Fabrication and size dependent properties of porous silicon nanotube arrays†

Xuezhen Huang, a Roberto Gonzalez-Rodriguez, a Ryan Rich, b Zygmunt Gryczynski b and Jeffery L. Coffer*a

A general method for the formation of a broad family of silicon nanotube arrays (Si NTAs) relevant to diverse fields – ranging from energy storage to therapeutic platforms – is described. Such nanotubes demonstrate a thickness-dependent dissolution behavior important to its potential use in drug delivery. Under selected conditions, novel porous silicon nanotubes can be prepared when the shell thickness is on the order of 12 nm or less, capable of being loaded with small molecules such as luminous ruthenium dyes associated with dye-sensitized photovoltaic devices. Dissolution. As outlined in Fig. 1, our process entails the use of ZnO nanowire array (NWA) templates, followed by the deposition of a selected coating layer for directing the composition of the desired nanotube product, and template removal via a novel gas phase etching process involving He-diluted HCl–NH3 gas mixtures at a relatively low temperature (450 °C). In this work, we describe, for elemental semiconductors such as silicon (Si) how the careful manipulation of fabrication parameters can induce formation of a wide range of nanotube diameters, including novel porous sidewall morphologies capable of nanoscale infiltration, release, and dissolution. Such structures were characterized by a combination of high-resolution transmission electron microscopy (HRTEM, JEOL-2100), energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM, JEOL-6100), and confocal fluorescence/time-resolved microscopy.

Semiconductor nanotubes (NTs) such as those comprised of silicon (Si) are attractive experimental targets because of their promising potential in applications in photovoltaics, battery technology, hydrogen storage, as well as extending into the realm of nanoscale drug delivery.1,4 While of theoretical interest for some time,5 few routes to formation of silicon nanotubes have actually been achieved experimentally.1 Routes explored to date often rely on incomplete filing of a porous alumina template, a process that is very difficult to control with product uniformity, as it is easy to overfill a given pore and produce solid nanowire structures. Another reported route employs gas phase condensation, a process that yields a large amount of amorphous, ill-defined particles and only a few nanotubes on a given surface.6 Thus it remains a challenge to produce relatively large area nanotube arrays in a straightforward manner, with sensitive control over feature size and composition, thereby permitting an analysis of size-dependent properties.

More recent investigations have identified templating methods based on ZnO nanowire7,8 (NW) or Ge NW9 cores as a promising strategy for subsequent nanotube (NT) formation upon NW core dissolution. As outlined in Fig. 1, our process entails the use of ZnO nanowire array (NWA) templates, followed by the deposition of a selected coating layer for directing the composition of the desired nanotube product, and template removal via a novel gas phase etching process involving He-diluted HCl–NH3 gas mixtures at a relatively low temperature (450 °C). In this work, we describe, for elemental semiconductors such as silicon (Si) how the careful manipulation of fabrication parameters can induce formation of a wide range of nanotube diameters, including novel porous sidewall morphologies capable of nanoscale infiltration, release, and dissolution. Such structures were characterized by a combination of high-resolution transmission electron microscopy (HRTEM, JEOL-2100), energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM, JEOL-6100), and confocal fluorescence/time-resolved microscopy.

Fig. 1 Si nanotube array (Si NTA) fabrication scheme. Si is brought into the system by CVD with silane onto ZnO NWs at 500 °C, with removal of the ZnO core by etching with HCl and NH3. Extent of NT crystallinity is affected by optional annealing.

† Electronic supplementary information (ESI) available: Additional details of ZnO nanowire (NW) fabrication; SEM images of ZnO NWA templates; EDX linescans of Si NTs (ESI†). See DOI: 10.1039/c3cc41913d
Control of nanotube shell thickness is a key parameter in terms of manipulation of sidewall structure and associated properties (optical, mechanical). In the experiments described here, sidewall thicknesses ranging from 10 nm to as thick as 100 nm (Fig. 2) have been produced. Significantly, when the sidewall thickness is ~12 nm or less, the resultant strain in the nanotube produces a unique morphology that appears uniformly porous across a given tube (Fig. 2d). Such voids appear to be in the 5–10 nm range, values associated with a mesoporous classification. Such porosification is presumably driven by a strain-influenced mechanism, whereby Ostwald-type coalescence into islands of Si occurs, with concomitant formation of void spaces in the nanotube. Moving to thicker shell structures (~25 nm) results in a relatively smooth, continuous surface lacking porous features (Fig. 2e). This is also evident in NTs with even thicker shells, as in the case of 70 nm (ESI†) and 100 nm (Fig. 2c) for two very different inner tube diameters (50 nm, 500 nm).

