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Effects of Organic Self-assembled Polymer and Metal Phthalocyanine Multilayers on the Surface Photovoltaic Properties of Indium Tin Oxide and Titanium Oxide

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Using a layer-by-layer self-assembly technique, we have deposited multilayers of nickel phthalocyanine tetrasulfonate (NiPc) and poly(diallyldimethylammonium chloride) (PDDA) onto indium tin oxide (ITO) and ITO/TiO_2 substrates, respectively. To probe charge-transfer properties of these self-assembled multilayers on conductive and semiconductive surfaces, Kelvin probe and surface photovoltage measurements have been carried out. The results showed an oscillating behavior of the surface potential or work function ($\Delta\Phi$) as the surface layer was alternated between PDDA and NiPc on both substrates with or without light. The average width of this surface potential oscillation was around 350 mV. These changes in surface potential, induced by self-assembled PDDA or NiPc, were due to the modulation of electron affinity rather than band bending at ITO surfaces. The photoinduced change in band bending ($\delta\Delta V$), however, has little correlation to the number of layers (PDDA or NiPc).

Introduction

The recently developed technique of layer-by-layer (LBL) assembly of oppositely charged polymeric and organic materials has been used to fabricate multilayers on various substrates. LBL assembly promises to enable the construction of materials with well-controlled, nanometer-scale architecture and tailored properties for applications in electronics, photonics, and optoelectronics.[1−6] The key to the construction of multilayers is the interface between adjacent layers, and hence, interface properties are crucial to the self-assembled systems [7,8] and their physical properties. Therefore, both interfacial chemistry and interfacial physics become the focal point for self-assembled multilayers. Such issues, however, have received little attention in the past.

To study the evolution of electronic properties as a function of molecular layers, we utilized a Kelvin probe, which has been previously used to measure work function difference between a conducting specimen and a vibrating tip.[9,10] It has been widely used for measuring surface potential of organic monolayers on conducting or semiconducting solids effectively by Cahen and coworkers.[11−17] The results indicated that surface electric properties were a function of molecular modifiers in systems composed of chemisorbed monolayers of dicarboxylic acids on CdTe, CdSe, $CuInSe_2$, GaAs, and InP. We recently employed Kelvin probe technique to measure work functions of organic and polymeric multilayers grown on conductive substrates.[18] In particular, we found that variation of the work function, as multilayers of PDDA [poly(dimethyldiallylammonium chloride)] and nickel phthalocyanine (NiPc) tetrasulfate were self-assembled, was periodic.

Nanostructured semiconductor metal oxide films have been widely studied as photoelectrochemical solar cells, ion-insertion batteries, and electrode materials[19−27] due

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to their obvious significant technological and commercial potentials. Metal oxides have a relatively large density of surface states, which yield very rich interfacial charge-transfer phenomena.[22] The photostimulated charge transfer will in turn give rise to a surface photovoltage at the surface or interface of a semiconductor/conductor oxide. As a result, surface photovoltage spectroscopy (SPS) is a very sensitive tool to study the change of charge distribution on semiconductor surfaces, buried interfaces, and heterojunctions.[10,28−34]

It is instructive, therefore, to build an inorganic−organic interface or a hard and soft interface and study charge-transfer phenomena at these interfaces. Here, we use positively charged PDDA and negatively charged NiPc, a highly absorbing dye, on two metal oxide substrates: conductive indium tin oxide (ITO) and semiconductive TiO_2. Because ITO has negatively charged surfaces, the LBL sequence is ITO/PDDA/NiPc/PDDA/NiPc, etc. Conversely, TiO_2 has positively charged surfaces, and the LBL sequence is ITO/TiO_2/NiPc/PDDA/NiPc/PDDA, etc. During the growth of these self-assembled multilayers on these two oxides, we use SPS to study the photovoltaic behavior of PDDA−NiPc multilayers. The selection of phthalocyanines is because they are hole conductors or electron donors and have received considerable attention as constituents in optoelectronic devices.[35,36] The choice of TiO_2 is due to its popularity as a candidate for solid-state solar cells.[19,20] We hope that studies of the effect of organic self-assembled multilayers on the surface work function of metal oxides will provide insightful information on materials design and lead to the control of electronic properties on conductive and semiconductive surfaces through molecular engineering.

