



**pH-Switchable Electroactive Composite Films of
Carboxylated Multi-walled Carbon Nanotubes and Prussian
Blue**

Journal:	<i>RSC Advances</i>
Manuscript ID	RA-ART-10-2015-021751.R1
Article Type:	Paper
Date Submitted by the Author:	20-Nov-2015
Complete List of Authors:	Tong, Ying; University of Science and Technology Beijing, Wang, Yuanyuan; University of Science and Technology Beijing, Gao, Bowen; University of Science and Technology Beijing, Su, Lei; University of Science and Technology Beijing, Research Center for Bioengineering and Sensing Technology, School of Chemistry and Biological Engineering Zhang, Xueji; University of Science & Technology Beijing, Research Center for Bioengineering and Sensing Technology
Subject area & keyword:	Films/membranes < Materials



Journal Name

ARTICLE

pH-Switchable Electroactive Composite Films of Carboxylated Multi-walled Carbon Nanotubes and Prussian Blue

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ying Tong, Yuanyuan Wang, Bowen Gao, Lei Su,* and Xueji Zhang,*

Here the combination of carboxylated multi-walled carbon nanotubes (CMWCNTs) and Prussian blue (PB) for fabricating pH-responsive electroactive composite thin films is reported. The as-prepared CMWCNT@PB composite films were found to change their electrochemical behaviors in response to the solution pH, including their cyclic voltammetric and the corresponding electrochromic behaviors. The electrochromic state of PB could be switched on and off by the solution pH. Furthermore, a linear relationship was found between the peak-to-peak potential separation of the cyclic voltammogram of PB and the solution pH, indicating that the composite film modified electrode might be useful for the development of novel pH sensors. The approach for the fabrication of pH-responsive electrochemical composite films demonstrated here should be generalizable to other redox nanomaterials.

1. Introduction

Stimuli-responsive materials, also known as “smart materials”, have attracted considerable research interest in recent years due to their enormous potential for many applications.¹ Stimuli-responsive materials have also provided an opportunity to the controllable alternation of electrochemical reactions by using external stimuli. For instance, functionalization of electrode surfaces with stimuli-responsive materials in the form of self-assembled monolayers or polymeric thin films² can produce switchable/tunable electrochemical properties controlled by external stimuli (e.g., heat, magnetic field, and pH). Many electrochemical reactions have been utilized in this way for developing novel electrochemical devices such as smart biosensors, switchable fuel cells and other novel electrochemical devices.^{1a, 1e, 2c-e, 3}

Prussian blue (PB) as the first known synthetic coordination polymers is a conventional pigment appearing in blue color and has been the subject of many applications including electrochemical sensors, ion batteries, and smart windows.⁴ Moreover, new and promising areas of application are still being explored.^{4d-4f, 5} However, so far there have been very few reports⁵ on controllable alternation of the electrochemical reactions of PB by using external stimuli.

On the other hand, carbon nanotubes (CNTs) are the typical one-dimensional nanocarbon materials that have had a profound impact on a wide range of applications. Recently, it has been known that the introduction of defects into CNTs or the doping of CNTs can be used to manipulate the electrical property of CNTs.⁷ The resultant CNTs (e.g., carboxylated CNTs) show the pH-sensitive electrical property,^{7a-7d, 8} making them promising candidates for use as pH-responsive materials. However, despite their attractive pH-sensitive electrical property, the CNTs have received only limited attention as a kind of pH-responsive material for the design of modified electrodes.

In the present study, we report for the first time the use of carboxylated multi-walled carbon nanotubes (CMWCNTs) for fabricating pH-responsive electrochemical CMWCNT@PB composite thin films. Layer-by-layer (LBL) assembly method is used to deposit CMWCNTs multilayers onto an indium tin oxide (ITO) substrate electrode, followed by chemical deposition of PB layer. The electrochemical behaviors of the as-prepared CMWCNT@PB composite film modified electrode in response to the solution pH, including their cyclic voltammetric and the corresponding electrochromic behaviors, are studied.

