IOP PUBLISHING

J. Phys.: Condens. Matter **20** (2008) 362203 (5pp)

IOP FTC ▶▶▶

JOURNAL OF PHYSICS: CONDENSED MATTER

doi:10.1088/0953-8984/20/36/362203

FAST TRACK COMMUNICATION

Fabrication and optical properties of gold nanotube arrays

W R Hendren[1]**, A Murphy**[1]**, P Evans**[1]**, D O'Connor**[1]**, G A Wurtz**[2]**,
A V Zayats**[1] **and R J Pollard**[1,3]

[1] Centre for Nanostructured Media, IRCEP, The Queen's University of Belfast,
Belfast BT7 1NN, UK
[2] Department of Chemistry and Physics, University of North Florida, 1 UNF Drive,
Jacksonville, FL 32224, USA

E-mail: r.pollard@qub.ac.uk

Abstract
Arrays of gold nanotubes with polypyrrole cores were grown on glass substrates by
electrodeposition into thin film porous alumina templates. Measurements of optical
transmission revealed strong extinction peaks related to plasmonic resonances, which were
sensitive to the polarization state and angle of incidence. On prolonging the electrodeposition of
gold, the polypyrrole core became fully encapsulated and this had a dramatic effect on the
optical properties of the arrays, which was rationalized by finite element simulation of the local
field intensities resulting from plasmon excitation.

(Some figures in this article are in colour only in the electronic version)

Metal nanoparticles exhibit distinctive optical properties that are highly sensitive to their size, shape, orientation and environment. Underlying these properties are surface plasmons, collective oscillations of the conduction electrons of the metal. Plasmonic nanoparticles have increasing technological relevance and are finding diverse applications in areas such as cancer treatment [1, 2], sensors [3–5], metamaterials [6–8], optoelectronics [9–11] and sub-wavelength photonics [12–14]. In spite of the high level of interest in plasmonic nanoparticles of various shapes and sizes there have been relatively few reports on nanotubes. Yet they have potential applications as electrodes for nanoscale devices [15], in metal enhanced luminescence [16–18] and as SERS substrates [19].

Most methods for making metal nanotubes employ a porous alumina or polycarbonate membrane as a template. A typical approach is to chemically pretreat the template to promote plating of the pore walls in an electrochemical or electroless reaction [20–22]. Thus nanotube length is determined by template thickness and the inner diameter depends on deposition time. Recently, alternative approaches

that avoid chemical modification of the template and give independent control over nanotube length have been developed and used successfully [15, 16, 19, 23–27]. These either involve very specific deposition conditions [19, 23–26], or coaxial composite nanowires with sacrificial cores [15, 27], which once removed leave tubular shells.

This paper reports the fabrication of vertically aligned arrays of gold nanotubes on glass substrates, which exhibit distinct plasmonic optical behaviour. The method of manufacture extends proven techniques originally developed to produce substrate supported nanowire arrays for optical studies [28–30].

The method for fabrication of gold nanotube arrays is summarized in figure 1. An anodic alumina (AAO) template was prepared by anodizing a specially developed thin film multilayer structure, incorporating an electrode and a 400 nm thick aluminium layer, in 0.3 M sulfuric acid [28]. Polypyrrole was deposited into the AAO template using a standard three electrode cell at a relatively high electropolymerization voltage of +1.5 V versus a Pt wire reference. The electrolyte was an acetonitrile solution containing 0.5 M pyrrole monomer and 0.3 M tetraethylammonium-p-toluene sulfonate [31]. After

