ChemComm

Cite this: Chem. Commun., 2011, 47, 10067-10069

www.rsc.org/chemcomm

COMMUNICATION

Redox-active π -conjugated polymer nanotubes with viologen for encapsulation and release of fluorescent dye in the nanospace[†]

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Received 28th June 2011, Accepted 20th July 2011 DOI: 10.1039/c1cc13853g

We report the encapsulation of negatively charged Au nanoparticles and anionic fluorescent (FL) dye in the inner cavity of redox-active cationic polymer nanotubes with viologen *via* electrostatic interaction and the release of the FL dye from the FL dye confined in the cavity of the polymer nanotubes by electrochemical and chemical reduction.

Nanotubes (NTs) and metal nanoparticles (NPs) represent a rapidly emerging field of significant fundamental and practical interest and are receiving worldwide attention.¹⁻³ It is advantageous or required to modify the nanotubes by physical or chemical methods to optimize their use in many applications. Recently, we reported new metal NP-polythiophene hybrid NTs from the electropolymerization of thiophene-modified metal NPs and the hybrid nanotube-catalyzed carbon-carbon bond forming reaction in the nanocavity.⁴ Conducting polythiophenes are indispensable materials for the development of displays, electronic and energy storage devices, actuators, sensors, and neural interfaces. The nanotubular structure of polythiophene is one of the ideal structures that can enhance the device performance by improving the charge-transport rate as well as increasing the surface area. The templatesynthesized conducting polymer NTs can have relatively large cavities and tunable interior chemical functionality.⁴ Especially, impregnation of the hollow NTs with guest materials provides a potentially fascinating route to create functional nanomaterials for a variety of applications. The development of a generalized method for the controlled encapsulation/ release of a molecule in the conducting polymer NTs remains an important and challenging issue.

We have performed the synthesis of new polythiophene (PT) NTs with redox-active viologen and the nanotube membranes, and the encapsulation or release of metal NPs or a guest molecule by the NTs (Chart 1 and Fig. 1). We have chosen the cationic viologen (N,N'-disubstituted-4,4'-bipyridinium salt: VL²⁺) group to achieve the assembly in nanopores *via electrostatic attraction* as a noncovalent approach.^{5–7}



Fig. 1 Fabrication of PT (polythiophene)-NTs and their composites: (a) bare alumina membrane (AM). (b) Modification of the nanopore of AM with PT-NTs generated by template-based electropolymerization of $1-VL^{2+}$ leads to $1-VL^{2+}$ -PT-NT-AM as a polymer nanotube membrane. The PT-NT-modified nanopore of AM: $1-VL^{2+}$ -PT-NT-AM. (c) SF⁻-AuNPs or Pyra encapsulated in the PT-NT-modified AM: SF⁻-AuNP@ $1-VL^{2+}$ -PT-NT-AM and Pyra@ $1-VL^{2+}$ -PT-NT-AM. (d) Release of Pyra from Pyra@ $1-VL^{2+}$ -PT-NT-AM by reduction.

The template-based electropolymerization of cationic viologen-linked terthiophene $(1-VL^{2+})$ in a nanoporous alumina membrane (AM) as a template gave the corresponding polythiophene NT-modified alumina membranes, which were converted into the redox-active cationic polythiophene NTs $(1-VL^{2+}-PT-NTs)$ upon dissolution of the alumina membranes by a sodium hydroxide solution (Chart 1 and Fig. 1).⁸ The redox-active cationic polythiophene NT-modified alumina membrane (denoted as 1-VL²⁺-PT-NT-AM) as a *polymer* nanotube membrane was utilized to incorporate the anionic fluorescent dye, pyranine (8-hydroxyl-1,3,6-pyrene-trisulfonate: Pyra), in which the Pyra was expelled from the Pyra confined within 1-VL²⁺-PT-NT-AM (denoted as Pyra@1-VL²⁺-PT-NT-AM) by electrochemical and chemical reductions of the viologen units in the cationic NTs (Fig. 1d and Scheme 1).⁹ There is currently considerable interest in using functional nanotube membranes in molecular storage and release, and sensing applications. This communication describes the encapsulation of ionic metal NPs or Pyra into the cavity of the redox-active π -nanotubes *via* electrostatic interaction, and the preliminary realization of the electron-supply induced the release of the Pyra from Pyra@1-VL²⁺-PT-NT-AM.



 $Chart\,1\,$ Structure of viologen-linked terthiophene $(1\text{-}VL^{2+})$ and protective ligand (SF^) for gold NPs.

