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2013 Nanotechnology 24 045605

(http://iopscience.iop.org/0957-4484/24/4/045605)

Nanotechnology **24** (2013) 045605 (8pp) doi:10.1088/0957-4484/24/4/045605

ZnO nanowire array-templated LbL self-assembled polyelectrolyte nanotube arrays and application for charged drug delivery

Weiyong Yuan[1], Zhisong Lu[1,2], Jinping Liu[3], Huili Wang[4] and Chang Ming Li[1,2]

[1] Institute for Clean Energy and Advanced Materials, Southwest University, Chongqing 400715, People's Republic of China
[2] Chongqing Key Lab for Advanced Materials and Technologies of Clean Electrical Power Sources, Chongqing 400715, People's Republic of China
[3] Institute of Nanoscience and Nanotechnology, Department of Physics, Central China Normal University, Wuhan 430079, People's Republic of China
[4] School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

E-mail: ecmli@swu.edu.cn

Received 5 August 2012, in final form 29 October 2012
Published 8 January 2013
Online at stacks.iop.org/Nano/24/045605

Abstract
Vertically oriented and robust polyelectrolyte nanotube arrays with high density, large area and high uniformity were successfully grown on substrates by a ZnO nanowire array-templated layer-by-layer (LbL) self-assembly approach for the first time, and were further used to deliver charged drugs, showing that they not only possess pH-responsive loading property, but also significantly enhance the loading capacity and sustained release time. This work could be extended to fabricate polyelectrolyte nanotube arrays with different polyelectrolyte combinations, including weak polyelectrolyte/weak polyelectrolyte, weak polyelectrolyte/strong polyelectrolyte and strong polyelectrolyte/strong polyelectrolyte. With the great versatility to use various substrates and building blocks, the polyelectrolyte nanotube arrays may have great potential for broad applications such as biosensor arrays, bioreactor arrays and optoelectronics.

S Online supplementary data available from stacks.iop.org/Nano/24/045605/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Polymeric nanostructures with controlled morphology and chemical composition have attracted great interest due to their large specific surface area, unique physical and biological properties, tailorable functionalities, environmental responsiveness and low cost [1–7]. Among them the polymeric nanotubes (outer diameter smaller than 100 nm) offer additional advantages such as large inner surface area, possibility of differently functionalized inner and outer walls and unique mass and energy transport properties [8–12]. There are great needs to robustly assemble large-area and high-density polymeric nanotubes on a substrate in an ordered and vertically oriented array structure for broad applications such as biosensor arrays, bioreactor arrays, implantable drug delivery devices and optoelectronics [13–18]. In particular, for an implantable localized drug delivery, a macroscale substrate is able to provide implantability, while a nanotube array

structure could offer large surface area and high porosity for significantly increased loading capacity and sustained release time [19–23].

Templating approaches by using conventional track-etched polycarbonate (PC) membrane or nanoporous anodic aluminum oxide (AAO) have been employed to fabricate polymeric nanotubes [24–27]. However, the nanotubes are randomly distributed in a solution with difficulty to form an arrayed structure, and the tube size is also restricted to several hundred nanometers because of easy blockage of small pores by polymers with nonuniform coating [6, 24–27]. Electrochemical synthesis and peptide self-assembly have been reported, but only disordered nanotubes of polymers with specific chemical structures are obtained on a substrate or in a solution [4, 28, 29]. Although lithography has been used to fabricate arrayed structures, it is very hard to make nanoscaled polymeric tubes, due to not only the complex process and harsh environment required, but also the easy collapse of flexible polymeric nanotubes on substrates [30–32]. ZnO nanowire arrays have been fabricated on various substrates with high density and in large area via metal–organic chemical vapor deposition, vapor phase transport and wet chemical growth [33–37]. They can be controllably dissolved with acid or base treatment [38, 39], and could be used as a template to fabricate nanotube arrays. However, it is very challenging to form a uniform, defect-free, chemically and mechanically robust coating to withstand the harsh template removal conditions for desired nanotube arrays, and thus to date only inorganic ones such as metal oxide, carbons, and metals can be obtained [39–41]. Nevertheless, polymeric nanostructured arrays provide great promising potential in many areas, particularly as implantable medical devices for localized drug delivery [19–23], thus rendering great significance in both fundamentals and applications.