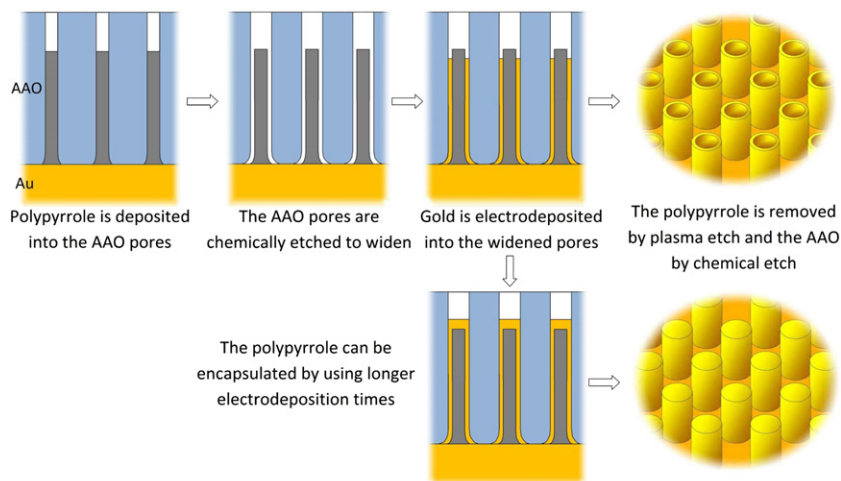[3] Author to whom any correspondence should be addressed.

Figure 1. The process for the fabrication of gold nanotube arrays.

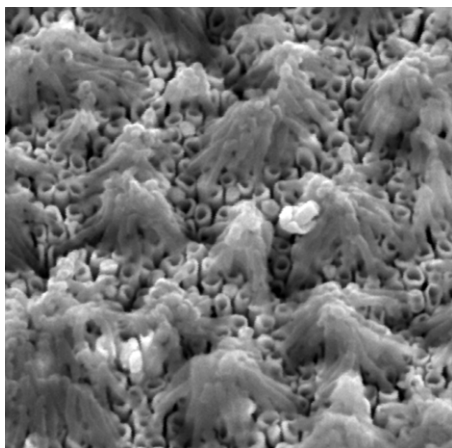**Figure 2.** SEM micrograph of a gold nanotube array before plasma etching. Polypyrrole cores can be seen emerging from inside the nanotubes.

Figure 3. SEM micrographs of (a) an uncapped nanotube array (b) a capped nanotube array, after template removal and plasma etch. Nanotube array dimensions estimated from the images are as follows: inside diameter 16 nm, outside diameter 35 nm and spacing 52 nm.

electropolymerization, the AAO pores were widened in sodium hydroxide to create space around the polypyrrole nanowires. Gold was electrodeposited from a thiosulfate–sulfite bath [32] to form gold nanotubes. To expose the nanotubes, the AAO template was dissolved in sodium hydroxide. The polypyrrole nanowires were removed by plasma etching in a 3:1 argon–oxygen atmosphere.

