Photochemistry

DOI: 10.1002/anie.201302062

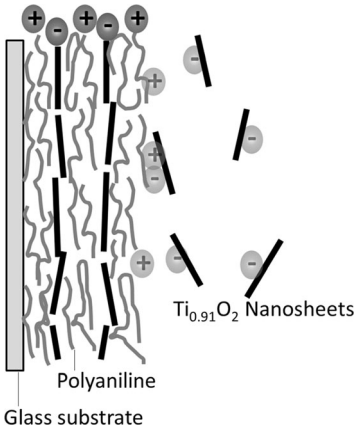
An n-Type to p-Type Switchable Photoelectrode Assembled from Alternating Exfoliated Titania Nanosheets and Polyaniline Layers

*Brian Seger, Jonathan McCray, Aniruddh Mukherji, Xu Zong, Zheng Xing, and Lianzhou Wang**

Polyaniline is a quite complex molecule because of the various redox states the polymer can be in, and the corresponding conductivity changes that accompany these states. However, by understanding this material, one can take advantage of the complexities of this molecule for applications in fields such as supercapacitors, sensors, diodes, and many others.[1] The most widely investigated and probably the most commercially applicable redox state of polyaniline is the emeraldine form. The emeraldine state consists of a polymer with 50% of the nitrogen reduced and another 50% oxidized and protonated.[1] When the emeraldine salt is in an acidic solution, the reduced nitrogen can be protonated and oxidized. The protonation of the polymer partially depopulates the π electrons with the end result being a highly conjugated system, which entails the polymer is highly conductive and potentially more stable because of its multiple resonance structures.[2] Thus the conductivity of polyaniline is both a function of the redox state and the pH value. It should be noted that both the fully reduced state (pernigraniline) and the fully oxidized state (leucoemeraldine) have shown to be insulators irrespective of the pH value.

Another interesting property of polyaniline is its ability to act as a semiconductor. When it is in the doped emeraldine state, polyaniline acts as a p-type semiconductor, while in its pernigraniline structure, it is an n-type semiconductor.[3] In this work we take advantage of the layer-by-layer (LBL) multilayer film assembly technique of exfoliated two-dimensional titania ($Ti_{0.91}O_2$) nanosheets[4] to show that a new type of alternating PANI-$Ti_{0.91}O_2$ multilayer thin films can be assembled successfully (Scheme 1). While a number of polyelectrolytes and inorganic nano-objects have been used for LBL film growth of titania nanosheets,[4–6] to our knowledge this is the first example of a conductive polymer being used. Interestingly, the resultant thin films can act as either an n-type or p-type photoelectrode depending on the electrolyte conditions.

The preparation procedure of exfoliated $Ti_{0.91}O_2$ nanosheets was conducted according to a modified reported method (Figure S1a).[7] An aqueous polyaniline (PANI) solution of 2 mg mL^{-1} at pH 3 solution was made using a method developed by Cheung et al.[8] A more detailed experimental procedure is given in the Supporting Information. While the point of zero charge of PANI is at pH 4, it is stable at pH 3 having a positive charge under this condition.[9] This allows for the PANI to be LBL deposited with a negative counterion.[8]



Scheme 1. Layer-by-layer deposition of a polyaniline-titania composite.

Multilayer film growth of alternating PANI-$Ti_{0.91}O_2$ layers on quartz glass substrates was accomplished using an established LBL technique.[6] This deposition was based on an electrostatic driving force of PANI being positively charged ($\zeta \approx +20$ mV at pH 3[9]) and $Ti_{0.91}O_2$ being negatively charged ($\zeta = -39$ mV at pH 8;[10] Scheme 1). UV/Vis spectra taken from a PANI-$Ti_{0.91}O_2$ electrode with various layers are shown in Figure 1. The 1st layer to be deposited on the substrate was PANI, which can be seen spectroscopically by its broad absorption peak at 630 nm indicative of the emeraldine base form of polyaniline[11] as well as another peak at 310 nm. The 2nd layer deposited was $Ti_{0.91}O_2$, and the only change in the spectra is an added absorption of 265 nm, which is characteristic of exfoliated $Ti_{0.91}O_2$ nanosheets,[12] indicating the deposition of negatively charged nanosheets on the PANI bottom layer. The unchanged PANI peaks after $Ti_{0.91}O_2$ deposition indicates that the nanosheets do not appear to have an effect on the intrinsic redox state of the PANI. An AFM image verifies the deposition of $Ti_{0.91}O_2$ nanosheets on substrate using PANI as binder (Figure S1b).