2. Experimental

2.1 Chemicals and materials

$K_3Fe(CN)_6$ was obtained from Sigma and used as received. Multi-walled CNTs (MWCNTs, 20-40 nm in diameter, 5-15 μm in length, purity > 97%) were purchased from Shenzhen Nanotech Port Co., Ltd. (China). All other chemicals of at least analytical reagent grade were obtained from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). The electrolyte solution was prepared by using Britton-Robinson buffer solutions. In brief, 25 mL of a 0.4 M solution of

Research Center for Bioengineering and Sensing Technology,
School of Chemistry and Biological Engineering,
University of Science and Technology Beijing,
Beijing 100083, China.
E-mail: sulej@ustb.edu.cn; zhangxueji@ustb.edu.cn

Electronic Supplementary Information (ESI) available: [Characterizations of the CMWCNTs multilayers and the CMWCNTs@PB composite film; Effect of pH on cyclic voltammetric curves of the PB modified electrode; Pictures of the electrochromic behaviors of the PB modified electrode; EIS of the PB modified electrode]. See DOI: 10.1039/x0xx00000x

H₃PO₄ and acetic acid were added to 75 mL of a mixture of KOH (1.0 M) and KCl (1.0 M). Buffer solutions of different pH were obtained by modifying the proportion between KOH and KCl.

2.2 Carboxylation of MWCNTs

MWCNTs were carboxylated using the well-known acid oxidation method.⁹ In brief, pristine nanotubes were firstly purified with 2 M nitric acid under stirring for 36 h. Then, the purified nanotubes were carboxylated using a mixture of concentrated H₂SO₄ and HNO₃ (v/v, 3:1) at 70°C for 4 h. Finally, the carboxylated MWCNTs were collected on a 220 nm pore filter membrane and washed up to neutral pH, followed by drying in vacuum at 60°C overnight.

2.3 Fabrication of films

Polycrystalline indium tin oxide (ITO) glass (Nippon Sheet Glass Co., Ltd., Japan) were cut into small pieces and then were treated with Piranha solution (7:3, vol/vol 96% H₂SO₄/30%H₂O₂) for 30 min. (CAUTION: piranha solutions are very aggressive, corrosive solutions, and appropriate safety precautions should be utilized including the use of acid resistant gloves and adequate shielding.) These treated ITO glasses were successively washed in acetone and deionized water under ultrasonication each for 10 min, and finally dried with nitrogen. Before use, the upper part of the ITO glass was covered with the double side tapes so that a square about 8 mm × 8 mm remained bare at the lower part of the ITO glass.

The CMWCNT multilayers films were fabricated by alternately immersing the cleaned ITO substrates into an aqueous solution of positively charged poly(diallyldimethylammonium chloride) (PDDA) (Mw 400,000 ~ 500,000, 1 wt%) containing 0.5 M NaCl and a dispersion of negatively charged CMWCNTs (1 mg mL⁻¹) for 20 min. After each immersing step the electrodes were carefully rinsed with deionized water to remove the excess of adsorption materials. The ITO covered with six or twelve bilayers of (PDDA/CMWCNTs) with PDDA as the outmost layer, *i.e.*, the CMWCNT modified ITO electrodes, were used for further PB deposition.

The CMWCNTs@PB modified electrodes were prepared by immersing the CMWCNT multilayers film modified electrodes into the freshly prepared mixture solution consisting of 10 mM FeCl₃·6H₂O, 10 mM K₃Fe(CN)₆ and 10 mM HCl for 20 min. Then, they were rinsed with 10 mM HCl and dried in an oven at 100°C for 2 h. For control experiments, a PB modified ITO electrode was prepared using a bare ITO electrode as the substrate according to this procedure. In addition, another PB modified ITO electrode was prepared according to a galvanostatic deposition procedure previously reported.¹⁰ In brief, a bare ITO electrode was immersed in a mixture solution consisting of 2 mM HCl, 2 mM K₃Fe(CN)₆ and 2 mM FeCl₃·6H₂O for galvanostatic deposition of PB by passing a current of 40 μA cm⁻² for 180 s. Then, they were rinsed with 10 mM HCl and dried in an oven at 100°C for 2 h.

