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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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### Molecular Assembly by Sequential Ionic Adsorption of Nanocrystalline TiO<sub>2</sub> and a Conjugated Polymer

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Online publication date: 10 July 2003

**To cite this Article** Kim, Young-Gi , Kim, Jaehyun , Ahn, Heejoon , Kang, Bongwoo , Sung, Changmo , Samuelson, Lynne A. and Kumar, Jayant(2003) 'Molecular Assembly by Sequential Ionic Adsorption of Nanocrystalline TiO<sub>2</sub> and a Conjugated Polymer', *Journal of Macromolecular Science, Part A*, 40: 12, 1307 – 1316

**To link to this Article:** DOI: 10.1081/MA-120025310

**URL:** <http://dx.doi.org/10.1081/MA-120025310>

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## Molecular Assembly by Sequential Ionic Adsorption of Nanocrystalline TiO<sub>2</sub> and a Conjugated Polymer<sup>#</sup>

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### ABSTRACT

Cationic nanocrystalline TiO<sub>2</sub> particles have been synthesized for which the size and composition of the nanoparticles were analyzed by a transmission emission microscopy and energy dispersive x-ray spectrometer (EDXS). Multilayered films have been fabricated by sequential adsorption of TiO<sub>2</sub> nanoparticles and poly(3-thiophene acetic acid) (PTAA). Each layer of the nanoparticles and PTAA in the thin film has also been characterized by x-ray photoelectron spectroscopy, atomic force microscopy, and UV-visible spectroscopy. These types of multilayered nanocomposite films may find applications in the fabrication of efficient light harvesting photovoltaic cells.

*Key Words:* PTAA; TiO<sub>2</sub>; Molecular assembly; ELBL; Multilayered nanocomposite; Conjugated polymer; Nanoparticle.

<sup>#</sup>Dedicated to the memory of Professor Sukant K. Tripathy (deceased).

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## INTRODUCTION

Recently, fabrication of nanostructured materials and organic/inorganic nanocomposites<sup>[1]</sup> by electrostatic layer-by-layer (ELBL) adsorption<sup>[2]</sup> and electrospinning<sup>[3]</sup> has attracted great attention due to their high degree of control. They provide for nano-level manipulation. Research on materials using EBL adsorption has been utilized for different coating applications,<sup>[4]</sup> optoelectronic devices,<sup>[5]</sup> and biomedical uses.<sup>[6,7]</sup> One of the most interesting subjects in EBL molecular assembly is to build nanometer scale multilayers using alternating conductive organic and semiconductive inorganic molecules. The organic layers usually provide flexibility with tunable electroactive properties while inorganic materials provide high thermal and mechanical stability with unique electronic properties. These multilayered films can be used for the fabrication of sensors, capacitors, and solar cells.<sup>[8,9]</sup>

The semiconducting inorganic nanoparticle TiO<sub>2</sub> has elicited tremendous interest in dye sensitized solar cells (DSSCs) due to the relatively large efficiency.<sup>[10-15]</sup> Photo-induced charge transfer in different particle sizes and crystal morphology of TiO<sub>2</sub> has been investigated in DSSC. In these cells, though TiO<sub>2</sub> is processed using spin coating, screen printing, or doctor blade coating, all of which can only provide macroscopic understanding of charge transfer processes.<sup>[16]</sup>

The EBL technique is useful for preparing well defined and ordered multilayer films with controllable thickness. Recently, He et al. reported that the photovoltaic efficiency of the solar cells made by EBL molecular assembly of nanocrystalline TiO<sub>2</sub> particles and polyelectrolytes was comparable to those of cells fabricated by other methods such as spin casting.<sup>[17]</sup> Ding et al. have also reported that alternating thin layers of TiO<sub>2</sub> and poly(3-thiophene acetic acid) (PTAA) showed interesting photoelectrochemical properties.<sup>[18]</sup>

In this paper, synthesis and processing of nanocrystalline TiO<sub>2</sub> particles will be discussed. The focus of this study will be to investigate the feasibility to build up nanometer scale molecular structures.

