applications hitherto not foreseen, such as optical coding, where the rich and layered diffraction patterns resulting from these 2 dimensional quasi-crystals can be utilised.

Figure Legend

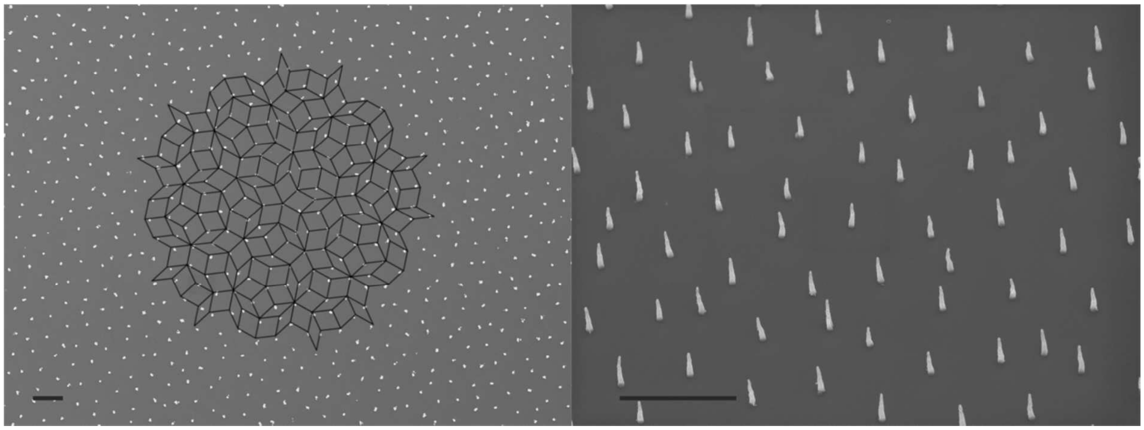

Figure 1: SEM images of a quasi-periodic array of carbon nanotubes. Left panel: Normal view, with Penrose tile scheme overlaid. Right panel: Array tilted by 45˚. Scale bars 2µm. CNT heights are ~700nm. On observation after growth the arrays, which cover an area of 2.5 mm^2, are seen to be strongly diffracting ambient light indicating that the arrays are well-ordered and metallic with low dielectric losses