2.4 Characterization of Films

For UV-vis absorption characterization, quartz slides were used instead of ITO substrates to fabricate the films. The layer deposition process was characterized by using UV-vis spectroscopy (SHIMADZU UV-1800, Japan). Surface morphology was characterized by using a field emission scanning electron microscopy (FE-SEM) (ZEISS Supra 55, German).

2.5 Measurements

Electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT302N, Metrohm, Switzerland) in an electrolytic cell with a three-electrode configuration. The modified electrodes were used as the working electrode, an Ag/AgCl (KCl-saturated) electrode as the reference electrode, and a platinum sheet as the counter electrode. Due to the well-known instable property of PB in neutral and alkaline solutions,^{4c} buffer solutions with pH values ranging from 2 to 6 were used in the electrochemical experiments. Before recording the voltammograms, all of the freshly prepared PB modified electrodes were cycled in 0.10 M KCl aqueous solution (pH 3.0) for 15 cycles around the PB↔ES redox system for obtaining a stable voltammogram of soluble PB, K⁺Fe³⁺Fe²⁺(CN)₆. During this process the insoluble PB, Fe₄³⁺[Fe²⁺(CN)₆]₃, formed *via* galvanostatic deposition can be converted to the soluble PB.^{5e} Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequencies range between 10⁴ and 0.1 Hz and 5 mV of signal amplitude, and the stabilization potential was set to 0.2 V vs Ag/AgCl. The electrochromic process of the CMWCNTs@PB composite film modified electrode at potentials ranging from + 0.60 to + 0.10 V vs Ag/AgCl at pH 2 and pH 6 were videotaped, respectively, using a digital camera.

3. Results and Discussion

Fig. 1a shows the fabrication process of the CMWCNT@PB composite film modified electrode. Negatively charged CMWCNTs were firstly assembled with a strong electrolyte, *i.e.*, positively charged poly(diallyldimethylammonium chloride) (PDDA), *via* the LBL self-assembly method. Then, a PB layer was deposited electrolessly on the CMWCNT multilayers to form the films of the

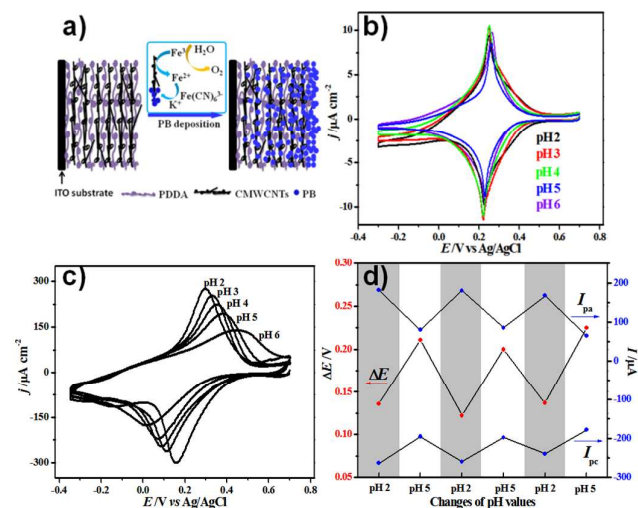


Fig. 1 a) Schematic illustration of the preparation of the CMWCNTs@PB composite films. The reactions in the light blue frame reveal *in situ* electroless deposition process of PB on a conductor surface. Reduction reaction of ferri ions is catalyzed by CMWCNTs and driven by the subsequent formation of PB according to previous studies.^{4a} b) Cyclic voltammograms of the PB modified ITO electrode at different pH values at a scan rate of 20 mV s⁻¹. c) Cyclic voltammograms of the CMWCNTs@PB composite film modified electrode with six bilayers at different pH values at a scan rate of 20 mV s⁻¹. d) Plots of the anodic and cathodic peak currents, *I*_{pa} and *I*_{pc}, and the Δ*E* of the CMWCNTs@PB composite film modified electrode versus the pH recycles.