Experimental Section

Materials and Preparation of Self-Assembled Multilayers. NiPc and PDDA were purchased from Aldrich and used without further purification. As negatively or positively charge materials, respectively, they were used to prepare self-assembled bilayers. The concentration of PDDA polymer and NiPc aqueous solutions were 10 mM and 1 mM, respectively. ITO substrates (sheet resistance $\leq 40\ \Omega/\square$) were purchased from Delta Technologies Company and were cleaned by ultrasonication in an acetone solution for 10 min. Then, they were rinsed several times in deionized water and dried by N_2. ITO/TiO_2 substrates were prepared by a chemical solution deposition method. The results from X-ray diffraction showed an anatase phase with an average TiO_2 film thickness of 70 ± 5 nm. First, the ITO substrates were immersed in the PDDA solution for about 5 min. The attractive force between positively charged PDDA polymer and negatively charged (Sn−O^- terminated) ITO surface is expected to coat the ITO surface with a monolayer of PDDA. The coated sample then was washed with deionized water several times to remove all of the nonadsorbed materials. Next, the PDDA-coated substrate was immersed in a NiPc aqueous solution for another 2 min, followed by washing with deionized water. At this time, a PDDA−NiPc bilayer is formed on the ITO substrate. With the repetition of the above steps, additional bilayers of PDDA and NiPc were deposited and a multilayer began to emerge on the ITO substrate.

Accordingly, positively charged TiO_2 surfaces were immersed in an aqueous NiPc solution for 2 min for growing the first NiPc monolayer. Subsequent immersion in a PDDA solution for 5 min formed a NiPc−PDDA bilayer on ITO/TiO_2 substrate.

Instrumentation and Measurements. A commercial Kelvin probe system (KP-6500 Digital Kelvin Probe System, McAllister Technical Services) was used to measure work-function changes and integrated with a light source for surface photovoltage measurements. This apparatus measures the contact potential difference (CPD) between a reference plate and the sample's surface. CPD is defined as the work function of the reference plate connected to the preamplifier minus the work function of the sample, i.e., $\phi_m - \phi_{sam}$ (where ϕ_m is the work function of the reference plate (a constant) and ϕ_{sam} is the work function of sample). By comparing the work function before and after deposition of PDDA or NiPc onto an ITO or TiO_2 substrate, the change in work function, $\Delta\phi$, after the deposition is obtained. The probe plate is made of stainless steel with a diameter of 2 mm. It was electrically connected via ground to the sample during the measurement with an accuracy of 2.5 mV. The typical distance between the reference plate of the probe and the sample was less than ~1 mm. The oscillation frequency of the probe was chosen at 100 Hz. A CPD measurement was obtained by the Kelvin Probe system under ambient conditions for each new monolayer (PDDA or NiPc) deposited onto the substrate.

The SPS measurements were carried out on a home-built setup. ITO and ITO/TiO_2 were chosen as the substrates that were illuminated through the transparent backside by monochromatic light, which was obtained by passing light from a 450 W xenon lamp through a double-prism monochromator (SPEX FL3-21). The Kelvin probe was employed to pick up the photovoltage signal. Photoinduced surface photovoltage spectra were obtained by scanning the wavelength of the incident light from the visible to UV range (250−800 nm) at a typical scanning rate of 30 nm/min. The raw SPS data were not corrected for the spectrum of the xenon lamp.

Results and Discussion

The surfaces of ITO show negatively charged characteristics due to the formation of dangling Sn−O^- bonds on bare ITO.[18] Therefore, in an aqueous solution, positively charged PDDA forms a monolayer on the substrate surfaces through self-organization or self-association of oppositely charged pairs, a process that assembles solution-solvated polymer into monolayer solid thin films. Similarly, negatively charged NiPc macrocycles will bind to the dispersed positively charged polymeric PDDA monolayer. Multilayer thin films can be obtained by alternately dipping the substrate into the solutions of PDDA and NiPc. Conversely, TiO_2

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surfaces always have characteristics of positive charges due to oxygen defects on surfaces.[29] Therefore, the initiation layer for the multilayer growth must be NiPc, which is then followed by the immersion in PDDA solution for the second layer formation. Multilayers prepared on TiO_2 surfaces have a sequence that are reversed from multilayers prepared on ITO surfaces.

The formation of both ionic multilayers and covalent multilayers was well-characterized previously.[5,18,37] We refer the readers to those references, and in this paper, we will concentrate on the electronic properties and photoinduced electronic property changes at interfaces.

Here, we use SPS to monitor the change of band bending of ITO and ITO/TiO_2 at the inorganic–organic interface under UV–vis illumination with or without PDDA and NiPc surface-layer modification. Typically, surface photovoltage and photovoltaic effects are very sensitive to the change of charge redistribution on semiconductor surfaces, in buried interfaces, or between heterojunctions, because the photoexcited electron–hole pairs will migrate under the intrinsic electric field to mitigate the space charge at the interface, thus changing band bending. Therefore, it seems attractive to study the electronic properties of the inorganic and organic interfaces and understand how the self-assembled multilayers affect the properties of metal oxides.