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 $[\]dagger$ Electronic supplementary information (ESI) available: Synthesis of 1-VL^2+ and SF⁻-AuNPs, and the spectral and microscopic data. See DOI: 10.1039/c1cc13853g



Scheme 1 Proposed mechanism for the encapsulation and release of Pyra in $1-VL^{2+}$ -PT-NT-AM.

The electropolymerization was performed by attaching the alumina membrane (AM) (Whatman Anodisc; pore diameter of about 200-250 nm, thickness of 60 µm) to a Pt electrode, another Pt electrode was used as the counter electrode, and Ag/0.1 M AgNO₃ was used as the reference electrode. The electrolysis solution contains $1-VL^{2+}$ (5 mM) in 0.1 M Bu₄NClO₄-MeCN (1 mL). A voltage of +0.75 V (vs. Ag/ 0.1 M AgNO₃) was applied for 20 min. The 1-VL²⁺-PT-NTmodified nanopore of AM (1-VL²⁺-PT-NT-AM) was formed. After the electropolymerization, removal of the alumina membrane of 1-VL²⁺-PT-NT-AM with 1 M NaOH led to the release of 1-VL²⁺-PT-NTs. Scanning and transmission electron microscopies (SEM and TEM), and energy-dispersive X-ray (EDX) spectroscopy were used for the analysis of the NTs. Fig. 2a shows an SEM image of the 1-VL²⁺-PT-NTs. which were grown using the nanoporous alumina template; most of them have outer diameters of about 200-230 nm. The elemental composition of the 1-VL²⁺-PT-NTs was confirmed by an EDX analysis, which reveals the presence of C, O, and S (Fig. 2b). The redox behaviour of 1-VL²⁺-PT-NTs was studied by cyclic voltammetry (vide infra).

In order to confirm the electrostatic interaction between an anionic guest material and the inner surfaces of the cationic NTs, 4-(10-mercapto-decyloxy)-benzenesulfonic acid sodium salt (SF⁻: Chart 1) and the SF⁻-stabilized gold NPs (SF⁻-AuNPs) were prepared.⁸ We used the NT-modified alumina membrane for the encapsulation of the Au NPs or Pyra into the inner surfaces of the NTs because the outer surfaces of the NTs are in contact with the pore wall of the alumina membrane and thus masked.

The encapsulation of SF⁻-AuNPs (4.6 ± 0.5 nm, Fig. S1a and b: ESI†) into 1-VL²⁺-PT-NTs was conducted as follows (Fig. 3).⁸



Fig. 2 (a) SEM image and (b) EDX spectrum of $1-VL^{2+}$ -PT-NTs. Scale: 100 nm. (c) Cyclic voltammogram of $1-VL^{2+}$ -PT-NTs on a GC electrode in 0.1 M Bu₄NClO₄-MeCN; scan rate 100 mV⁻¹.



Fig. 3 Photographs of a solution of SF^-AuNPs in (a) the presence of bare AM, (b) the absence of bare AM, and (c) the presence of $1-VL^{2+}$ -PT-NT-AM. (a-0, b-0, c-0) before and (a-1, b-1, c-1) after overnight storage. (d) Each UV-vis spectrum (d-i, red line) corresponds to the photograph of c-0 and (d-ii, blue line) corresponds to the photograph of c-1.

The UV-vis spectra of SF⁻-AuNPs in H₂O showed a plasmon resonance at 533 nm in the absence and the presence of the bare alumina membrane (Fig. 3d-i). Interestingly, in contrast, in the presence of 1-VL²⁺-PT-NT-AM (Fig. 3d-ii), the absorption intensity decreased with the storage time, suggesting the continuing encapsulation of the Au NPs into the inner cavity of the 1-VL²⁺-PT-NT-AM. The colour of the solution turned from pink to colourless after overnight storage (Fig. 3c-0 and c-1). The immersion of the 1-VL²⁺-PT-NT-AM into a solution of SF⁻-AuNPs was done, and any Au NPs remaining in solution were removed by filtration and washed several times with water. After removal of the alumina membrane template by the 1 M NaOH solution, the Au NPs confined inside the NTs (denoted as SF⁻-AuNP@1-VL²⁺-PT-NTs) were obtained by filtration. The composite, SF--AuNP@1-VL2+-PT-NTs, contains Au and S, as evidenced by the EDX analysis (Fig. S1c, ESI[†]). Thus, the electrostatic interaction should be effective for fabricating a metal NP-PT-NT composite in the nanopore. Importantly, this approach based on the electrostatic interaction provides an efficient method to attach other nanostructures to functionalized polythiophene NTs and can be used as an illustrative detection of functional groups on the inner walls of polythiophene NTs.