CMWCNT@PB composite. The obtained CMWCNT multilayers films showed a light grey color (inset of Fig. S1a, item ii). Fig. S1a shows the UV-vis absorption spectra of the as-prepared CMWCNTs multilayers films. As revealed, the multilayers presented an absorption intensity at around 260 nm associated with the CMWCNTs. The absorption intensity increased with the increase of the number, n , of the bilayers, i.e., (CMWCNTs/PDDA) $_n$. The presence of a linear relationship between the absorption values and n , as shown in Fig. S1b, indicates that the assembly growth of the CMWCNTs layer was uniform spectroscopically.¹¹ SEM image shown in Fig. S1c indicates that the CMWCNT multilayers had the randomly assembled networks. After PB deposition, the obtained CMWCNT@PB composite films showed a blue color (inset of Fig. S2a, item ii). The composite films also presented a broad absorption centered at around 730 nm corresponding to the characteristic mixed-valence charge-transfer absorbance of the polymeric [Fe(II)-C-N-Fe(III)]_i,¹² as shown in Fig. S2a. Further SEM characterization (Fig. S2b) also indicated that the CMWCNT layers were covered by the PB layer. The apparent thickness of the deposited PB layer with six bilayers was estimated to be ~100 nm according to the electrogeneration electrical charge equation:

$$L = L_0 N_A Q / (4FA) \quad (1)$$

where Q represents the electrical charge, L_0 the unit cell length (~10 Å), N_A the Avogadro's number, F the Faraday's constant and A the electrode area.

It is well-known that electrochromic PB is mainly operated between its oxidized form (PB state) and its reduced form (Prussian White state, also called as Everitt's salt (ES)), which correspond to its blue and colorless states, respectively.¹³ In addition, such electrochemical and electrochromic properties of PB are pH-independent. These properties of PB can be reflected from Fig. 1b with the use of a bare ITO substrate electrode covered by electrolessly deposited PB with a thickness of ~3 nm. The deposited amount of PB on conductive glasses was usually very small, as reported previously.^{4b} So, the galvanostatic deposition was used to prepare another PB modified ITO electrode with more PB amount corresponding to ~100 nm thickness calculated according to equation 1 for electrochemical and electrochromic studies, as shown in Fig. S3 and S4. From Fig. 1b and Fig. S3, it can be seen that

the voltammetric behaviors of PB were essentially pH-insensitive, regardless of PB film thickness; from Fig. S4, the electrochromic behaviors of PB were also essentially pH-insensitive. For instance, at both pH 2 and pH 6, the potential cycling between +0.6 and +0.1 V vs Ag/AgCl could cause the common potential-dependent color changes between the blue color of the PB and the colorlessness of the ES.¹³ However, as shown in Fig. 1c, the CMWCNT@PB composite film modified electrode presented the pH-responsive cyclic voltammograms. As revealed, as the solution pH value increased, the electrochemical responses of the composite film modified electrode decreased, for instance, the values of the peak-to-peak potential separation, ΔE , and the half peak widths increased, and the peak current values decreased. These changes in the cyclic voltammograms are characteristic of the sluggish charge transfer kinetics, indicating that the increase of pH could induce the increase in the charge transfer resistance (vide infra). On the other hand, as the solution pH value decreased, the responses were restored, as shown in Fig. 1d. And as revealed, the changes in the I_{pa} , I_{pc} , and ΔE in response to pH were recyclable.

Meanwhile, it was found that the change of the solution pH could alter the electrochromic behavior of the CMWCNT@PB composite film modified electrode. Fig. 2 shows the pictures of the electrolytic cell taken at different potentials applied to the composite film modified electrode. As revealed from Fig. 2a, b, at pH 2, under the potential cycling from +0.6 to +0.1 V vs Ag/AgCl, the composite film modified electrode exhibited the common potential-dependent color changes between the blue color of the PB and the colorlessness of the ES.¹³ Note: the light grey was the color of the CMWCNT multilayers-coated ITO glass. However, at higher pH, the electrochromics of the composite film modified electrode was turned off. As revealed from Fig. 2c, d, at pH 6, under the same potential cycling conditions, the composite film modified electrode remained the blue color regardless of the changes in the external applied voltages.