1. Surface and Interfacial Electronic Properties of Self-Assembled Multilayers on ITO. The photovoltaic behavior of PDDA–NiPc multilayers on ITO is shown in Figure 1. For reference purposes, blank ITO SPS was employed as a calibration baseline (curve g in Figure 1). Only one peak at 310 nm, related to the band gap of ITO ($E_g = 3.7-4.3$ eV),[38–40] has been observed, and its photovoltage is more than ΔV_p (310 nm) = 500 mV. The negative photovoltaic response indicates a typical n-type material with an upward band bending near the surface. The photovoltage of ΔV_p (310 nm) = 500 mV is obtained by measuring the difference [ΔV_p(310 nm) = V_p (310 nm) − V_p (600−700 nm)] between photovoltage at the band gap [V_p (310 nm)] and photovoltage away from the band gap [V_p (600−700 nm) or the baseline]. After one layer of polymeric PDDA is deposited, the photovoltaic response is significantly decreased to ΔV_p (310 nm) = 150 mV at 310 nm. The reduction of the photovoltaic effect is also accompanied by an offset of the whole spectrum due to electron affinity effects generated by charge characteristics of the PDDA layer. When we grew a NiPc layer and form the first PDDA–NiPc bilayer on ITO, a photovoltaic response of ΔV_p (310 nm) = 80 mV was observed, also accompanied by another offset of the whole spectrum due to electron affinity effects generated by the NiPc layer. Similar photovoltage patterns were observed with the deposition of the second and third PDDA–NiPc bilayers. What is remarkable is that the photovoltage response over the entire spectra depends only on the last layer of the nanometer-thick self-assembled multilayer films. For example, all the spectra from PDDA-terminated layers resemble each other, and all the curves from NiPc-terminated layers trace each other closely (Figure 1). The nearly constant gap in the surface work functions between the two groups (PDDA-terminated and NiPc-terminated) over the entire spectra is due to the change of electron affinity on substrates by PDDA and NiPc. The significance of this result is that surface work functions can be modulated by organic self-assembled multilayers.

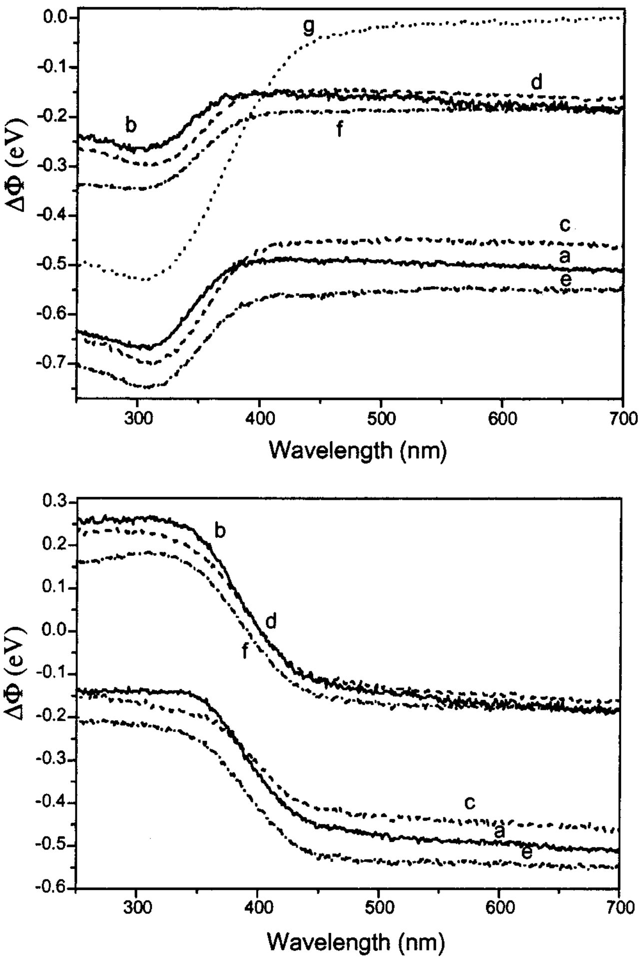

Figure 1. Top: surface photovoltage spectra (SPS) dependence on the terminating layer of PDDA and NiPc of (a) ITO/PDDA; (b) ITO/PDDA/NiPc; (c) ITO/PDDA/NiPc/PDDA; (d) ITO/PDDA/NiPc/PDDA/NiPc; (e) ITO/PDDA/NiPc/PDDA/NiPc/PDDA; (f) ITO/PDDA/NiPc/PDDA/NiPc/PDDA/NiPc; (g) blank ITO. Bottom: SPS data after the correction from blank ITO, i.e., $\phi_{sam} - \phi_{ITO}$.