Figure 1a presents the LBL growth of alternating PANI-$Ti_{0.91}O_2$ layers measured after each deposition layer. The inset in Figure 1 monitors the absorption at the three peaks (265, 310, and 630 nm) and shows that they increase at a steady rate. The nearly linear increase in absorbance after eight LBL cycles verifies the successful growth of multilayer thin films.

[*] B. Seger, J. McCray, A. Mukherji, X. Zong, Z. Xing, L. Wang
ARC Centre of Excellence for Functional Nanomaterials
School of Chemical Engineering and AIBN
University of Queensland
St Lucia, 4072, Queensland (Australia)
E-mail: l.wang@uq.edu.au

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201302062.

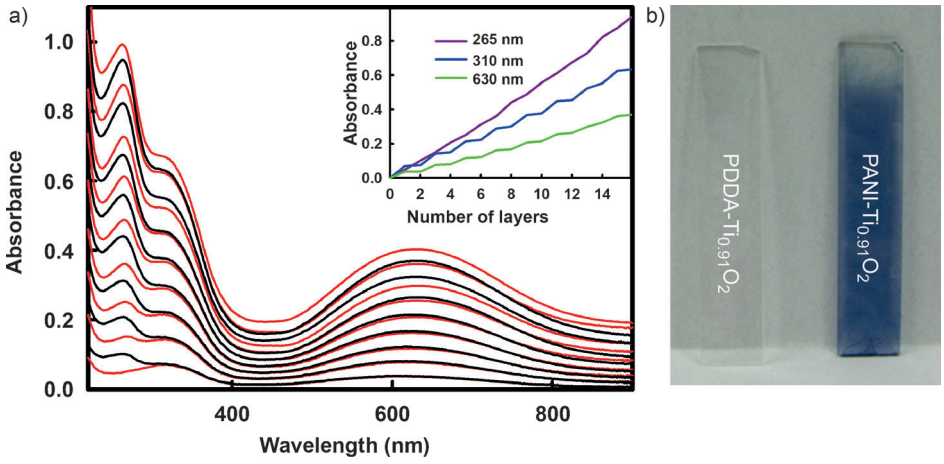


Figure 1. a) UV/Vis absorption spectra of multilayer films of PANI-$Ti_{0.91}O_2$ prepared on quartz glass substrates. The insets of (a) shows the absorbance of a particular wavelength as a function of the number of single layers deposited. b) Quartz substrates deposited with eight layers of (PPDA-$Ti_{0.91}O_2$) and (PANI-$Ti_{0.91}O_2$), respectively.