Electrochemical impedance spectroscopy (EIS) is a very useful tool in the study of charge transport processes in a film-modified electrode where the electroactive species is assumed to be fixed at the surface of the electrode.¹⁴ So EIS was performed to study the electrochemical behaviors of the CMWCNT@PB composite film modified electrode with six bilayers in response to pH. As shown in Fig. 3, at pH 2, the composite film modified electrode exhibited a small semicircle at high frequencies with a vertical branch at low frequencies in the complex impedance plane. The semicircle

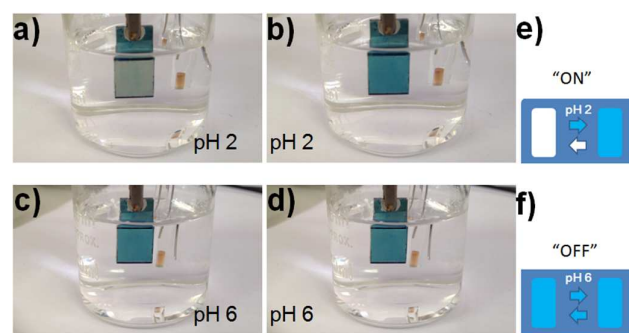


Fig. 2 Screen pictures captured from the videotapes of the CMWCNTs@PB composite film modified ITO electrode undergoing cyclic potential sweeps between 0.6 and 0.1 V vs Ag/AgCl at a scan rate of 20 mV s⁻¹. a) pH 2, 0.1 V; b) pH 2, 0.6 V; c) pH 6, 0.1 V; d) pH 6, 0.6 V. The videotapes are provided in the Supporting Information. e and f) Schematic illustration of the pH-switchable electrochromic behaviors of the composite films between the "ON" and "OFF" states, respectively.

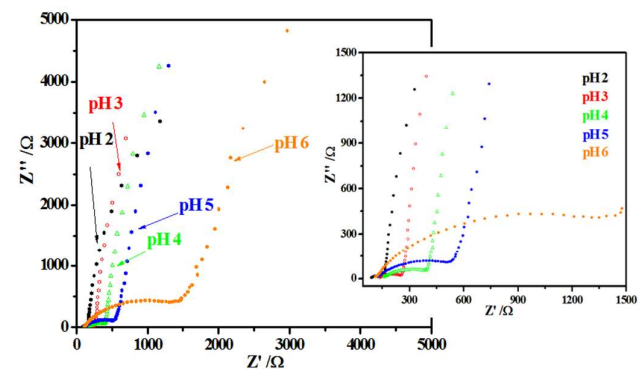
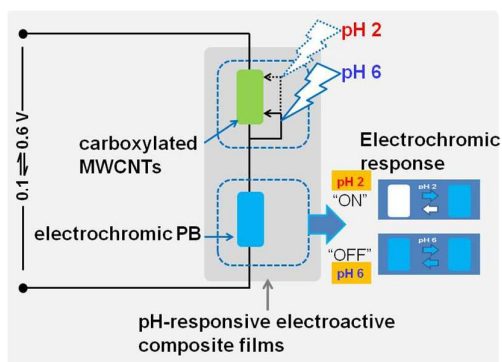


Fig. 3 Electrochemical impedance spectra of the CMWCNTs@PB composite film modified electrode at different pH. Inset shows the enlarged image for the high frequency region.