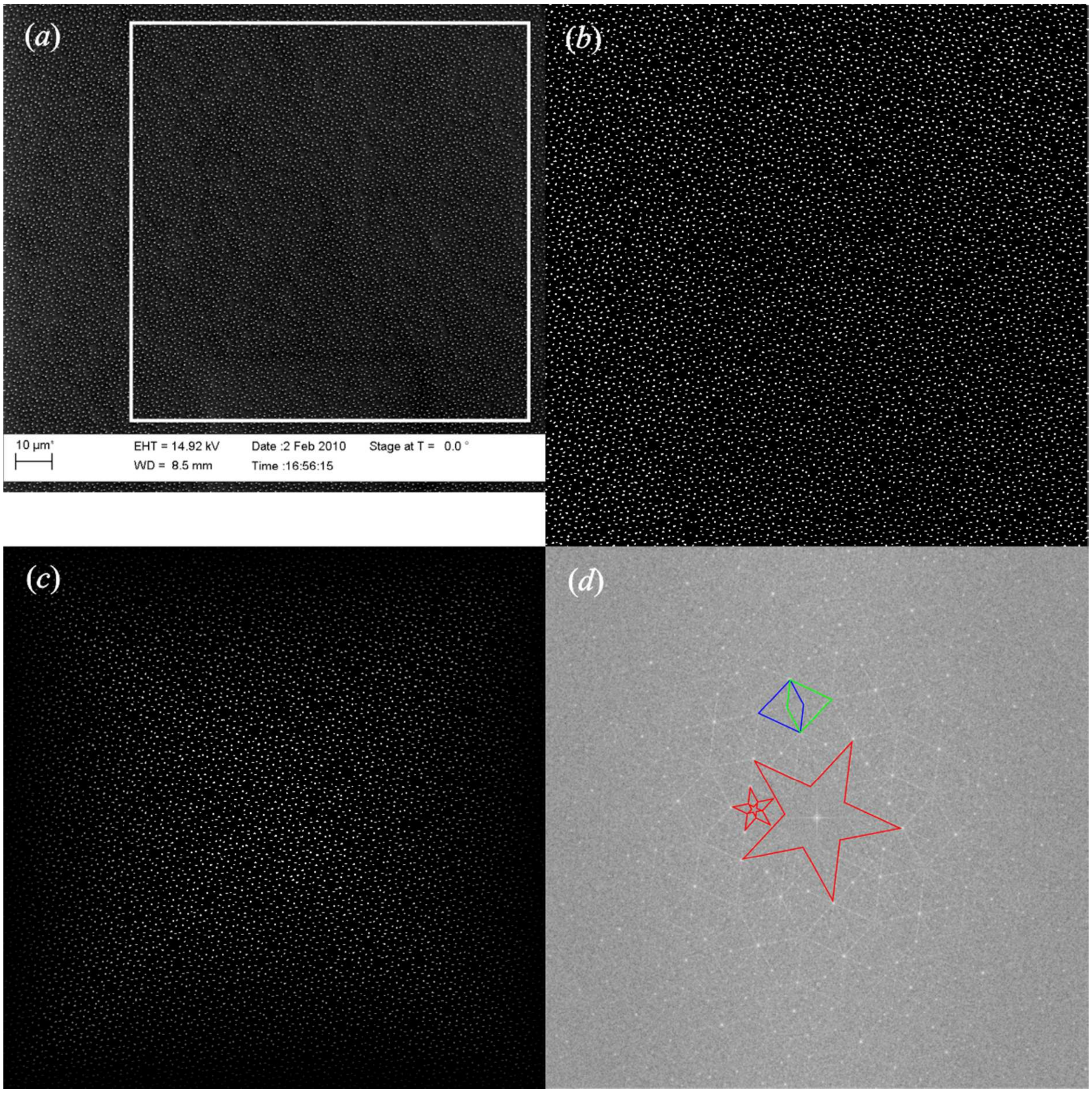

Figure 2: 2D Fourier transform of pentagonal nanotube array image. (*a*) SEM image of CNT array. (*b*) Square section of array thresholded to binary image. (*c*) Blending of edges. (*d*) 2D FFT. The square image is imported into an image processing program (ImageJ) for FFT generation. Red pentagrams have been overlaid to accentuate the fractal fivefold symmetry of the pattern, the green and blue shapes show the kite and dart and fat and skinny units from which the real space tiling is generated.