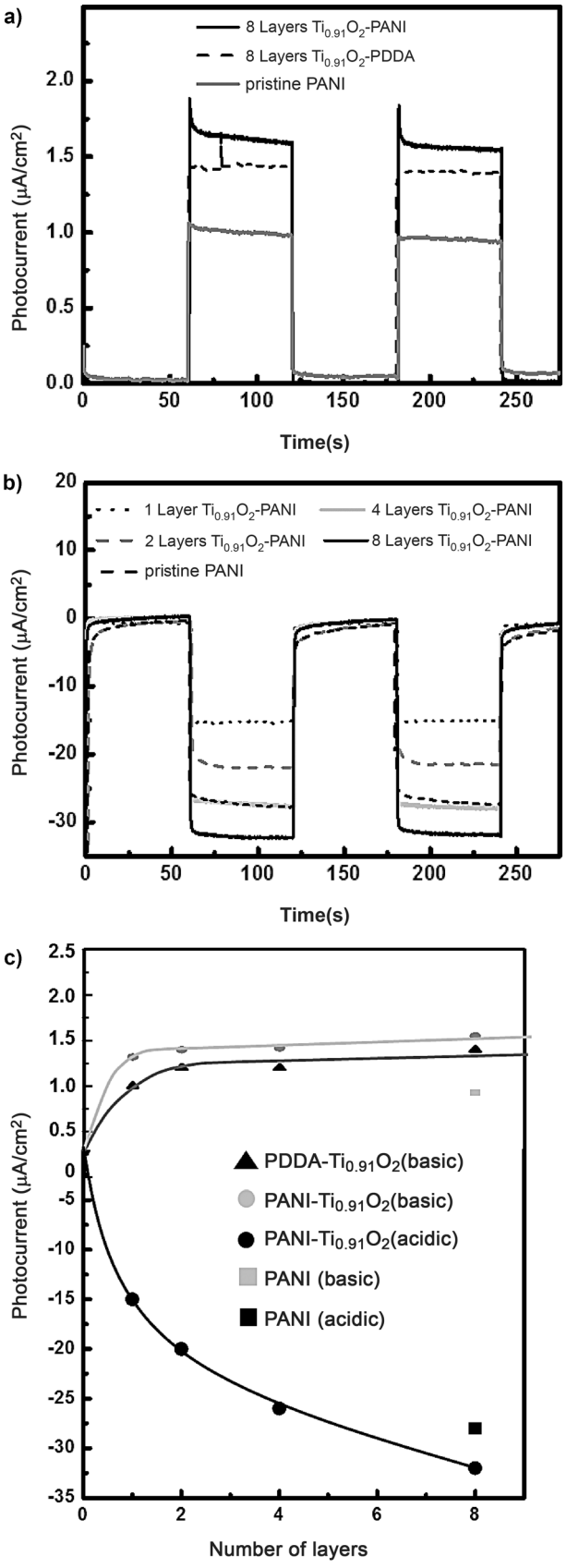
For comparison, insulating polyelectrolyte poly(diallyldimethylammonium chloride) (PDDA) was also used to assemble $Ti_{0.91}O_2$ nanosheets. The UV/Vis spectra of the PDDA-$Ti_{0.91}O_2$ thin films are shown in Figure S2. Figure 1 b displays an image of the two types of thin films deposited on quartz glasses. The most obvious feature is the deep blue color that the PANI-$Ti_{0.91}O_2$ sample possesses compared to the colorless film of PDDA-$Ti_{0.91}O_2$. The sandwich-like lamellar structure of the films is further elucidated in the Supporting Information by XRD (Figure S3). In fabricating the PDDA-$Ti_{0.91}O_2$ and PANI-$Ti_{0.91}O_2$ multilayer thin films, it was found that the nanosheets absorb better on PDDA than PANI. The possible reason for such difference is that PDDA is hydrophilic and has a charge independent of pH,[13] while PANI is hydrophobic and its charge is very sensitive to pH conditions.[1] XPS analysis on the PANI-$Ti_{0.91}O_2$ multilayer film revealed the ratio of PANI to $Ti_{0.91}O_2$ is roughly 3.2 (Figure S4), suggesting PANI is quite effective in adsorbing nanosheets from solution.

For photoelectrochemical testing, LBL deposition of PDDA-$Ti_{0.91}O_2$ and PANI-$Ti_{0.91}O_2$ multilayer films were deposited on conductive fluorine-doped tin oxide (FTO) substrates. For better comparison under nearly the same conditions, the substrates were simply deposited in $Ti_{0.91}O_2$ nanosheet solution for a shorter time after a PDDA deposition compared to a PANI deposition. This allowed the absorbance at 265 nm to be nearly the same for both PDDA-$Ti_{0.91}O_2$ and PANI-$Ti_{0.91}O_2$ at a given number of $Ti_{0.91}O_2$ layers. The electrodes were initially placed in an aqueous 1 M NaOH, 1 M methanol solution and held at −0.2 V vs. Ag/AgCl. The potential of −0.2 V vs. Ag/AgCl was used because of the clear redox state of PANI at this potential as well as its known stability.[2] The samples were photoirradiated with 100 mW cm^{-2} from a xenon lamp (Oriel-Newport, MA) at 60 s intervals and the photocurrent was measured. Figure 2 a shows the photocurrent of the electrodes with eight bilayers of polymer and $Ti_{0.91}O_2$. For comparison, Figure 2 a also shows the photocurrent of a drop-cast pristine PANI thin film with the same PANI absorbance as the PANI-$Ti_{0.91}O_2$ sample. (Figure S5 shows a cyclic voltammogram of the PANI and PANI-$Ti_{0.91}O_2$ samples.)