We have succeeded in the encapsulation and release of an organic molecule, such as Pyra, using the redox-active $1-VL^{2+}$ -PT-NTs via an electron transfer process.^{7,9} We postulate that the positively charged inner surfaces of the 1-VL²⁺-PT-NTs strongly accelerate the encapsulation of the negatively charged Pyra via an electrostatic interaction. In contrast, such an interaction between Pyra and the viologen neutral form generated by the two-electron reduction of the viologen dication is unfavourable (Scheme 1); accordingly, the release of Pyra from the Pyra confined within the 1-VL²⁺-PT-NTs will be confirmed by the reduction (Fig. 1d). To prove this concept, the encapsulation of Pyra into the 1-VL²⁺-PT-NTs was examined. The UV-vis spectra of a Pyra solution in the absence or the presence of a bare alumina membrane in water showed the characteristic absorption due to the Pyra (Fig. 4a); while no absorption in the UV-vis region was observed in the presence of 1-VL²⁺-PT-NT-AM (Fig. 4b), indicating the formation of $Pyra@1-VL^{2+}$ -PT-NT-AM by the encapsulation of Pyra into the NTs. On the other hand, the cyclic voltammogram of the 1-VL²⁺-PT-NTs in



Fig. 4 Structure of Pyra. UV-vis spectra and photographs of a solution of Pyra (a) after overnight storage in the presence of bare AM and (b) after overnight storage in the presence of 1-VL²⁺-PT-NT-AM in water. The photograph of (a) shows a typical colour of Pyra in water.



Fig. 5 Photographs of a solution of (a-0) before electrochemical reduction of Pyra@1-VL²⁺-PT-NT-AM in water and (a-1) after electrochemical reduction of Pyra@1-VL2+-PT-NT-AM in water. The fluorescence of Pyra was monitored by irradiation at 365 nm UV light. (b) Photographs for monitoring reaction of $Pyra@1-VL^{2+}$ -PT-NT-AM with dithionite: (b-0) before addition, (b-1) after 120 s, and (b-2) after 180 s. The fluorescence of Pyra was monitored by irradiation at 365 nm UV light. The photographs of b-1 and b-2 showed the fluorescence of the released Pyra.

0.1 M Bu₄NClO₄-MeCN at a glassy carbon (GC) electrode exhibited two reversible redox peaks corresponding to the VL²⁺ dication–VL⁺ radical cation–VL neutral system at $E_{1/2}$ = -0.69 and -1.13 V (vs. Ag/0.1 M AgNO₃) (Fig. 2c). Thus, the electronic state of the 1-VL²⁺-PT-NTs can be electrochemically controlled. Consequently, at 1200 s, a potential of -1.25 V $(Ag/0.1 \text{ M AgNO}_3)$ was applied to the Pyra@1-VL²⁺-PT-NT-AM. At this potential the viologen is present in the neutral form by the reduction (Scheme 1), consequently, the Pyra would be released from Pyra@1-VL²⁺-PT-NT-AM. Actually, after the electrochemical reduction of the Pyra@1-VL²⁺-PT-NT-AM, the Pyra was released from the NT-alumina membrane as evidenced from the UV-vis spectra and the observed fluorescence due to the released Pyra (Fig. 5a-0 and a-1). Moreover, the injection of sodium dithionite $(Na_2S_2O_4)$ as a reductant into the Pyra@1-VL2+-PT-NT-AM induced the release of the Pyra;¹⁰ *i.e.*, the fluorescence of the released Pyra from $Pyra@1-VL^{2+}-PT-NT-AM$ was observed when a solution of sodium dithionite in water was injected into the Pyra@1-VL²⁺-PT-NT-AM using a syringe pump (Fig. 5b-0-b-2). It is noteworthy that the redox-active viologen-functionalized polythiophene NT membrane is very unique from the standpoint of electrochemical control of the reversible encapsulation/ release system. Further studies on this preliminary examination for the encapsulation and release of Pyra in the redox-active polythiophene NTs are now in progress.

In summary, we have shown that the nanopore functionalization by the electropolymerization of terthiophene with a positively charged pendant in the alumina membrane provides new functional polymer NTs and their polymer NT membranes. We have demonstrated the encapsulation and release of an anionic Pyra fluorescent dye in the redox-active cationic polymer NTs containing viologen via an electrostatic interaction. We believe that this approach will have broad implications in the reversible encapsulation/release of molecules using redox-active polymer NTs. We expect this research to yield a broad range of potential applications in catalysis, nanoelectrochemistry, molecular separation, drug delivery, controlled-release devices, and sensor developments.

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas (No. 21108522 and 23108723, "pi-Space") from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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- 8 See the ESI[†].
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