Scheme 1. Schematic illustration of the pH-induced electrochemical responses of CMWCNT@PB composite films.

corresponds to the charge transfer resistance, R_{ct} , at the CMWCNT|PB interface. With increasing pH, the semicircle became remarkably larger, indicating the increase in the charge transfer resistance at the CMWCNT|PB interface. For instance, at pH 6, the increase in the right intercept of the semicircle with the Z' axis was more than 1 k Ω , indicating remarkably sluggish electron transfer kinetics at the CMWCNT|PB interface, in accordance with the obtained voltammetric results (see Fig. 1c). In comparison, Fig. S5 shows the EIS of the PB modified ITO electrode. It can be seen that in the absence of CMWCNT the charge transfer resistance of PB was small, not more than 200 Ω . These results clearly indicate that the pH increase resulted in the increase in the charge transfer resistance at the CMWCNT|PB interface. It has been known that the carboxylation of CNTs can introduce the saturated sp³ carbon centers which act as scattering sites to alter the electronic and transport properties of the nanotubes and that the scattering strength of the sp³ carbon centers is associated with the local charge density. At pH 2, the carboxyl groups are protonated, resulting in a low local charge density and thus low scattering effect; At higher pH, the carboxyl groups dissociate, resulting an increasing local charge density and thus increasing scattering effect.¹⁵ It has also been reported that the conductance of carboxylated CNTs decreases exponentially with the increase of pH due to the hole doping/undoping effects.^{7a, 7d} Therefore, it is reasonable that the changes in the solution pH affected the protonation/deprotonation of the CMWCNTs layer, resulting in the changes in the charge transfer resistance at the CMWCNTs | PB interface, as schematically illustrated in Scheme 1.

In addition, the electrochemical behaviors of the composite film modified electrode in response to the solution pH were found to be sensitive to the bilayer number of the CMWCNTs multilayers. As shown in Fig. 4a, the CMWCNT@PB composite film modified electrode with twelve bilayers showed similar pH-responsive behaviors. However, in comparison with the composite film modified electrode with six bilayers (see Fig. 1c), the changes in the voltammetric behaviors of the composite film modified electrode with twelve bilayers in response to the solution pH were more remarkable. For instance, at pH 6, both the oxidative and reduction peaks of the PB at the latter were totally suppressed, clearly indicating the dramatic effect of pH on the electrochemical responses of the composite film modified electrode. Interestingly, it was also found that there was a linear relationship between the ΔE and the solution pH at the CMWCNT@PB composite film modified electrode. Fig. 4b shows the plots of the ΔE of the composite film modified electrodes with six and twelve bilayers, respectively,

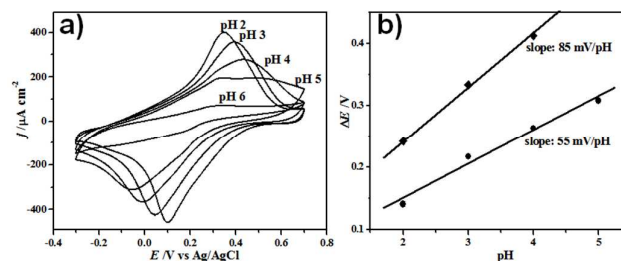


Fig. 4 Cyclic voltammetric curves of the CMWCNTs@PB composite film modified electrode with twelve bilayers at different pH values at a scan rate of 20 mV s⁻¹. b) Plots of the ΔE of the CMWCNTs@PB composite film modified electrode with six (\blacklozenge , $R^2=0.97$) and twelve bilayers (\bullet , $R^2=0.99$) versus pH.

against the solution pH. The response slopes were 55 and 85 mV pH⁻¹, respectively. At present, the exact mechanism of the presence of the linearity between the ΔE and the solution pH is still unknown. However, such a linear relationship indicates that the composite film modified electrode might be useful for the development of novel pH sensors.

4. Conclusions

In conclusion, we have demonstrated the pH-responsive voltammetric and electrochromic behaviors of the composite films fabricated via combining the CMWCNTs and PB. The electrochromic state of PB could be switched on and off by the solution pH. Meanwhile, a linear relationship was found between the ΔE of the cyclic voltammogram of PB and the solution pH, indicating that the composite film modified electrode might be useful for the development of novel pH sensors. On the other hand, although the potential application of the composite films could be limited by the instability of PB in nonacidic solutions at present, various methods for improvement of the stability of PB in nonacidic solutions are being developed worldwide, which will broaden the potential application of the composite films. In addition, the approach for the fabrication of pH-responsive electrochemical composite films demonstrated here should be generalizable to other redox nanomaterials.