The photoelectrochemical experiments employed 1 M methanol as a hole scavenger and 1 M NaOH as the electrolyte (Figure 2 a). NaOH acts as a base, thus preventing any of the imine nitrogen of PANI from being protonated. This entails that in the aniline monomer unit the nitrogen atom forms a double bond with a carbon, thus preventing the continuous conjugation of the benzene rings. Without the conjugation, polyaniline becomes an electrical insulator. This electronic structure has also been shown to result in polyaniline acting as an n-type semiconductor.[14] Thus, in this case, both PANI and $Ti_{0.91}O_2$ act as n-type semiconductors, which means that both should produce an anodic photocurrent. $Ti_{0.91}O_2$ is also affected by NaOH, which varies the conduction band through the well-established ratio of 59 mV per pH.[15] The variation in the conduction band allows for an increased potential of the $Ti_{0.91}O_2$ conduction band electrons to transfer to the electrode. However the current redox state of PANI is insulating and its LUMO is higher than that of $Ti_{0.91}O_2$.[16] This indicates that any photogenerated $Ti_{0.91}O_2$ electrons would probably have to tunnel through the PANI, resulting in a decreased photocurrent.

Figure 2 a shows that the PANI-$Ti_{0.91}O_2$ films provides the best result with 1.5 μA cm^{-2}, but PDDA-$Ti_{0.91}O_2$ produces very similar results with 1.35 μA cm^{-2}. The pure PANI film produces notably less current at 0.9 μA cm^{-2}. The slight better performance of the PANI-$Ti_{0.91}O_2$ over the PDDA-$Ti_{0.91}O_2$ electrodes can most likely be attributed to the extra light absorbance attained by PANI since its absorption peak is at 310 nm, compared to the 265 nm for $Ti_{0.91}O_2$. PDDA is nonconductive, and it was found that removing this layer by thermal treatment significantly enhanced the photocurrents by more than an order of magnitude (Figure S6). Thus, while it is clear that these structures produce an anodic photocurrent, the values are quite low. By using Figure 1 a as a guide, a single layer of PANI-$Ti_{0.91}O_2$ should absorb about 20% (Abs = 0.1) of incoming photons while eight layers should absorb about 89% (Abs = 0.95) of all incoming photons at 265 nm. When going from one to eight layers, the absorbed photons increased by 400%, but Figure 2 c shows that the photocurrent increases only by 15%. This clearly shows that photons being absorbed further from the electrode are not able to reach the electrode and produce current. This reinforces the electrical insulating effect of PANI.

In Figure 2 b and 2 c the same electrodes were used at −0.2 V vs. Ag/AgCl, but the solution was switched to a 1 M HCl and 0.1 M $NaNO_3$ solution. The change to an acidic



solution transforms PANI from an n-type material to a p-type material. For this reason an electron scavenger was needed instead of a hole scavenger, thus the change from methanol to $NaNO_3$. (Preliminary results using methanol with HCl showed no photocurrent.) Figure 2b shows cathodic photocurrent for samples with a varying number of layers of PANI-$Ti_{0.91}O_2$. In comparison to the results in the basic solution, Figure 2b shows that the photocurrent in an acidic solution is drastically increased by more than an order of magnitude. Figure 2c shows that the increase in the number of layers also vastly increases the photocurrent in acidic solution, while having an negligible effect in basic solution. Note that in the acidic solution an approximately 400% increase in light absorption between one and eight layers only results in a 120% increase in photocurrent. This denotes that there are still some losses attributed to having to traverse through the multiple layers.

The slight photocurrent increase in the PANI-$Ti_{0.91}O_2$ system compared to pure PANI may be because of the presence of $Ti_{0.91}O_2$ helping the PANI to form more uniform layers compared to the drop-cast prepared PANI. Since $Ti_{0.91}O_2$ is an n-type semiconductor, preliminary tests verified a PDDA-$Ti_{0.91}O_2$ film that is ineffective in the presence of an electron scavenger.