Layer-by-layer (LbL) self-assembly of polyelectrolytes is able to conformally assemble stable polymeric nanostructures with tailorable chemical composition, molecular organization and desired properties on any substrate from a theoretical point of view [2, 42–50]. Since both the ZnO nanowire and the substrate could be uniformly assembled, we expect that a unique approach combining ZnO nanowire array templating and LbL self-assembly could be used to grow well-defined polymeric nanotube arrays on substrates. In this work, various polyelectrolyte combinations, including weak polyelectrolyte/weak polyelectrolyte (W/W), weak polyelectrolyte/strong polyelectrolyte (W/S) and strong polyelectrolyte/strong polyelectrolyte (S/S), were studied to produce vertically oriented polymer nanotube arrays on substrates. The loading and release of charged drugs were further examined to demonstrate their potential applications as medical devices for localized drug delivery.

2. Experimental details

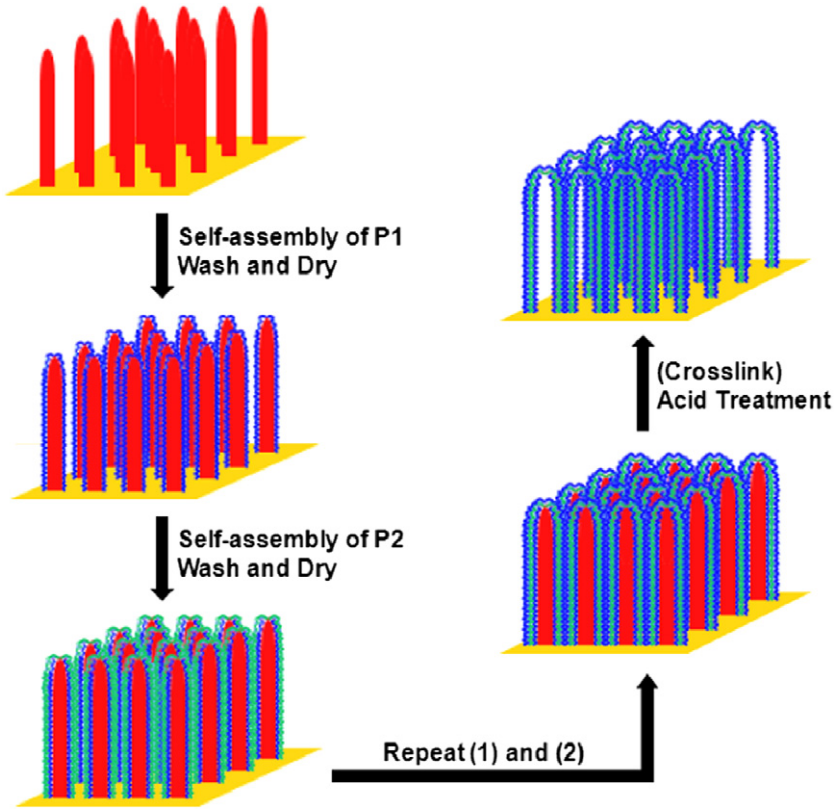
Poly(ethylenimine) (PEI) solution (50 wt% in water, M_w 750 000), poly(acrylic acid) (PAA) solution (35 wt% in water, M_w 100 000), poly(diallyldimethylammonium chloride) (PDDA) solution (20 wt% in water, medium molecular weight), poly(sodium 4-styrene-sulfonate) (PSS, M_w 70 000), $Zn(NO_3)_2 \cdot 6H_2O$ (98%), $NH_3 \cdot H_2O$ (28%–30% in water), and crocein orange G (CG) were all purchased from Sigma-Aldrich. Methylene blue (MB) was obtained from Research Chemicals Ltd. Stainless steel (Fe–Co–Ni alloy, purity > 99.5%) was obtained from Shanghai Chemical Reagent Co. Ltd. Phosphate buffered saline (PBS) was prepared by dissolving PBS dry powder (Sigma-Aldrich) in DI water. The DI water (18.2 MΩ cm) was obtained from a Millipore Milli-Q water purification system.