We also measured the CPDs after each deposition of a PDDA or NiPc layer on ITO in the dark. Figure 2a (top) shows the surface work-function values *vs* the total number of PDDA and NiPc layers, *N*, *N* = 1 indicating that the surface potential of ITO electrodes changed after the deposition of PDDA or NiPc. For example, after a single layer of PDDA was deposited onto an ITO substrate, its CPD value increased by ~500 mV (work function decreased by 0.5 eV) in reference to blank ITO. After deposition of NiPc onto PDDA-coated ITO, the CPD value decreased to around 200 mV (work function increased by 0.2 eV) in reference to blank ITO. Subsequent deposition of PDDA and NiPc layers continue the trend of increasing and decreasing the CPD by ~300 mV. The oscillation of the work function with layer deposition demonstrates that the relationship between surface potential and layer deposition (whether PDDA

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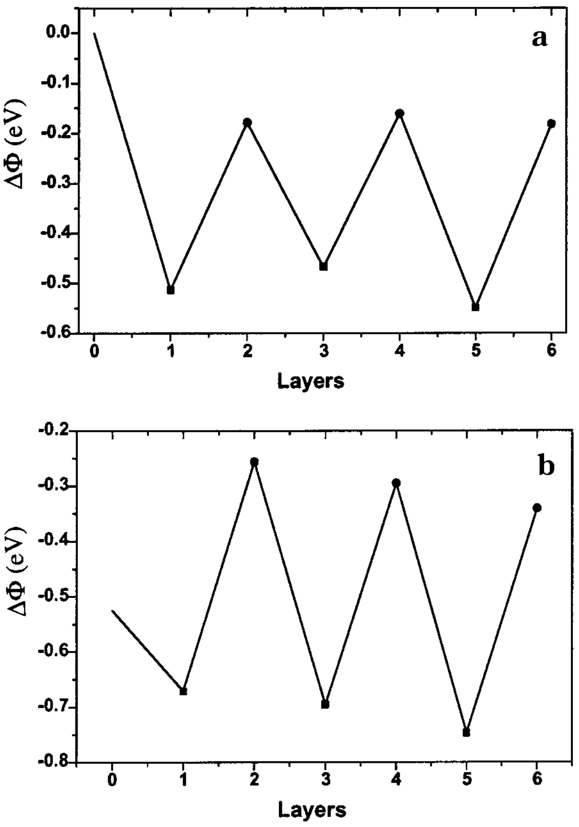

Figure 2. Surface work-function (ϕ eV) dependence on the terminating layer of PDDA (squares) or NiPc (circles) *vs* the number of total individual layers (i.e., the number of PDDA layers plus NiPc layers): top, without illumination; bottom, at 310 nm, under illumination.

or NiPc) is periodic, following the cycle of charge characteristics of the alternating layers. Therefore, the surface work function of a multilayer is the same in an ideal situation regardless of the number of charged layers or charged bilayer pairs in the structure. Conversely, the observation of this periodic surface potential or work function is a sign of the reproducibility and consistency of the charged layer pair structure.[18]

Surface work-function change can be due to modification in electron affinity and/or an alteration in band bending at surfaces/interfaces (see eq 1). Therefore, the total change in surface work function is equal to the sum of the modulation in band bending and electron affinity. Since the interaction between PDDA and ITO oxide are weak charge−charge bindings, we expect that changes in the surface work function from deposition of oppositely charged polymer or macrocycles on ITO result predominantly from electron affinity contribution. The presence of a dipole layer, interacting weakly with surfaces, affects the electron affinity of the substrate only. Both band bending and electron affinity can be changed simultaneously if a dipole layer interacts strongly with surfaces. Because the same dipole effect keeps repeating itself as deposition of PDDA−NiPc multilayers continues, we concluded that this oscillating pattern of surface work function was mainly due to modulation in ITO's electron affinity. If this modification of the work function were mainly due to an alteration of ITO band bending, we would not have observed the oscillation pattern of CPD values after the deposition of the first layer since the subsequent layers were not bound to the substrates. The same oscillation behavior was also observed under light illumination. For instance, the photovoltage spectra in Figure 1 can be divided into two groups: those terminated with PDDA and those terminated with NiPc. The average value of work-function difference with light illumination is about 300 mV, consistent with the CPD measurements without light. In Figure 2b (bottom), the oscillation pattern was plotted at $\lambda = 310$ nm. It is obvious that the oscillation patterns in Figures 2a and 2b resemble each other very much.