## EXPERIMENTAL

### Synthesis of a Carboxylated Polythiophene and Nanocrystalline TiO<sub>2</sub> Particles

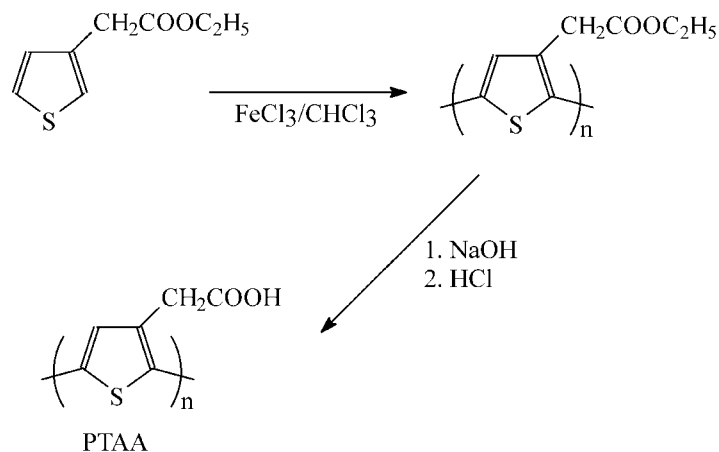
#### Materials

Titanium tetrachloride (Aldrich), 3-aminopropyltrimethoxysilane (APS, Aldrich), hydrochloric acid (Fisher Scientific), and monomer ethyl-(3-thiophene acetate) (Fisher Scientific) were used without any further purification.

### Synthesis of a Carboxylated Polythiophene

Poly(3-thiophene acetic acid) was synthesized as described earlier.<sup>[19]</sup> The structures of the polymers are shown in Fig. 1. Poly(3-thiophene acetic acid) has been synthesized





**Figure 1.** Structure of PTAA and schematic representation of performed reactions.

from monomer ethyl-(3-thiophene acetate) by chemical dehydrogenation method using anhydrous ferric chloride.

### Synthesis of Cationic Nanocrystalline $\text{TiO}_2$ Particles<sup>[20]</sup>

$\text{TiCl}_4$  was slowly added to a 6 M aqueous HCl under vigorous stirring. The concentration of HCl in the resulting solution is 0.5 M. After completion of the addition, the temperature of the round bottom flask was kept at  $80^\circ\text{C}$  for 4 h. The resulting solution was transparent and stable over six months.

### Characterization of Nanocrystalline $\text{TiO}_2$ Particles

The particle images of nanocrystalline  $\text{TiO}_2$  were measured at 120 kV using a transmission electron microscopy (TEM, Philips EM400T) which is equipped with an energy dispersive x-ray spectrometer (EDXS, Noran Instrument).

### Fabrication of Multilayer via Molecular Assembly

Aqueous PTAA solution was prepared at the concentration of 10 mmol/L using deionized water (resistivity of  $18 \text{ M}\Omega/\text{cm}$ ). The concentration was calculated based on the number of monomer units in the polymers. The range of pH of these solutions was pH 1.5~11.5. The pH was determined using an Orion pH meter (model 420), and was adjusted using hydrochloric acid and sodium hydroxide.

The substrates, quartz and glass, that were used for self-assembled multilayers of the polymers, were cleaned using Piranha solution at  $80^\circ\text{C}$  for 1 h. The substrates were rinsed with deionized water and ethanol, and dried in vacuum oven for 2 days. After cleaning of the substrates, they were immersed in a solution of 5% APS in toluene for 15 h. This was



followed by sonicating in toluene (30 min), methanol/toluene (1 : 1, 30 min), and methanol (30 min), and finally, the sample was rinsed with deionized water, and dried. For the fabrication of ionically adsorbed multilayers of the polymers and  $\text{TiO}_2$ , the substrates were dipped in PTAA solution and  $\text{TiO}_2$  solution (aq.) at various pH and concentrations followed by washing and drying. Multilayer films were used for measuring UV-VIS absorption.

### Characterization of Multilayers

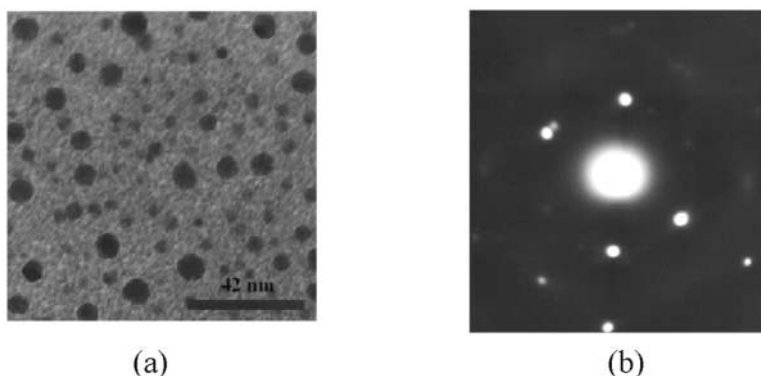
Atomic force microscopy (AFM) characterization was performed with an AFM (Park Scientific, CA) operated in the contact mode using a standard silicon nitride cantilever in ambient air. The scan rate is 1 line/s, and the set point is 50 nN. The samples on silicon wafer were used for this AFM scanning.