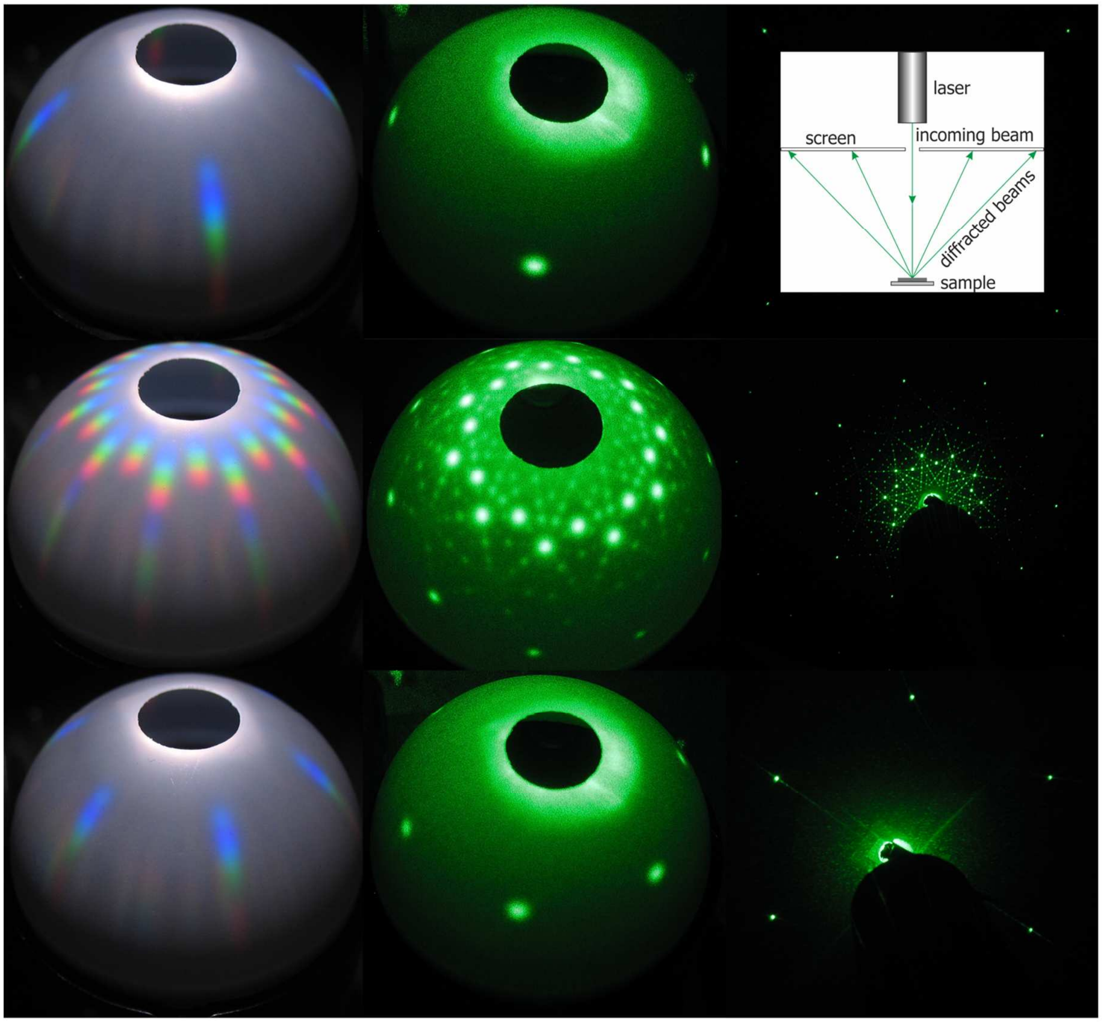

Figure 3. Columns: Left, white light diffraction. Middle, 532nm light diffraction. Right, diffraction patterns projected onto a flat screen. Rows: Top, Square array. Middle, pentagonal array. Bottom, hexagonal array. Inset, top right: Experimental setup for screen projection – note that the four diffraction spots form the square array are outside the corners of the inset .