The manufacturing route enables some control over the nanotube spacing (40–70 nm), length (<400 nm), inside diameter (10–40 nm) and outside diameter (30–60 nm). Figure 2 shows gold nanotubes with growth terminated at approximately half the polypyrrole wire length. The figure clearly demonstrates that the tubes grow from the substrate and not directly onto the polypyrrole. If the gold nanotube growth is not terminated before it reaches the top of the polypyrrole wires, overgrowth will occur and a new capped structure is formed. This is illustrated in figure 3, which shows capped and uncapped nanotubes after the removal of the alumina template and plasma etching.
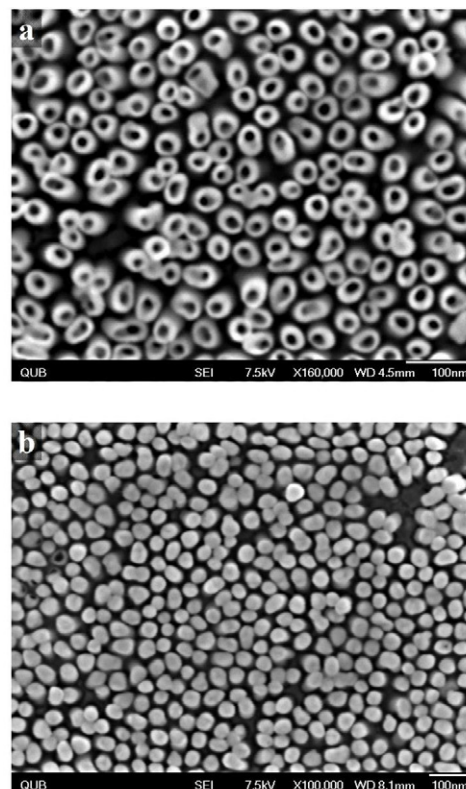
The optical properties of the arrays were investigated using measurements of transmission. In figures 4(a) and (b), the results for uncapped nanotubes are expressed as extinction spectra for s- and p-polarized light at several angles of incidence. A broad peak extends over most of the observable range and extinction increases with angle of incidence for both polarization states; however, the effect is more pronounced for
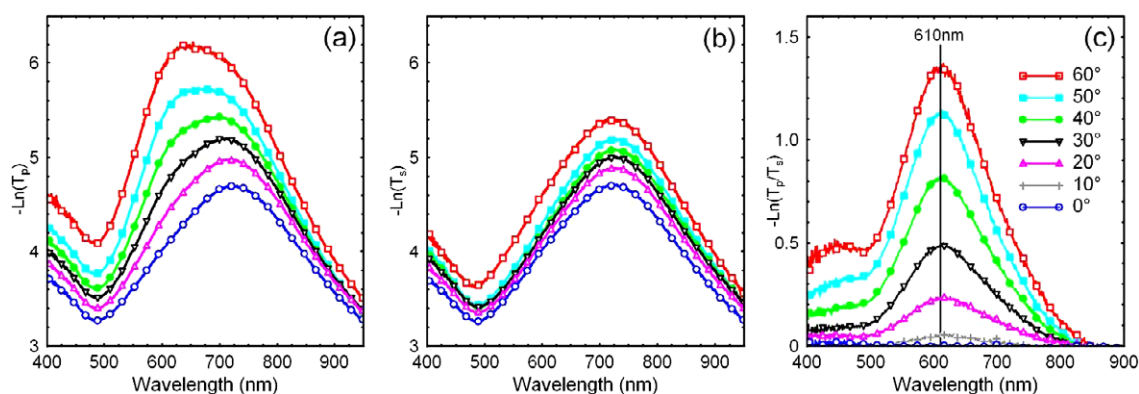
Figure 4. Extinction spectra for an uncapped nanotube array, taken at angles of incidence in the range 0°–60°, before the polypyrrole cores and AAO template were removed. The graphs are (a) p-polarized light; (b) s-polarized light; (c) the difference between the p- and s-polarized extinctions illustrating that the p-polarized spectrum is composed of two peaks. Nanotube dimensions were estimated to be as follows: inner diameter 24 nm; outer diameter 40 nm; length 150 nm; spacing 55 nm.

p-polarized light, which also shows an increasing asymmetry. The latter appears to be due to the existence of two peaks in the p-polarized spectra: the first is similar to that seen in s-polarized light; the second is sharper, occurs at a shorter wavelength, and is more sensitive to angle of incidence. To illustrate the point, the p-polarized spectra has been normalized with respect to the s-polarized spectra in figure 4(c), revealing a peak at a wavelength of 610 nm, which increases with angle of incidence. The optical characteristics of the nanotubes show some similarities to those of gold nanowire arrays [28, 33]. The latter also exhibit two extinction peaks, one appearing in both p and s-polarized spectra and the other, highly dependent on angle of incidence, appearing in p-polarized spectra only. In the nanowire case both peaks are plasmon related, the former due to a resonance across the nanowires and the latter associated with resonance along the nanowires. Consequently, it is sensible in the first instance to consider something similar as the origin of the optical effects in the nanotubes.

A second peak at shorter wavelengths also occurs when nanotubes are capped; only in this case, it can also be seen at normal incidence. Figure 5 compares the extinction spectra for a nanotube array, before, during and after capping, clearly showing the development of a peak between 500 and 600 nm.