UV-VIS absorption spectra were obtained with a Perkin-Elmer Lambda-9 spectrophotometer (Norwalk, CT). A VG ESCALAB MK II photoelectron spectrometer equipped with a concentric hemispherical analyzer and a  $\text{MgK}\alpha$  x-ray source was used for a x-ray photoelectron spectroscopy (XPS).

## RESULTS AND DISCUSSION

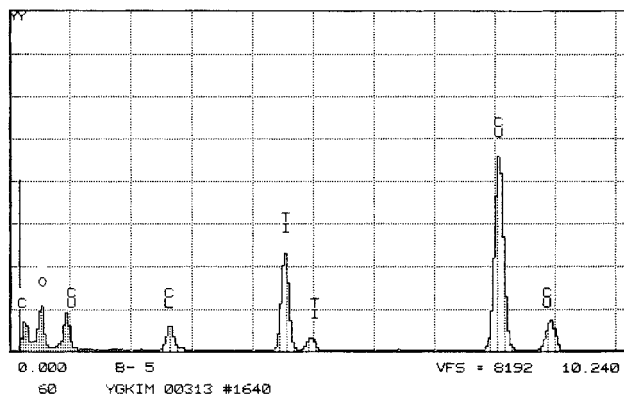
### Nanocrystalline $\text{TiO}_2$ Particles

As shown in Fig. 2, the particle size of nanocrystalline  $\text{TiO}_2$  in aqueous HCl solution was approximately 10 nm. The electron diffraction pattern in Fig. 2(b) shows the presence of crystalline  $\text{TiO}_2$ . Energy dispersive x-ray spectrometer (Fig. 3) revealed the composition of the  $\text{TiO}_2$  particles. Elements such as Ti, O, Cu, Cl, and C are present. Ti and O peaks are attributed to  $\text{TiO}_2$  and Cl peak is from the reaction medium (that is, aqueous HCl solution). Cu peak is from Cu grid that holds the samples in the TEM.



**Figure 2.** Transmission electron microscopy and crystallography for cationic  $\text{TiO}_2$  particles. Particle size: 10 nm, (a) bright field image and (b) electron diffraction pattern.