The growth of the ZnO nanowire array was carried out according to the reported work [36]. In a typical process, a piece of an ethanol/water-washed Fe–Co–Ni alloy was suspended in 200 ml aqueous solution containing 0.035 M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.65 M $NH_3 \cdot H_2O$ followed by heating at 70 °C for 24 h. After the reaction, the substrate was taken out, rinsed with ethanol and finally dried in air.

For the fabrication of polyelectrolyte nanotube arrays, the selected polyelectrolyte pairs were first LbL self-assembled on the ZnO nanowire array. As an example, the ZnO nanowire array template was first immersed in 1 mg ml^{-1} PEI solution (pH 9.5) for 15 min, subsequently rinsed with DI water five times and then blown dry gently with N_2. Then the ZnO nanowire array was immersed in 1 mg ml^{-1} PAA solution (pH 3.2) for 15 min, rinsed with DI water five times and further dried gently with N_2. This procedure was repeated to obtain a polyelectrolyte multilayer coating (denoted by $(PEI/PAA)_{n/2}$, where n is the number of layers of the coated polyelectrolyte). The as-prepared weak polyelectrolyte multilayer coating was further crosslinked with glutaraldehyde by immersing in 2% glutaraldehyde aqueous solution for 2 h. The procedures for LbL self-assembly of PDDA and PAA, and of PDDA and PSS, were similar except that the polyelectrolyte deposition time was 10 min and no crosslinking step was performed. To remove the ZnO template, the polyelectrolyte assembled ZnO nanowire arrays were immersed in 0.01 M HCl for 40–60 min without any agitation, and were sequentially immersed into DI water for 1 h, ultrasonicated in DI water for 2 min, and dried in air for the final polymer arrayed tubes on a substrate. The fabrication process is shown in scheme 1, and mainly involves two steps: self-assembly of polyelectrolyte multilayers on the ZnO nanowire array substrates followed by template removal by acid treatment.

The surface and cross-section morphologies of the polymer nanotube arrays were characterized by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F), which has an energy dispersive x-ray (EDX) unit for the element analysis. The nanotube arrays for characterization were surface-coated by a thin Pt layer using an Auto Fine Coater (JEOL) at 20 mA for 100 s. The transmission electron microscopy (TEM) characterizations were performed with a JEOL 2010 microscope at 200 kV. The tested polyelectrolyte nanotubes were scraped from the substrate. After vigorous shaking in DI water, the nanotube suspension was dropped on the carbon-coated Cu grid, followed by evaporation to remove solvent in ambient environment.

To load the model drugs MB and CG, the polymer nanotube arrays were immersed in 0.5 mg ml^{-1} MB and



Scheme 1. Schematic illustrations of the fabrication procedures for polyelectrolyte nanotube arrays on solid substrates. P1 and P2 denote two polyelectrolytes used for assembly.

1 mg ml^{-1} CG solution for 1 h respectively, followed by rinsing with water three times. In the release experiment, the drug-loaded polymer nanotube arrays were immersed into PBS (pH 7.4, 10 mM, 137 mM NaCl) at 37 °C. After releasing for pre-designed times, 1 ml of the solution was taken out to determine the released drug amount by the measured UV–visible (UV–Vis) absorbance through comparison with a calibration curve of the model drugs obtained by measuring absorbances in solutions with a series of drug concentrations. To eliminate the effect of released model drugs on the release profile, the PBS solution was replaced frequently with a fresh one for each characterization.