Figure 3 further explains the photocurrent difference of PANI-$Ti_{0.91}O_2$ samples between acidic and basic conditions. (The basis/reference for setting the potential levels is given in the Supporting Information.) By looking at the chemical

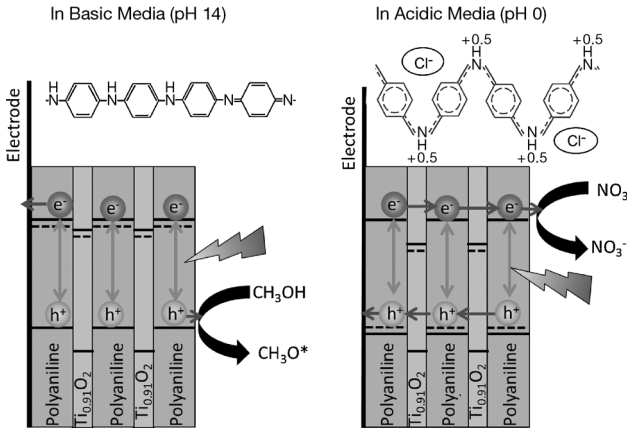


Figure 3. Structures of PANI molecules and the possible electron transfer pathways in the PANI-$Ti_{0.91}O_2$ multilayer films used as photoelectrodes under both basic and acidic conditions.

Figure 2. a) Photocurrent versus time for the electrodes prepared with eight bilayers of PDDA-$Ti_{0.91}O_2$ and PANI-$Ti_{0.91}O_2$, and pristine PANI, respectively. Solution: aqueous 1.0 M methanol and 1.0 M NaOH solution. b) Photocurrent versus time for the electrodes prepared with different bilayers of PDDA-$Ti_{0.91}O_2$ and PANI-$Ti_{0.91}O_2$, and pristine PANI. Solution: aqueous 0.1 M $NaNO_3$, 1.0 M HCl solution. c) Sustained photocurrents for various electrodes of one and eight layers of $Ti_{0.91}O_2$ nanosheets. For all the data in the figures, the amount of pristine PANI deposited matched an equivalence PANI absorbance of eight bilayers of PDDA-$Ti_{0.91}O_2$ or PANI-$Ti_{0.91}O_2$.

structure of PANI, it is clear that variations in the pH value will have large effects on the structure. Under basic conditions the structure is electron rich, which results in PANI acting as an n-type semiconductor. However it can also be seen by this structure that there is no continuous conjugation of the electronic levels. Since the photoexcitation at 354 nm is due to the excitation from a π to π^* orbital in the benzene rings,[17] without conjugation it is quite difficult to conduct these electrons to the electrode.

On the other hand, under acidic conditions all the nitrogen atoms are protonated. In protonating the remaining nitrogen atoms the double bond between nitrogen and the benzene ring is broken. This allows for total conjugation throughout the polymer, and hence increases the conductivity of PANI from the order of 10^{-10} to 10^{0} S cm^{-1}.[18] However by protonating the nitrogen, the system becomes electron poor, and hence becomes a p-type semiconductor. Thus, the protonation can explain both the switch to p-type photocurrent and the enhanced photocurrent seen in Figure 2b.

Given that the basic conditions of PANI have a much lower efficiency, the $Ti_{0.91}O_2$ was expected to help in increasing the anodic photocurrent. Since $Ti_{0.91}O_2$ is always a n-type semiconductor, this should have no effect on the cathodic photocurrent. Thus it could be interesting to see if the additional photocurrent from $Ti_{0.91}O_2$ could help to balance out the difference between the anodic and cathodic currents from this device. However, this work showed that the variation in conductivity of the PANI was the dominant factor in determining photocurrent.

In summary, PANI can be used as a conductive polymer binder to assemble exfoliated $Ti_{0.91}O_2$ nanosheets in a controlled manner through layer-by-layer deposition. While PANI can switch from a n-type to p-type semiconductor on its own by varying potentials,[3] this work shows that the alternating PANI-$Ti_{0.91}O_2$ films used as photoelectrodes can be switched by simply varying the electrolyte. The growth of multiple layers also allows a controllable magnification of the generated photocurrent. These findings may shed light on the potential photo-electronic applications of n–p switchable devices.