Finite element modelling was used to gain insight into the nature of the electromagnetic resonances in these structures. Figure 6, shows the normalized electromagnetic field distribution for nanotube arrays, 120 nm long, with and without 12 nm thick caps, excited by plane waves at normal incidence. At shorter wavelengths, the fields are contained inside the nanotubes, whereas at longer wavelengths the inside is screened and the fields are concentrated outside. Also of note is the large field enhancement around the rim of uncapped nanotubes that occurs across the wavelength range, which is promising for applications where strong localized fields are desirable, such as SERS substrates. On capping, the calculations show electromagnetic fields enhanced mainly around the cap region for shorter wavelengths. This is in the region that the development of a second peak during capping is seen experimentally (see figure 5). Informed by the near field calculations, the spectra can be explained qualitatively,
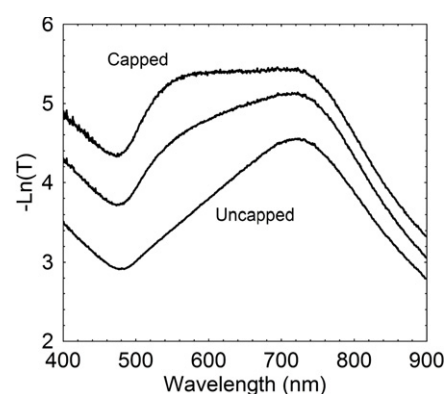

Figure 5. Extinction spectra taken at normal incidence of a gold nanotube array during capping. Final length approximately 270 nm. For other dimensions see figure 3.

by considering the capped nanotubes as quasi-spherical gold particles sitting on nanotubes. Gold particles with dimensions of the order of the caps are expected to exhibit a plasmon resonance around 550 nm [34]. Thus we might expect the extinction spectra to be composed of a nanotube peak at longer wavelengths and a peak due to the caps at shorter wavelengths.