3. Results and discussion

The weak polyelectrolytes PEI and PAA have been widely used as building blocks to study the mechanism and applications of LbL self-assembly of weak polyelectrolytes [51–53], and they are selected here as model building blocks to study whether a polymeric nanotube array could be successfully fabricated. Different assembly pH values as described in 'Experimental details' were selected, since the LbL self-assembly of PEI and PAA on flat substrates under these conditions has been demonstrated with superior drug loading and release performance [53, 48]. Figure 1 shows the top-view FE-SEM images of the ZnO nanowire array after assembling different layers of PEI and PAA. The surface of the ZnO nanowire with one layer of PEI is very smooth, similar to that of the bare ZnO nanowire (figure S1 available at stacks.iop.org/Nano/24/045605/mmedia). After modification of the second-layer PAA, the surface becomes rougher with appearance of nanowire interconnection, suggesting an efficient assembly of polyelectrolytes. Interestingly, the third layer of polyelectrolyte assembly makes the nanowire smooth again, and the interconnection becomes more apparent. After the fourth-layer polyelectrolyte assembly, a high degree of nanowire interconnection is observed. The surface morphology evolution of ZnO nanowire arrays with layer number clearly illustrates a successful self-assembly process. The assembly with PAA as the first layer was also studied, showing the polyelectrolytes could be assembled. However, the coated multilayer is much less uniform and the interconnection of nanowires is much more prominent with the same number of assembled layers (figure S2 available at stacks.iop.org/Nano/24/045605/mmedia).

The three-layer-coated nanowire array with PEI as the first layer was adopted to fabricate the nanotube array because of its uniform coating and less interconnection of nanowires. To improve the stability of the weak polyelectrolyte multilayer coating, a crosslinking step was performed before removal of the ZnO template. The surface morphology of the nanostructured array after acid etching was examined using top-view FE-SEM imaging (figure 2(a)), showing that the interstices between nanoscaled structural units on the substrate were reduced after removal of the template. This is very likely to be caused by the slight collapse of the

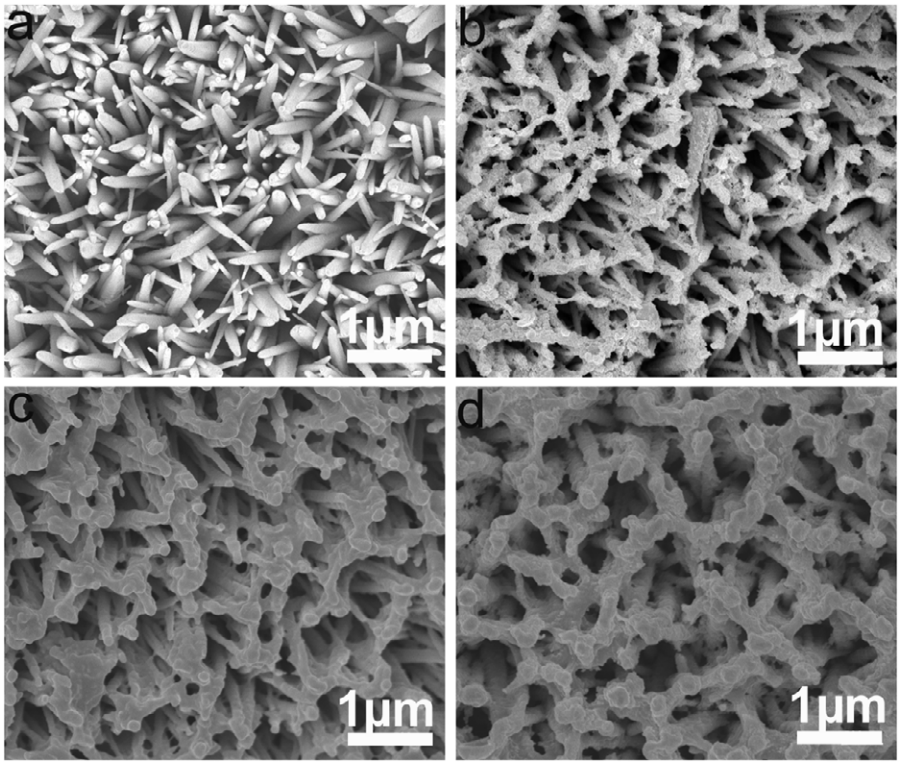


Figure 1. Top-view FE-SEM images of ZnO nanowire array coated with different layers of PEI and PAA. (a) One layer, (b) two layers, (c) three layers, and (d) four layers.