Acknowledgements

The support from the National Natural Science Foundation of China (Grant No. 21175010, 21545012 and 21275017), the Project-sponsored by SRF for ROCS, SEM, and the grant from Beijing Municipal Science and Technology Commission (z131102002813058) is highly appreciated.

Notes and references

- a) E. Katz, S. Minko, J. Halamek, K. MacVittie, K. Yancey, *Anal. Bioanal. Chem.* 2013, **405**, 3659-3672; b) Q. M. Zhang, D. Berg, S. M. Mugo, M. J. Serpe, *Chem. Commun.* 2015, **51**, 9726-9728; c) J. Chen, P. Xiao, J. C. Gu, D. Han, J. W. Zhang, A. H. Sun, W. Q. Wang, T. Chen, *Chem. Commun.* 2014, **50**, 1212-1214; d) X. Chen, L. Mahadevan, A. Driks, O. Sahin, *Nat. Nanotechnol.* 2014, **9**, 137-141; e) K. Aran, J. Parades, M. Rafi, J. F. Yau, A. P. Acharya, M. Zibinsky, D. Liepmann, N. Murthy, *Adv. Mater.* 2015, **27**, 1433-1436.

- 2 a) P. K. Deshmukh, K. P. Ramani, S. S. Singh, A. R. Tekade, V. K. Chatap, G. B. Patil, S. B. Bari, *J. Control. Release* 2013, *166*, 294-306; b) A. Zhuk, S. A. Sukhishvili, *Soft Matter* 2013, *9*, 5149-5154; c) X. Zhao, Y. Liu, J. Lu, J. H. Zhou, J. H. Li, *Chem. - Eur. J.* 2012, *18*, 3687-3694; d) T. K. Tam, M. Pita, M. Motornov, I. Tokarev, S. Minko, E. Katz, *Adv. Mater.* 2010, *22*, 1863-1866; e) T. K. Tam, M. Ornatska, M. Pita, S. Minko, E. Katz, *J. Phys. Chem. C* 2008, *112*, 8438-8445.
- 3 a) O. Parlak, A. P. F. Turner, A. Tiwari, *Adv. Mater.* 2014, *26*, 482-486; b) Z. Y. Jin, G. Guven, V. Bocharova, J. Halamek, I. Tokarev, S. Minko, A. Melman, D. Mandler, E. Katz, *ACS Appl. Mater. Interfaces* 2012, *4*, 466-475; c) Y. B. Dou, T. Pan, A. W. Zhou, S. M. Xu, X. X. Liu, J. B. Han, M. Wei, D. G. Evans, X. Duan, *Chem. Commun.* 2013, *49*, 8462-8464; d) L. Peng, A. C. Feng, M. Huo, J. Y. Yuan, *Chem. Commun.* 2014, *50*, 13005-13014; e) P. B. Wan, X. D. Chen, *ChemElectroChem.* 2014, *1*, 1602-1612.
- 4 a) J. D. Qiu, H. Z. Peng, R. P. Liang, J. Li, X. H. Xia, *Langmuir* 2007, *23*, 2133-2137; b) K. Itaya, T. Ataka, S. Toshima, *J. Am. Chem. Soc.* 1982, *104*, 4767-4772; c) F. Ricci, G. Palleschi, *Biosens. Bioelectron.* 2005, *21*, 389-407; d) B. Kong, C. Selomulya, G. Zheng, D. Zhao, *Chem. Soc. Rev.* 2015, *44*, 7997-8018; e) P. Yu, X. L. He, L. Q. Mao, *Chem. Soc. Rev.* 2015, *44*, 5959-5968; f) H. Sun, H. B. Sun, W. Wang, H. D. Jiao, S. Q. Jiao, *RSC Adv.* 2014, *4*, 42991-42995.