In summary, gold nanotube arrays on glass substrates were fabricated using thin film AAO templates and polypyrrole nanowires, which acted as cores. Polypyrrole and gold were electrochemically deposited into the AAO templates from electrolytic baths using standard three electrode cells. Control of the length of polypyrrole cores and gold shells made it possible to make uncapped and capped nanotubes, the latter produced by allowing the gold to overgrow the polypyrrole wires. Extinction spectra for uncapped structures showed a broad plasmon resonance centred at a wavelength of approximately 700 nm. On capping a second extinction peak emerged near 550 nm. Finite element calculations show a high degree of field localization and screening depending on wavelength. Both model and experimental evidence indicate that the top on a capped nanotube behaves optically like a gold nanoparticle of similar size: consequently, the observed long
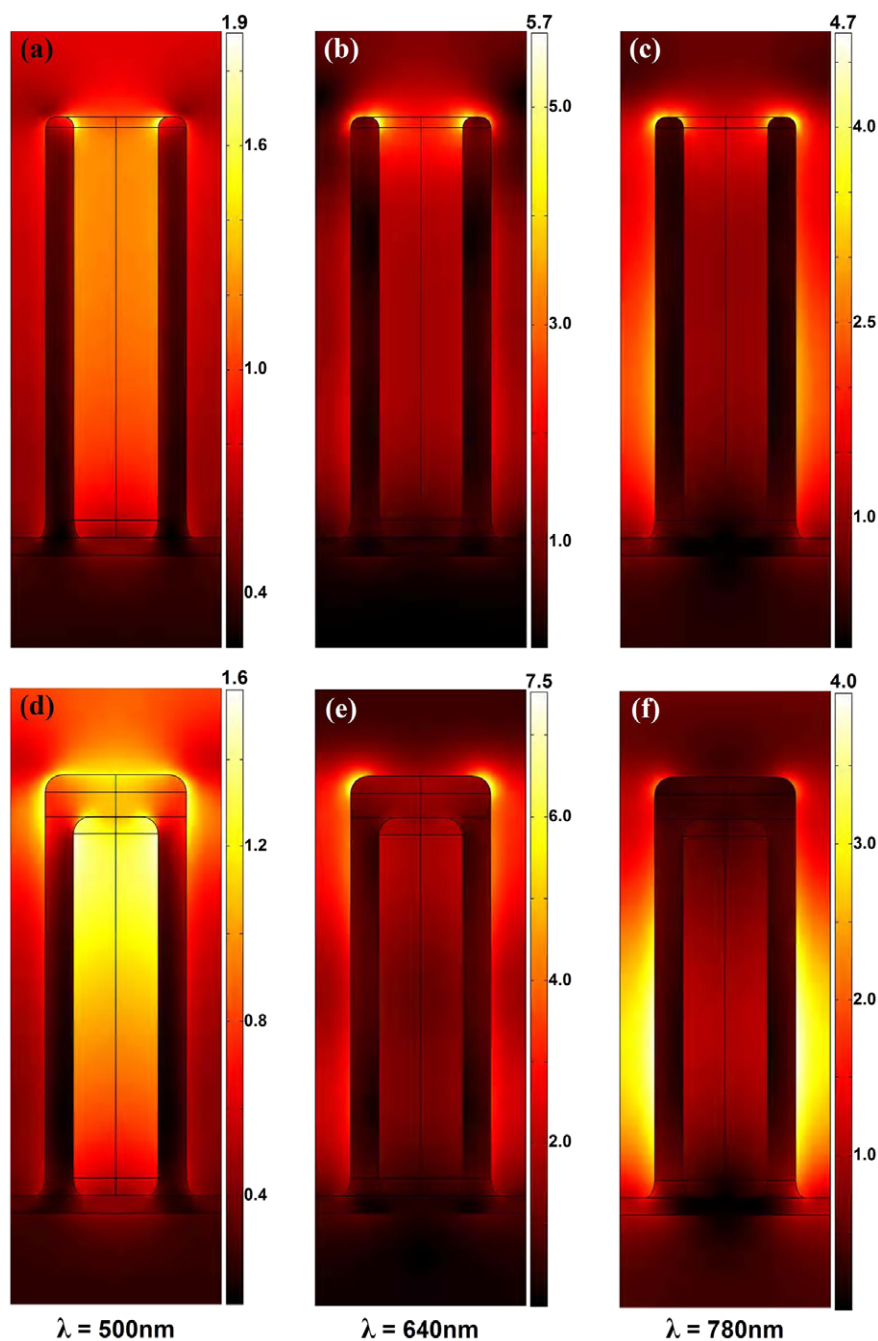
Figure 6. Finite element simulations of electromagnetic field distribution in ((a)–(c)) uncapped and ((d)–(f)) capped gold nanotube arrays in AAO, showing localization of field inside, outside and around the rim of the nanotubes at different wavelengths. Linearly polarized light is incident at normal incidence through air (from the top of the figure). The nanotubes are 120 nm long with a 24 nm inner diameter, 8 nm wall thickness and 60 nm spacing. Caps are 12 nm thick.

and short wavelength peaks are related to the nanotube and cap respectively.

References

[1] Stern J M and Cadeddu J A 2008 *Urol. Oncol.* **26** 93
[2] Hirsch L R, Stafford R J, Bankson J A, Sershen S R, Rivera B, Price R E, Hazle J D, Halas N J and West J L 2003 *Proc. Natl Acad. Sci. USA* **100** 13549
[3] Stewart M E, Anderton C R, Thompson L B, Maria J, Gray S K, Rogers J A and Nuzzo R G 2008 *Chem. Rev.* **108** 494
[4] Aslan K, Lakowicz J R and Geddes C D 2005 *Curr. Opin. Chem. Biol.* **9** 538
[5] Haick H 2007 *J. Phys. D: Appl. Phys.* **40** 7173
[6] Shalaev V M, Cai W, Chettiar U K, Yuan H K, Sarychev A K, Drachev V P and Kildishev A V 2005 *Opt. Lett.* **30** 3356
[7] Kussow A G, Akyurtlu A and Angkawisittpan N 2008 *Phys. Status Solidi* b **245** 992
[8] Grigorenko A N, Geim A K, Gleeson H F, Zhang Y, Firsov A A, Khrushchev I Y and Petrovic J 2005 *Nature* **438** 335
[9] Evans P R, Wurtz G A, Hendren W R, Atkinson R, Dickson W, Zayats A V and Pollard R J 2007 *Appl. Phys. Lett.* **91** 043101