$$\Delta\phi = \Delta\chi \pm \Delta V \qquad (\text{“+” for n-type; “−” for p-type}) \quad (1)$$

In eq 1, we describe that the total change in surface work function ($\Delta\phi$) for a semiconductor comes from two terms: the change in electron affinity, $\Delta\chi$, and the change in band bending, ΔV. Because ITO forms an n-type depletion layer, we have $\Delta\phi$ that equals the sum of $\Delta\chi$ and ΔV. Without light illumination (labeled with superscript (1)), we measured the surface work-function change (eq 2), which is shown in Figure 2a.

$$\Delta\phi^{(1)} = \Delta\chi^{(1)} + \Delta V^{(1)} \qquad (2)$$

With light illumination (labeled with superscript (2)), we measured photoinduced effects on the change of surface work function (eq 3), which is plotted in Figure 1.

$$\Delta\phi^{(2)} = \Delta\chi^{(2)} + \Delta V^{(2)} \qquad (3)$$

Since we expect that the electron affinity will remain constant with or without light illumination, i.e., $\Delta\chi^{(1)} = \Delta\chi^{(2)}$, we can deduce the photoinduced change of band bending $\delta\Delta V = \Delta V^{(2)} - \Delta V^{(1)} = \Delta\phi^{(2)} - \Delta\phi^{(1)}$. Accordingly, we have calculated the photoinduced change of band bending $\delta\Delta V$ at the ITO band gap (310 nm). For bare ITO substrates, we have $\delta\Delta V$ (310 nm) = −525 meV, which confirms that photoexcitation at the band gap has a more pronounced photovoltaic effect. After the formation of a PDDA monolayer, the $\delta\Delta V$ (310 nm) value shifts to −158 meV. When a bilayer of PDDA−NiPc is formed, the photoinduced photovoltage response value is $\delta\Delta V$ (310 nm) = −78 meV. The photoinduced changes in band bending for the second and third bilayers are, respectively, as follows: 2nd PDDA's $\delta\Delta V$ (310 nm) = −229 meV and NiPc's $\delta\Delta V$ (310 nm) = −134 meV; 3rd PDDA's $\delta\Delta V$ (310 nm) = −198 meV and NiPc's $\delta\Delta V$ (310 nm) = −159 meV. Figure 2 shows the plot of surface work function (ϕ) against the terminating layer of PDDA or NiPc in the dark as well as with light illumination at 310 nm, and it is clear that the work functions are periodic either with or without light.

As shown in Figure 3, the photoinduced change in photovoltage, $\delta\Delta V$, which is the difference between work functions with and without light, have very little dependence on the terminal layer of the self-assembled multilayers of PDDA−NiPc. The photovoltage was decreased to around negative 100−200 mV after the formation of the first PDDA monolayer on ITO and began to converge with small amplitude of oscillations as more layers were deposited. These results suggest that the photoinduced effects ($\delta\Delta V$) are dictated by the change in band bending. Although the presence of PDDA does not affect band bending in the dark, it does

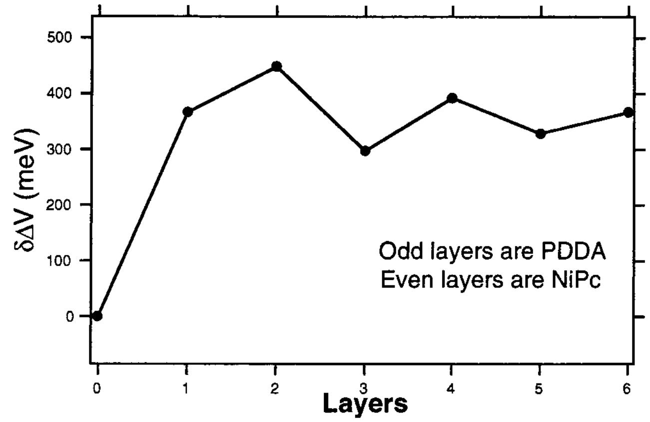

Figure 3. Photoinduced band bending $\delta\Delta V$ (meV) dependence on self-assembled multilayer of PDDA and NiPc on ITO at 310 nm excitation after the correction from blank ITO.

affect how much the band bending can be recovered under illumination. The convergence of this photoinduced effect as more layers are deposited leads us to conclude that the photoinduced change in photovoltage comes from the change in band bending influenced mainly by the first PDDA layer. Therefore, we deduce this photovoltaic response change is due to the decrease in efficiency of charge transfer and/or the separation of electron−hole pairs at this inorganic/organic interface. The small-amplitude oscillating behavior mainly comes from the change of ITO's electron affinity through long-range dipole influence on photovoltaic effects. In other words, the change in photovoltage ($\delta\Delta V$) is not a strong periodic function of the self-assembled layers on conductive ITO because the first PDDA monolayer contributes most of the change on photovoltaic response.