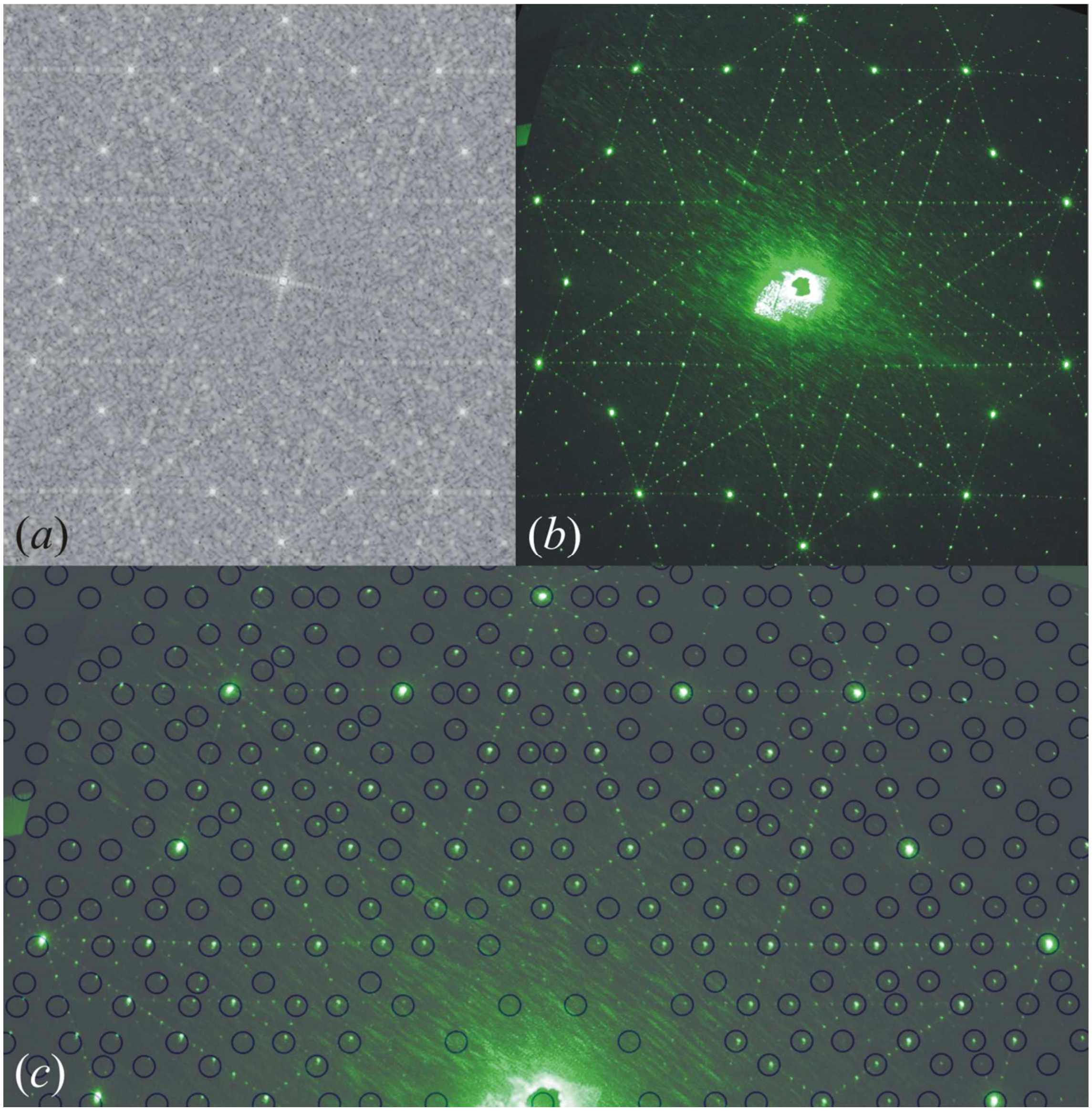

Figure 4: Comparison of (*a*) FFT of SEM image of pentagonal array nanotube tips and (*b*) diffraction of normally-incident green laser light (the dark central spot is the aperture in the screen through which the laser shines; the image has been corrected for distortion). (*c*) shows an overlay of the reciprocal lattice points as calculated in MATLAB onto half of the laser diffraction pattern.