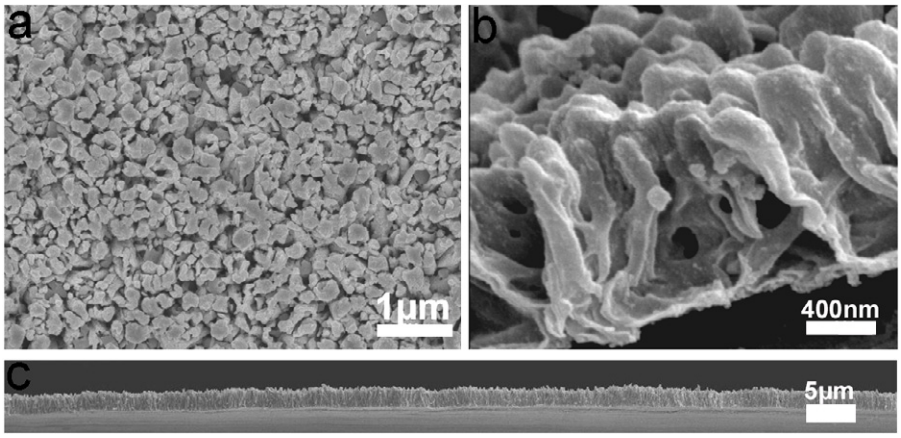


Figure 2. Top-view FE-SEM image (a), cross-section FE-SEM image (b), and low magnification cross-section FE-SEM image (c) of the fabricated PEI/PAA nanotube array.

polymer-based nanostructure after losing the rigid ZnO nanowire supports, which is evidenced by its flexibly bendable nature as shown in figure 2(b). The high magnification cross-section FE-SEM image (figure 2(b)) shows clearly the retained individual nanostructural units and vertically oriented arrays even after the template removal, suggesting that the acid etching process does not significantly affect the assembled polymer nanostructure. The low magnification cross-section FE-SEM image (figure 2(c)) further reveals that the nanoarrays are homogeneously distributed over a large area of a substrate. TEM images illustrate that individual units (figure 3(a)) are nanotube-structured and the thickness of the nanotube wall is uniform, further confirming that a coating of polymers is homogeneously LbL self-assembled on ZnO nanowires. EDX analysis (figure 3(b)) indicates that no Zn element is detected in the etched sample. The Fe, Co, and Ni elements must come from the stainless steel substrate and the Pt element is from the Pt coated on the sample for SEM imaging. The result shows that the ZnO nanowire array template has been completely removed.

In terms of their ionization property in aqueous solution, polyelectrolytes can be divided into strong and weak polyelectrolytes and they have distinct behaviors during the LbL self-assembly [54–57]. As well as using

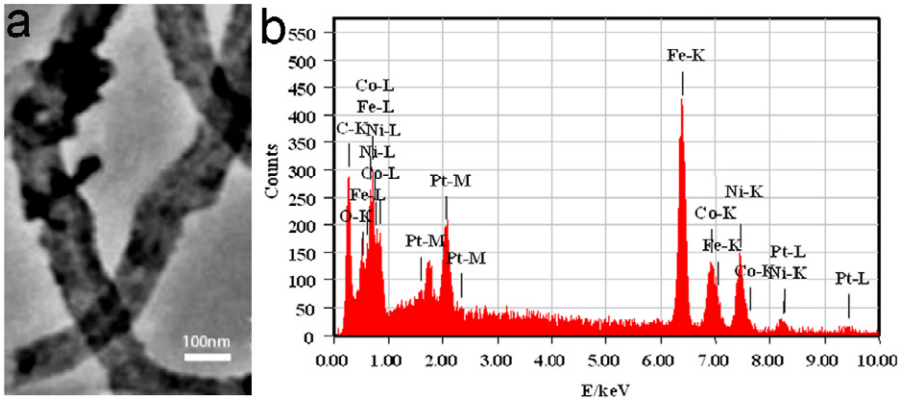


Figure 3. Typical TEM image of the individual nanostructure (a) and EDX spectrum of a selected area (b) of the fabricated PEI/PAA nanotube array.