2. Surface and Interfacial Electronic Properties of Self-Assembled Multilayers on TiO_2. Because TiO_2 is considered a dye-sensitized solar cell material,[19,20] it is important to understand the effects of surface modification on charge accumulation and compensation, and charge transport at the interfaces of nanostructured TiO_2, especially for anatase form. To address this, we first assembled a NiPc monolayer and then a PDDA monolayer on the surfaces of TiO_2 supported by ITO substrates, aiming at understanding the interface charge transport behaviors between TiO_2 and organic molecules. In Figure 4 (top), curve e shows the surface photovoltage spectrum of a blank ITO/TiO_2. There is a very broad peak centered at 650 nm. The photovoltage of this broad negative peak was around 20 mV. This photovoltaic response came from surface states at TiO_2 surface or ITO/TiO_2 interface. In addition, we observed a dramatic photovoltage increase at 500 nm reaching a peak value of 350 mV at 345 nm, which corresponded to the band gap of TiO_2. This broad onset of this super-band-gap surface photovoltage was due to two distinct absorption mechanisms for photons with the energy slightly below E_g. First, a non-negligible electric field was always associated with a significant surface charge region. Because sub-band-gap absorption was electric-field-assisted, it could be expected to blur the sharp onset of the absorption. Second, photoassisted charge transfer might take place between shallow states extending from the band gap, i.e., "tail states".[10]

After the adsorption of a NiPc monolayer onto TiO_2, no photovoltage was observed in the range from 450 to 800 nm (curve a), but rather a much sharper increase in photovoltage onset was observed at 450 nm. The strongest photovoltaic response was still at 350 nm, and intensity had essentially the same value of 340 mV. Once the first bilayer of NiPc and PDDA was formed (Figure 4, curve b), the photovoltage remained flat without any observable surface states in the region between 450 and 800 nm, resembling curve a from one NiPc monolayer on TiO_2, except the offset. We noticed that the strongest response shifted to 364 nm with the same intensity. The photovoltaic peaks for PDDA-terminated layers have a narrower peak than those of NiPc-terminated layers. A faster photovoltage drop is seen from 360 to 350 nm, which can be related to super-band-gap states or energy levels higher than the band gap of TiO_2. The second NiPc−PDDA bilayer duplicates the same behavior that we observed in the first bilayer. These results suggest that TiO_2 photovoltage can be modified by self-organized layers of organic dyes and/or polymers. Photovoltage phenomena, which arise from surface and/or sub-bandgap states, can be completely altered or erased by self-assembled monolayers. In Figure 4 (bottom), we plotted the difference spectra between TiO_2 with self-assembled layers and TiO_2 alone. These difference spectra reveal the exact photovoltage contributions due to NiPc and PDDA monolayers and multilayers on ITO/TiO_2 substrates.