Received: March 11, 2013
Published online: May 9, 2013

Keywords: layered compounds · nanosheets · photocatalysis · photochemistry · polyaniline

[1] E. T. Kang, K. G. Neoh, K. L. Tan, *Prog. Polym. Sci.* **1998**, *23*, 277 – 324.
[2] W. S. Huang, B. D. Humphrey, A. G. Macdiarmid, *J. Chem. Soc. Faraday Trans. 1* **1986**, *82*, 2385 – 2400.
[3] E. M. Genies, M. Lapkowski, *Synth. Met.* **1988**, *24*, 69 – 76.
[4] L. Z. Wang, Y. Ebina, K. Takada, T. Sasaki, *J. Phys. Chem. B* **2004**, *108*, 4283 – 4288.
[5] a) N. Sakai, T. Sasaki, K. Matsubara, T. Tatsuma, *J. Mater. Chem.* **2010**, *20*, 4371 – 4378; b) K. Zhang, L. L. Zhang, X. S. Zhao, J. S. Wu, *Chem. Mater.* **2010**, *22*, 1392 – 1401; c) T. Sasaki, Y. Ebina, M. Watanabe, G. Decher, *Chem. Commun.* **2000**, 2163 – 2164.
[6] T. Sasaki, Y. Ebina, T. Tanaka, M. Harada, M. Watanabe, G. Decher, *Chem. Mater.* **2001**, *13*, 4661 – 4667.
[7] a) T. Sasaki, M. Watanabe, H. Hashizume, H. Yamada, H. Nakazawa, *J. Am. Chem. Soc.* **1996**, *118*, 8329 – 8335; b) T. Sasaki, M. Watanabe, Y. Michiue, Y. Komatsu, F. Izumi, S. Takenouchi, *Chem. Mater.* **1995**, *7*, 1001 – 1007.
[8] J. H. Cheung, W. B. Stockton, M. F. Rubner, *Macromolecules* **1997**, *30*, 2712 – 2716.
[9] M. D. Butterworth, R. Corradi, J. Johal, S. F. Lascelles, S. Maeda, S. P. Armes, *J. Colloid Interface Sci.* **1995**, *174*, 510 – 517.
[10] Y. Wang, C. H. Sun, X. X. Yan, F. X. Xiu, L. Z. Wang, S. C. Smith, K. L. Wang, G. Q. Lu, J. Zou, *J. Am. Chem. Soc.* **2011**, *133*, 695 – 697.
[11] J. G. Masters, Y. Sun, A. G. Macdiarmid, A. J. Epstein, *Synth. Met.* **1991**, *41*, 715 – 718.
[12] T. Sasaki, M. Watanabe, *J. Phys. Chem. B* **1997**, *101*, 10159 – 10161.
[13] a) A. Baba, F. Kaneko, R. C. Advincula, *Colloids Surf. A* **2000**, *173*, 39 – 49; b) Y. Lvov, K. Ariga, M. Onda, I. Ichinose, T. Kunitake, *Colloids Surf. A* **1999**, *146*, 337 – 346.
[14] a) Y. H. Dong, S. L. Mu, *Electrochim. Acta* **1991**, *36*, 2015 – 2018; b) X. F. Ma, G. Li, M. Wang, R. Bai, F. Yang, H. Z. Chen, *Green Chem.* **2006**, *8*, 63 – 69.
[15] a) J. M. Bolts, M. S. Wrighton, *J. Phys. Chem.* **1976**, *80*, 2641 – 2645; b) M. Tomkiewicz, *J. Electrochem. Soc.* **1979**, *126*, 1505 – 1510.
[16] Z. Zhang, P. A. Maggard, *J. Photochem. Photobiol. A* **2007**, *186*, 8 – 13.
[17] T. Komura, H. Sakabayashi, K. Takahashi, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1269 – 1273.
[18] J. C. Chiang, A. G. Macdiarmid, *Synth. Met.* **1986**, *13*, 193 – 205.