weak polyelectrolyte pairs (PEI/PAA) as building blocks, we further used weak polyelectrolyte/strong polyelectrolyte (W/S) and strong polyelectrolyte/strong polyelectrolyte (S/S) pairs for LbL self-assembly to investigate whether W/S and S/S nanotube arrays could be fabricated. PDDA/PAA and PDDA/PSS were selected as model systems due to their broad applications in LbL self-assembly [55, 57, 58]. Both polyelectrolyte combinations were successfully assembled on ZnO nanowire arrays (data not shown). Like the PEI/PAA pair, one-dimensional nanostructured arrays were well retained after removal of the ZnO nanowire array template as shown in the top-view and cross-section FE-SEM images (figures 4(a), (b), 5(a) and (b)). It is noted that for both combinations, in particular for the S/S one, the interconnection of individual structural units is less than that of the PEI/PAA one, which is very likely to be caused by the stronger electrostatic interactions between ionic pairings and thinner polyelectrolyte films. Similarly, large-area vertically oriented nanostructure arrays for both combinations were obtained (figures S3 and S4 available at stacks.iop.org/Nano/24/045605/mmedia). The TEM images in figures 4(c) and 5(c) display the individual structural units of PDDA/PAA and PDDA/PSS polymeric nanostructure arrays, respectively. Hollow inner structures clearly illustrate the prominent nature of nanotube structures. No Zn element was also detected by EDX analysis for both polymeric nanotube arrays, revealing that the ZnO templates could be thoroughly removed from these two systems as well (figures S5 and S6 available at stacks.iop.org/Nano/24/045605/mmedia).

The stability of polymeric nanotube arrays is very important for their practical applications. All the fabricated nanotube arrays show no significant change in morphology after immersing in pH 3.2 aqueous solution, pH 10 aqueous solution, or PBS (pH 7.4, 10 mM, 137 mM NaCl) for at least one month, and even after ultrasonication for at least 3 min (data not shown), demonstrating their excellent stability. This stability further indicates the robustness of polyelectrolyte multilayers, not only composing the nanotubes but also attaching them to substrates.

To demonstrate the promising potential application of the polymer nanotube arrays, the PEI/PAA nanotube array

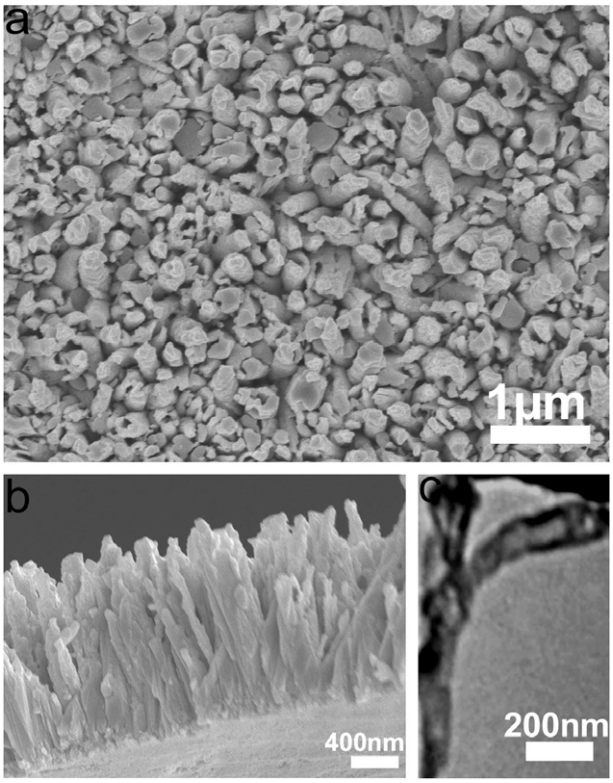


Figure 4. (a) Top-view FE-SEM image of the fabricated PDDA/PAA nanotube array, (b) cross-sectional FE-SEM image of the fabricated PDDA/PAA nanotube array, and (c) typical TEM image of the individual nanostructure of the PDDA/PAA nanotube array.