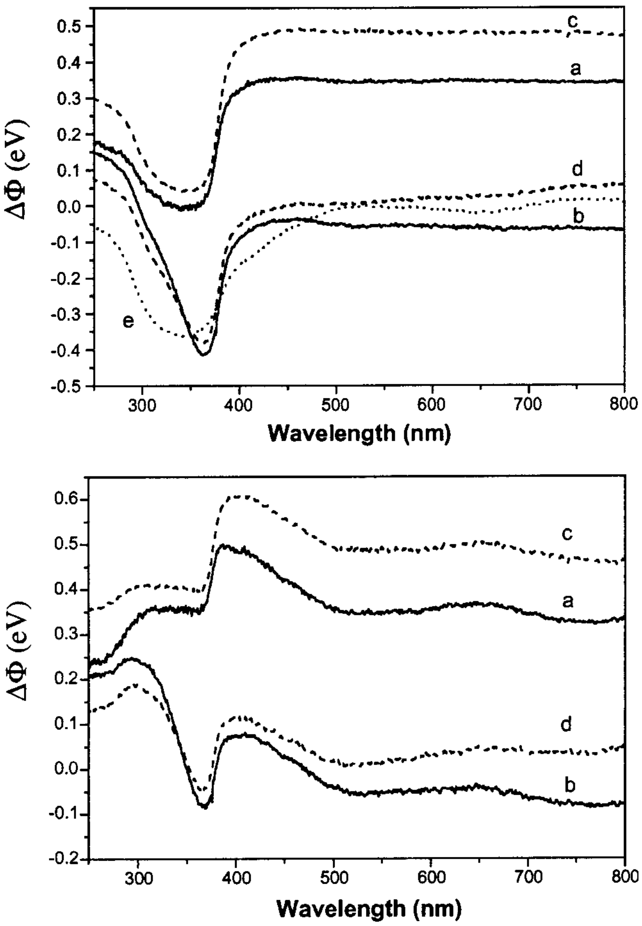

Figure 4. Top: surface photovoltage spectra (SPS) of NiPc and PDDA multilayers on ITO/TiO_2 of (a) ITO/TiO_2/NiPc; (b) ITO/TiO_2/NiPc/PDDA; (c) ITO/TiO_2/NiPc/PDDA/NiPc; (d) ITO/TiO_2/NiPc/PDDA/NiPc/PDDA; (e) ITO/TiO_2. Bottom: SPS data after the correction from ITO/TiO_2, i.e., $\phi_{\text{sam}} - \phi_{\text{ITO/TiO}_2}$.

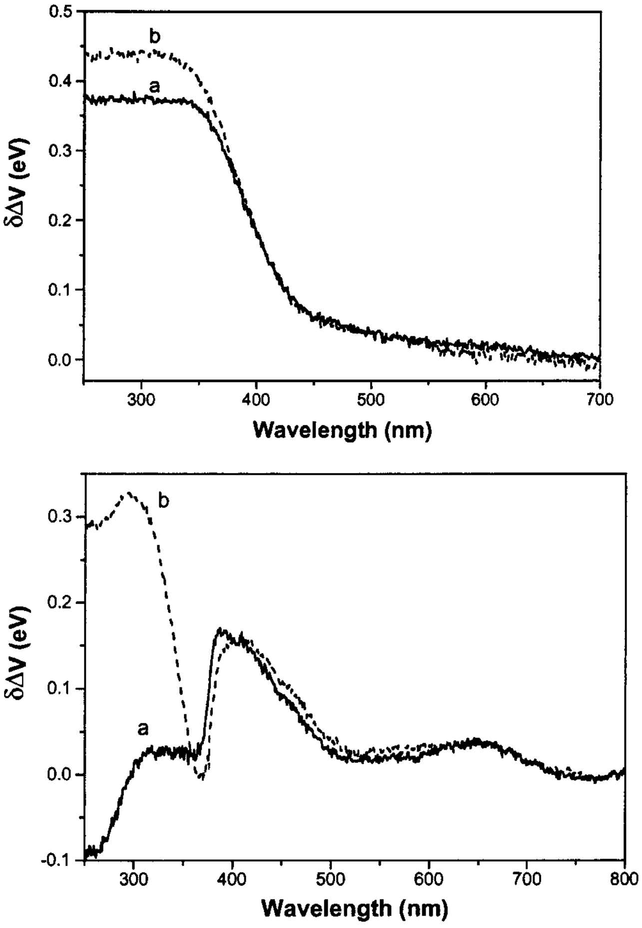

Figure 5. Photoinduced band bending $\delta\Delta V$ (eV) dependence on the excitation wavelength λ after the correction from: blank ITO (top) (a) one PDDA layer and (b) PDDA−NiPc bilayer; ITO/TiO$_2$ (bottom) (a) one NiPc layer and (b) NiPc−PDDA bilayer.

In Figure 5, we attempt to clarify the detailed contributions to photoinduced effects from each individual component in the self-assembled multilayers on both ITO and TiO$_2$ substrates. Below band gap excitation, there was very little photoinduced response for conductive ITO and some surface states were observed for semiconductive TiO$_2$. In this low energetic excitation region (λ = 400−800 nm), both PDDA and NiPc make no difference in terms of contribution to the photoinduced effects as demonstrated in Figure 5 (curves a and b are essentially same). While there was excitation at the band gaps or above the band gaps, however, there were stronger photoinduced activities in both ITO and TiO$_2$ systems. On ITO, the first PDDA layer made most of the contribution around the band gap at 310 nm. Subsequent layers only made minor modifications regardless of NiPc or PDDA (compare curve a and curve b in Figure 5, top).