Such manipulation of nanotube shell thickness, in conjunction with directing the inner diameter size (through control of ZnO NWA template width), provides a widely-tunable overall width of a given nanotube. For example, the overall width of the Si NT structures described above range from 80 nm in (a) to 610 nm in (d). This is a significant expansion of the range provided in earlier studies of SiNTs applied to Li storage and cycling (e.g. 60, 80 and 100 nm). The NTAs align in relatively dense films that can be readily fractured into free standing structures for further manipulation (ESI†).

The associated crystallinity of the Si in the as-formed nanotubes is strongly a function of deposition temperature. If the silane decomposition takes place at a temperature of ~500 °C, only an amorphous Si shell is formed on the surface of ZnO NWs (ESI†). Use of secondary annealing protocols at temperatures of 600 °C (30 min; He atmosphere) and beyond produces readily visible nanocrystalline domains of (111) orientation (ESI†) present in the nanotube wall.

In an observation of significance to therapeutic applications such as drug delivery and tissue engineering, these Si NTs are observed to dissolve in water (at room temperature) as a function of shell thickness and annealing temperature (Fig. 3; evaluated by molybdate-based spectrophotometric-based methods). For example, 23% of Si NTs with a 20 nm shell thickness dissolve in a 47 d period, in contrast to ~5% for the 80 nm thick variant; annealing Si NTs with a 20 nm thick shell drops the percent dissolution to a value of 11% in this same timeframe. Not surprisingly, use of buffered media at physiological temperature (37 °C) accelerates this process; for example, >80% of a porous Si NT (10 nm thick) sample (~60 µg) will resorb in a 48 h period, and complete dissolution within 72 h (ESI†). This novel dissolution behavior is reminiscent of bioactive nanostructured mesoporous silicon prepared by the anodization of single crystal silicon.

One method to probe the presence of porous sidewalls in such nanotubes is the infiltration of luminescent dyes into the hollow cavity and an evaluation of their photophysics. For this purpose the well studied ruthenium species tris(bipyridyl) ruthenium(II) was selected. Related derivatives of this complex
are often employed in dye-sensitized solar cells (DSSCs).\textsuperscript{15} A typical experiment involves the exposure of a given Si NT film to a dilute ethanolic solution of Ru(bpy)$_3$$^{2+}$, following ethanol rinse and air drying. Such films produce strong visible light that can be viewed via confocal fluorescence microscopy. Steady state emission measurements ($\lambda_{ex} = 470$ nm) reveal the expected 600 nm maximum feature associated with metal to ligand charge transfer (MLCT) in this type of complex.\textsuperscript{16} The corresponding fluorescence image consists of bright dots consistent with the overall nanotube diameter derived from SEM imaging (Fig. 4).

It is also instructive to examine the corresponding lifetimes associated with this emission when present in the nanotube. In thin film form, Ru(bpy)$_3$$^{2+}$ is known to possess two distinct components in its fluorescence decay curves, with $\tau_1$ ranging from 80 to 99 ns, and $\tau_2 = 329$ to 400 ns\textsuperscript{17} for films of Ru(bpy)$_3$$^{2+}$ alone ranging from 17 to 200 nm, a direct correlation between increasing film thickness and increasing emission lifetime has been observed.\textsuperscript{17} Such behavior has been attributed to size-dependent changes in the non-radiative component of the lifetime, $k_{nr}$ in turn mainly associated with effects on the quenching rate for Forster energy transfer (FET).

For Ru(bpy)$_3$$^{2+}$ loaded into Si NTs, the expected two decay regimes are observed. It is found that that the short lifetime component is significantly reduced to an average value of 10 ns, and the corresponding long lifetime species is lengthened slightly (relative to the above thin film values) to an average of 450 ns. The cause of such an extreme reduction in $\tau_1$ is consistent with previous studies of adsorption of Ru(bpy)$_3$$^{2+}$ onto oxide terminated semiconducting surfaces, where electron transfer between the Ru(bpy)$_3$$^{2+}$ and the oxide semiconductor results in a reduction in observed excited state lifetime to 12–20 ns, depending on the substrate.\textsuperscript{18}

In summary, it is clear that the formation of a broad family of nanotube structures is possible with the route demonstrated here. Sensitive control of shell structure has been demonstrated for the case of Si, including a thin-walled variant that dissolves at physiological temperature. Such structures have implications for sensitive drug delivery devices, along with broader electronic applications, at the nanoscale. Proof-of-concept experiments using Ru dye systems reveal strong interactions of the encapsulated complex with the NT surface. A number of additional opportunities for NTs that take advantage of these initial discoveries are currently under investigation.

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