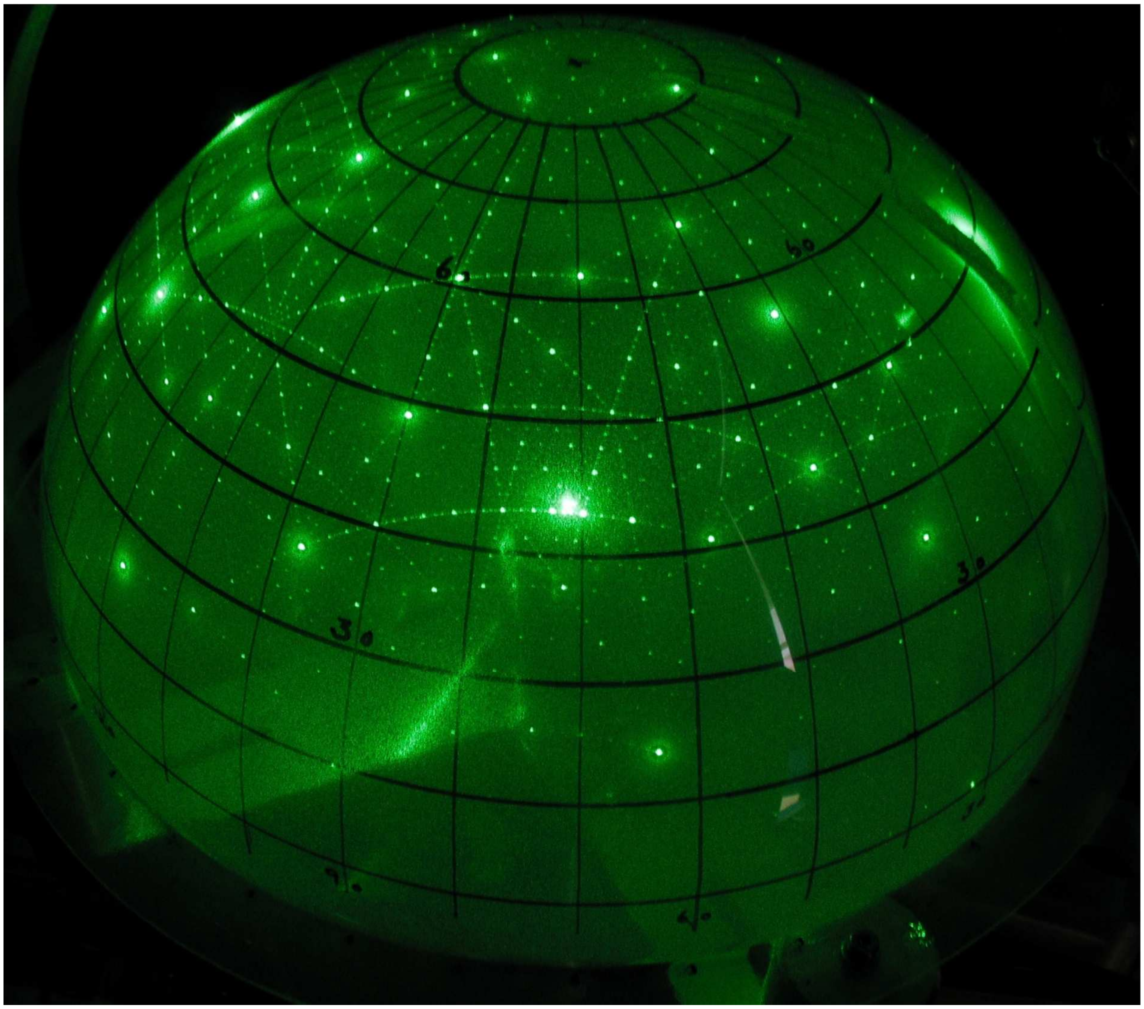

Figure 5: Penrose diffraction of 532nm laser, incident at an angle of 50˚ from the normal, captured with a semi-transparent dome.

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Methods

Penrose tile based quasi-periodic pattern generation

Periodic arrays of VACNTs can be produced via electron beam lithography by repeating a unit pattern over the area in which the nanotube array is desired. The lack of translational symmetry inherent in quasiperiodic structures precludes this approach, requiring the employment of a more complex method. Algorithms for the generation of complex, self-similar patterns as part of a theoretical treatment of biological development were proposed by Lindenmayer in 1968; known as L-systems, they use the concept of rewriting in which complex objects can be defined by recursive replacement of the parts of a simple object. An initial condition, known as the axiom, is provided then substitutions occur according to the rule set. The following set of rules produces a Penrose tiling of the fat and thin rhombus (P3) type [11]:

Axiom: +AF--BF---CF--DF

Rules:

A = CF++DF----BF[-CF----AF]++

B = +CF--DF[---AF--BF]+

C = -AF++BF[+++CF++DF]-

D = --CF++++AF[+DF++++BF]--BF

Where '-' means turn left 36˚, '+' turn right 36˚, 'F' move forward, '[' store location and ']' recall location. A 16th-order recursion with a tile side length of 1270nm will produce a quasiperiodic pentagonal pattern of several square millimeters.

A LOGO-style program was written to interpret the rules used to generate the Penrose array; the program produces a list containing the position of each of the vertices of the tiles, which is then converted to a format recognized by the electron beam lithography system.

Sample preparation

A 10x10mm Si substrate was cleaned and spincoated with a 150nm layer of PMMA. The sample was then patterned using a NanoBeam electron beam lithography system and developed for 70s in a solution of MIBK:IPA at a ratio of 1:2. A 5nm barrier layer of ITO followed by 15nm of Ni catalyst was sputtered in an Ar atmosphere at a pressure of 3.5mBar. Subsequently lift-off was carried out in acetone, leaving the desired pattern of catalyst dots. The nanotubes were grown in a NanoInstruments "Black Magic" PECVD system with acetylene as the feedstock gas and ammonia as the etchant. The plasma was maintained at a voltage of 650V and a current of 60mA. A growth time of 7.5 min at a pressure of ~3 mBar yielded a 2.5mm^2 quasiperiodic VACNT array with a tube length of approximately 700nm (Figure 1).