On TiO$_2$, the first NiPc layer did not really change the photovoltage intensity much at TiO$_2$'s band gap, but it erased the photovoltage response attributed to surface states completely. The second PDDA layer, however, also made pronounced contributions to the photovoltage through its charge influence to TiO$_2$'s super band gap (i.e., above the band gap of TiO$_2$). These photovoltaic response changes are due to the decrease in efficiency of charge transfer and/or separation of electron−hole pairs at this inorganic/organic interface.

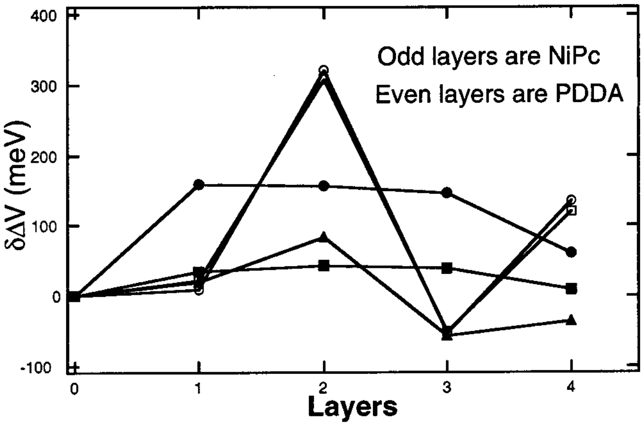

Figure 6. Photoinduced band bending $\delta\Delta V$ (meV) dependence on NiPc and PDDA multilayers on ITO/TiO$_2$ at 300 nm (open circles), 310 nm (open squares), 350 nm (solid triangles), 400 nm (solid circles), and 650 nm (solid squares) after the correction from ITO/TiO$_2$.

As shown in Figure 3, the photoinduced change in photovoltage oscillated around 350 mV after the formation of PDDA and NiPc monolayers on ITO. We found that PDDA monolayer does affect how much the band bending, manifested as photovoltage, can be recovered under illumination. We observed a similar effect when the PDDA monolayer was grown on NiPc-coated ITO/TiO$_2$, as shown in Figure 5, bottom. This seems to suggest that the PDDA polymers play a dominant role in affecting photovoltage response at the band gap or super band gap of TiO$_2$. Detailed photovoltage changes for the TiO$_2$/NiPc/PDDA/NiPc/PDDA system at 300, 310, 350, 400, and 650 nm are shown in Figure 6. The first and second NiPc monolayers made most of photovoltage alterations from 350 to 800 nm, which was particularly obvious at 400 and 650 nm, while the first and second PDDA layers contributed to most of the changes below 350 nm. Unlike the photovoltage response below the band gap, which were flat, the photovoltage response excited at the band gap has great sensitivity to the surface self-assembled multilayers. For semiconductive TiO$_2$ substrates, we found that not only did the first layer contribute to the photovotage response but the subsequent layers could modify the photovoltage responses as well.

Conclusions

To investigate the evolution of the surface physical properties of self-assembled multilayers, we applied Kelvin probe technique and surface photovoltage spectroscopy to monitor the growth of self-assembled PDDA and NiPc systems. Kelvin probe results indicated that the surface electronic potential was very sensitive to the presence of self-assembled molecular layers on surfaces. We found that there was an approximately constant gap of 300 meV between the work function of PDDA- and NiPc-terminated self-assembled multilayers on ITO and TiO$_2$ substrates either in dark or under illumination. In other words, the surface potential or surface work function ($\Delta\Phi$) is a periodic function of the terminating layer, oscillating between ~−500 mV for PDDA layers and ~−200 mV for NiPc layers on ITO and ~400 mV for NiPc layers and ~0 mV for PDDA layers on TiO$_2$. For photoinduced effects regarding band bending at interfaces, we observed little correlation to the terminating layer of the PDDA−NiPc system on ITO. On TiO_2, the effects of self-assembled multilayers appeared to be more complex in the region beyond band gap excitations, which might suggest that the self-assembled multilayers could influence the photoinduced effects to a greater degree.

Further implications are that work functions of electrodes can be modified with simple self-organized monolayers at surfaces so that charge injections can be systematically tuned using the functions of organic mono- or multilayers. In this work, the observation of surface work-function oscillation is correlated to the alternative pattern of dipoles. Logic prediction is that work function, within a range, should continue to change linearly with aligned polar multilayers, which could have advantageous technological potentials. However, chemical and thermal stability issues continue to be the focal point for the organic materials. For PDDA, we expect typical thermal stability similar to other organic materials. For phthalocyanine, thermal stability up to 400 °C was reported;[41] thus, proper engineering of organic materials can yield organic materials with reasonable thermal stability for tuning surface work functions.

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