was tested for delivery of charged drugs, using MB and CG as model drugs [53, 59–61]. PEI/PAA multilayer films with the same layer number assembled on flat stainless steel substrate (denoted as multilayer-1) and on a ZnO nanowire array without removing the template (denoted as multilayer-2) were used as controls. The PEI/PAA nanotube array shows an interesting pH-responsive loading behavior. At a low environmental pH, it could load negatively charged CG. At pH 3.2 the loading capacity of the nanotube array is ∼0.31 μg mm^{-2}, which is ∼5.3 and ∼1.4 times that

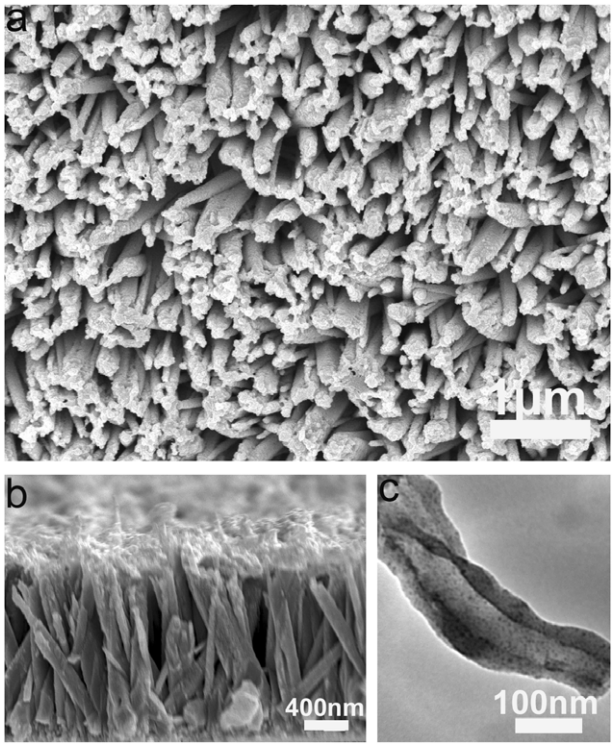


Figure 5. (a) Top-view FE-SEM image of the fabricated PDDA/PSS nanotube array, (b) cross-sectional FE-SEM image of the fabricated PDDA/PSS nanotube array, and (c) typical TEM image of the individual nanostructure of the PDDA/PSS nanotube array.

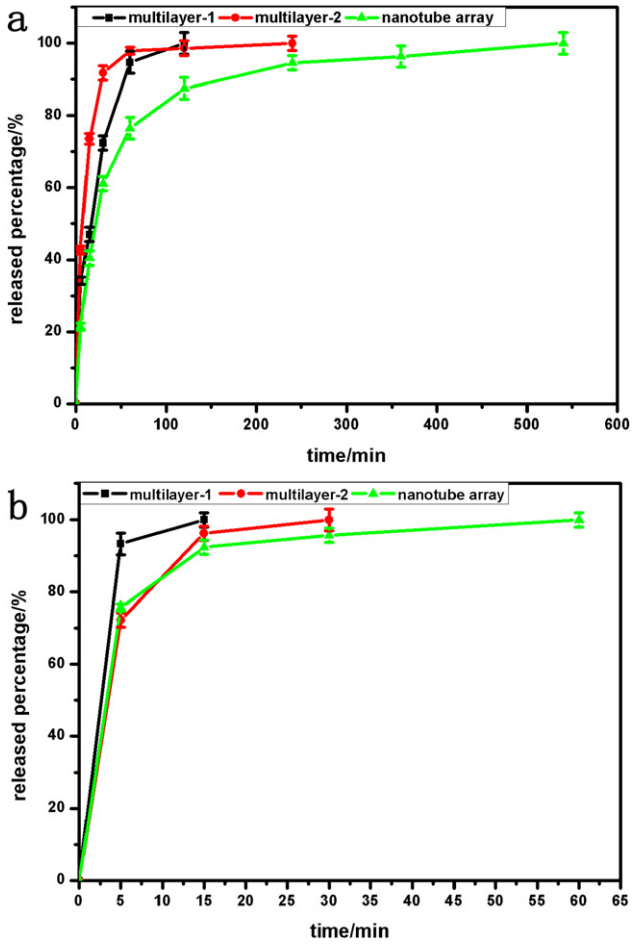


Figure 6. Release profiles of CG (a) and MB (b) from different samples, including multilayer film coated on flat substrates (multilayer-1), multilayer film coated on ZnO nanowire array without removing the template (multilayer-2), and polyelectrolyte nanotube array.