- 5 a) X. Cai, W. Gao, M. Ma, M. Wu, L. Zhang, Y. Zheng, H. Chen, J. Shi, *Adv. Mater.* 2015, DOI: 10.1002/adma.201503381; b) L. Zhang, H. B. Wu, S. Madhavi, H. H. Hng, X. W. Lou, *J. Am. Chem. Soc.* 2012, *134*, 17388-17391; c) B. Kong, J. Tang, Z. X. Wu, J. Wei, H. Wu, Y. C. Wang, G. F. Zheng, D. Y. Zhao, *Angew. Chem. Int. Edit* 2014, *53*, 2888-2892; d) Z. Q. Li, B. Li, L. W. Yin, Y. X. Qi, *ACS Appl. Mater. Interfaces* 2014, *6*, 8098-8107; e) Z. W. Wang, H. K. Yang, B. W. Gao, Y. Tong, X. J. Zhang, L. Su, *Analyst* 2014, *139*, 1127-1133; f) N. A. Sitnikova, M. A. Komkova, I. V. Khomyakova, E. E. Karyakina, A. A. Karyakin, *Anal. Chem.* 2014, *86*, 4131-4134; g) E. Nossol, A. J. G. Zarbin, *Sol. Energ. Mat. Sol. C* 2013, *109*, 40-46; h) D. Z. Yang, L. H. Han, Y. Yang, L. B. Zhao, C. Zong, Y. F. Huang, D. P. Zhan, Z. Q. Tian, *Angew. Chem. Int. Edit.* 2011, *123*, 8838-8841.
- 6 D. J. Schmidt, F. C. Cebeci, Z. I. Kalcioğlu, S. G. Wyman, C. Ortiz, K. J. V. Vliet, P. T. Hammond, *ACS Nano* 2009, *3*, 2207-2216.
- 7 a) D. Lee, T. Cui, *J. Vac. Sci. Technol., B* 2009, *27*, 842-848; b) D. J. Lee, T. H. Cui, *Biosens. Bioelectron.* 2010, *25*, 2259-2264; c) D. Lee, T. Cui, *Langmuir* 2011, *27*, 3348-3354; d) L. Ren, D. Yan, W. W. Zhong, *Carbon* 2012, *50*, 1303-1310; e) X. J. Zheng, J. Deng, N. Wang, D. H. Deng, W. H. Zhang, X. H. Bao, C. Li, *Angew. Chem. Inter. Edit.* 2014, *53*, 7023-7027.
- 8 J. H. Cheon, J. Lim, S. M. Seo, J. M. Woo, S. H. Kim, Y. Kwon, J. W. Ko, T. J. Kang, Y. H. Kim, Y. J. Park, *IEEE Trans. Electron Devices* 2010, *57*, 2684-2689.
- 9 X. C. Zhao, R. T. Liu, Z. X. Chi, Y. Teng, P. F. Qin, *J. Phys. Chem. B* 2010, *114*, 5625-5631.
- 10 J. J. Garcia-Jareno, D. Benito, J. Navarro-Laboulais, F. Vicente, *J. Chem. Educ.* 1998, *75*, 881.
- 11 M. N. Zhang, L. Su, L. Q. Mao, *Carbon* 2006, *44*, 276-283.
- 12 J. F. Zhai, Y. M. Zhai, L. Wang, S. J. Dong, *Inorg. Chem.* 2008, *47*, 7071-7073.
- 13 D. J. Yang, C. Y. Hsu, C. L. Lin, P. Y. Chen, C. W. Hu, R. Vittal, K. C. Ho, *Solar Energy Mater. Solar Cells* 2012, *99*, 129-134.
- 14 a) J. J. Garcia-Jareno, J. J. Navarro, A. F. Roig, H. Scholl, F. Vicente, *Electrochim. Acta* 1995, *40*, 1113-1119; b) B. W. Gao, L. Su, Y. Tong, M. Guan, X. J. Zhang, *J. Phys. Chem. B* 2014, *118*, 12781-12787.
- 15 a) M. Bockrath, W. Liang, D. Bozovic, J. H. Hafner, C. M. Lieber, M. Tinkham, H. Park, *Science* 2001, *291*, 283-285; b) H. Park, J. J. Zhao, J. P. Lu, *Nano Lett.* 2006, *6*, 916-919.