[10] Lim S H, Mar W, Matheu P, Derkacs D and Yu E T 2007 *J. Appl. Phys.* **101** 104309
[11] Kwon M K, Kim J Y, Kim B H, Park I K, Cho C Y, Byeon C C and Park S J 2008 *Adv. Mater.* **20** 1253
[12] Evlyukhin A B, Bozhevolnyi S I, Stepanov A L, Kiyan R, Reinhardt C, Passinger S and Chichkov B N 2007 *Opt. Express* **15** 16667
[13] Ditlbacher H, Hohenau A, Wagner D, Kreibig U, Rogers M, Hofer F, Aussenegg F R and Krenn J R 2005 *Phys. Rev. Lett.* **95** 257403
[14] Atwater H A, Maier S, Polman A, Dionne J A and Sweatlock L 2005 *MRS Bull.* **30** 385
[15] Lahav M, Weiss E A, Xu Q B and Whitesides G M 2006 *Nano Lett.* **6** 2166
[16] Joo J, Park D H, Jeong M Y, Lee Y B, Kim H S, Choi W J, Park Q H, Kim H J, Kim D C and Kim J 2007 *Adv. Mater.* **19** 2824
[17] Fort E and Gresillon S 2008 *J. Phys. D: Appl. Phys.* **41** 013001
[18] Moskovits M 1985 *Rev. Mod. Phys.* **57** 783
[19] Dickey M D, Weiss E A, Smythe E J, Chiechi R C, Capasso F and Whitesides G M 2008 *ACS Nano* **2** 800
[20] Brumlik C J and Martin C R 1991 *J. Am. Chem. Soc.* **113** 3174
[21] Kohli P, Wharton J E, Braide O and Martin C R 2004 *J. Nanosci. Nanotechnol.* **4** 605
[22] Wang W, Li N, Li X, Geng W and Qiu S 2006 *Mater. Res. Bull.* **41** 1417
[23] Kamalakar M V and Raychaudhuri A K 2008 *Adv. Mater.* **20** 149
[24] Wang H W, Shieh C F, Chen H Y, Shiu W C, Russo B and Cao G 2006 *Nanotechnology* **17** 2689
[25] Tourillon G, Pontonnier L, Levy J P and Langlais V 2000 *Electrochem. Solid-State Lett.* **3** 20
[26] Cheng C L, Lin J S and Chen Y F 2008 *Mater. Lett.* **62** 1666
[27] Wang Q, Wang G, Han X, Wang X and Hou J G 2005 *J. Phys. Chem.* B **109** 23326
[28] Evans P, Hendren W R, Atkinson R, Wurtz G A, Dickson W, Zayats A V and Pollard R J 2006 *Nanotechnology* **17** 5746
[29] Evans P, Hendren W R, Atkinson R and Pollard R J 2007 *J. Electrochem. Soc.* **154** K79
[30] Evans P R, Wurtz G A, Atkinson R, Hendren W, O'Connor D, Dickson W, Pollard R J and Zayats A V 2007 *J. Phys. Chem.* C **111** 12522
[31] Rapta P, Neudeck A, Petr A and Dunsch L 1998 *J. Chem. Soc. Faraday Trans.* **94** 3625
[32] Liew M J, Roy S and Scott K 2003 *Green Chem.* **5** 376
[33] Atkinson R, Hendren W R, Wurtz G A, Dickson W, Zayats A V, Evans P and Pollard R J 2006 *Phys. Rev.* B **73** 235402
[34] Rodriguez-Fernandez J, Perez-Juste J, Garcıa de Abajo F J and Liz-Marzan L M 2006 *Langmuir* **22** 7007