of multilayer-1 and multilayer-2, respectively. In contrast, at a high environmental pH the nanotube array could load positively charged MB. The loading capacity could reach $\sim$1.94 μg mm^{-2} at an environmental pH of 10.0. This loading capacity is $\sim$100 and $\sim$12 times more than that of multilayer-1 and multilayer-2, respectively. The result shows that no significant morphological changes of the multilayer film can be observed from either FE-SEM or TEM for the nanotube arrays after drug loading and release (data not shown), thus indicating its good stability. The excellent pH-responsive drug loading of the nanotube array could be ascribed to the synergistic effect of PEI and PAA, in which the charge density of PEI decreases and that of PAA increases with an increased environmental pH over a broad range [53, 62]. The greatly enhanced loading capacity is contributed from their ultrahigh surface area in comparison to that of the multilayered film assembled on flat substrates or on ZnO nanowire array. When the drug-loaded nanotube array was immersed in phosphate buffer saline solution (PBS) (pH 7.4, 10 mM, 137 mM NaCl), a physiological condition [47, 63], the model drugs were released with time. The time for the negatively charged CG release from the polyelectrolyte nanotube array could last for 540 min, which is significantly longer than those of multilayer-1 and multilayer-2 (figure 6(a)). Furthermore, the former released the drug more linearly than the latter ones (figure 6(a)). For MB, most of them were released in the first 5 min for all studied samples, possibly due to the weak electrostatic interaction between MB and the multilayer in PBS (figure 6(b)) [53, 59]. However, the release time of the nanotube array could last as long as 60 min, still significantly longer than those of multilayer-1 and multilayer-2 (figure 6(b)). The nanopores of the nanotube array structure and significantly increased diffusion length are very likely to be the main contributing factors to the sustained release for both CG and MB [64–66]. The excellent loading and release performance of the polyelectrolyte nanotube array in combination with implantability due to the substrate-attached large-area structure indeed demonstrate great potential to be used as an implantable device for localized drug delivery [19–23]. To further demonstrate the potential for this application, the zeta potential of the nanotube array was measured, showing a negative value of $\sim -$15 mV, which is favorable to reduce nonspecific adsorptions of proteins and cells for good biocompatibility [67, 68]. The cytotoxicity study of nanotube arrays with and without drug loaded is underway in our laboratory, and will be reported in due time.

4. Conclusions

ZnO nanowire array-templated LbL self-assembly has been developed to fabricate vertically oriented high-density and large-area robust polyelectrolyte nanotube arrays for the first time. The applications of polyelectrolyte nanotube arrays in delivery of charged drugs demonstrate that they not only possess pH-responsive loading property, but also significantly enhance loading capacity and sustained release time. This work demonstrates a universal approach to fabricate polymeric nanotube arrays with different kinds of polyelectrolyte combination including W/W, W/S and S/S on various substrates, thus providing great potential biomedical applications such as biosensor arrays, localized drug delivery, and bioreactor arrays. With the ability to precisely control film thickness via LbL self-assembly, the effects of wall thickness on the structure, morphology and drug loading capacity of nanotube arrays are being systematically investigated by changing layer number and assembly conditions such as pH and ionic strength, and promising preliminary results have been obtained. The work will be reported in the near future.

Acknowledgments

This work is jointly supported by the Institute for Clean Energy and Advanced Materials, Southwest University, Chongqing, China, the Chongqing Key Laboratory for Advanced Materials and Technologies of Clean Energies, China, and the Chongqing Science and Technology Commission (cstc2012gihz90002), China.

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