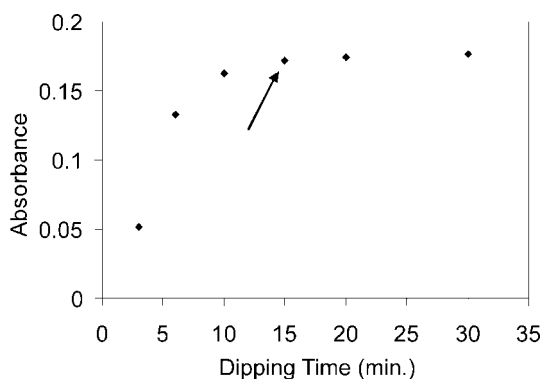


**Figure 3.** Energy dispersive x-ray spectrometer of cationic  $\text{TiO}_2$  particles.

### Optimization of the Process of Molecular Assembly

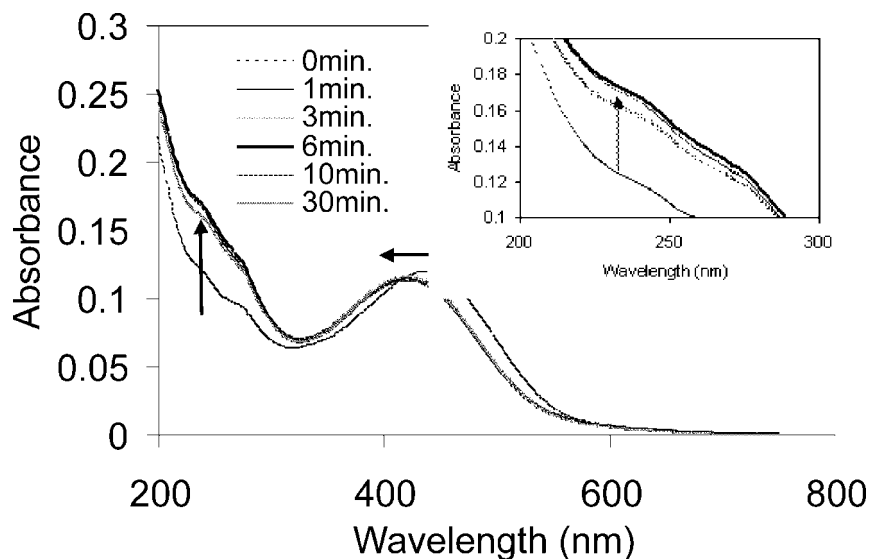
Optimized conditions for the fabrication of the  $\text{TiO}_2$ /PTAA multilayers have been established using UV-VIS absorption. As shown in Fig. 4, UV-VIS absorptions of PTAA adsorbed on APS substrate saturated at 15 min of dipping in the PTAA solution. After 15 min of dipping, a plateau of UV-VIS absorption was observed. The concentration of the PTAA solution used was 10 mmol/L, which was calculated based on the monomer unit of the polymer molecule. The pH of the polymer solution was adjusted to pH 6.5.

The coverage of the  $\text{TiO}_2$  nanoparticles was also measured using UV absorption in the range of 200–300 nm as shown in Fig. 5. The nanoparticle layer began to level off at 3 min. The maximum UV absorption of the nanoparticle was observed at 6 min of dipping time. As the dipping time increased, slight desorption of the  $\text{TiO}_2$  particles was observed and consequently, decreases in the UV absorptions were observed. On applying the aqueous  $\text{TiO}_2$  nanoparticle solution, maximum UV-VIS absorption curves of the resultant  $\text{TiO}_2$ /PTAA films showed blue shift ( $\sim 16$  nm, Fig. 6) due to the interaction between the



**Figure 4.** Time dependence of adsorption of PTAA obtained by UV-VIS absorption of APS-glass substrate.



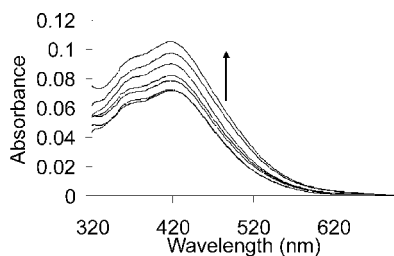


**Figure 5.** UV-VIS absorptions of  $\text{TiO}_2$  at different dipping time on PTAA layer. Inset: magnified absorptions in the region of 200–300 nm.

polymer and  $\text{TiO}_2$  nanoparticle. The interaction can induce changes in conformation of the polymer resulting in these spectral shifts. Highly acidic (6 M HCl)  $\text{TiO}_2$  solutions can also change the conformation of the polymer and leading to a blue shift of the spectrum. Consequently, the dipping time of the PTAA layers on the  $\text{TiO}_2/\text{PTAA}$  was fixed at 5 min. After 5 min of dipping, there was no significant change in the absorption maximum.

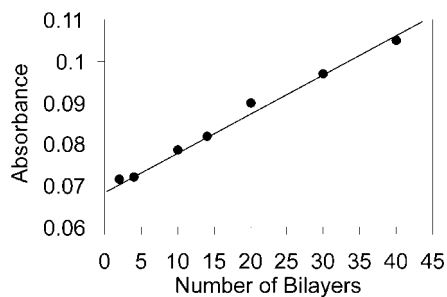
### Multilayers of Nanocrystalline $\text{TiO}_2$ Particles and a Conjugated Polymer

Multilayers of  $\text{TiO}_2/\text{PTAA}$  were built up using the optimized conditions described in the previous section. As alternate layers of PTAA and  $\text{TiO}_2$  were increased, the UV-VIS absorptions of PTAA in the multilayer also increased showing a linear relationship as shown in Figs. 6 and 7. The linear increments of UV-VIS absorption vs. layers support the formation of a reproducible  $\text{TiO}_2/\text{PTAA}$  multilayer. Atomic force microscopic images show different phases of the alternating layers of PTAA and  $\text{TiO}_2$  on APS. Each image of

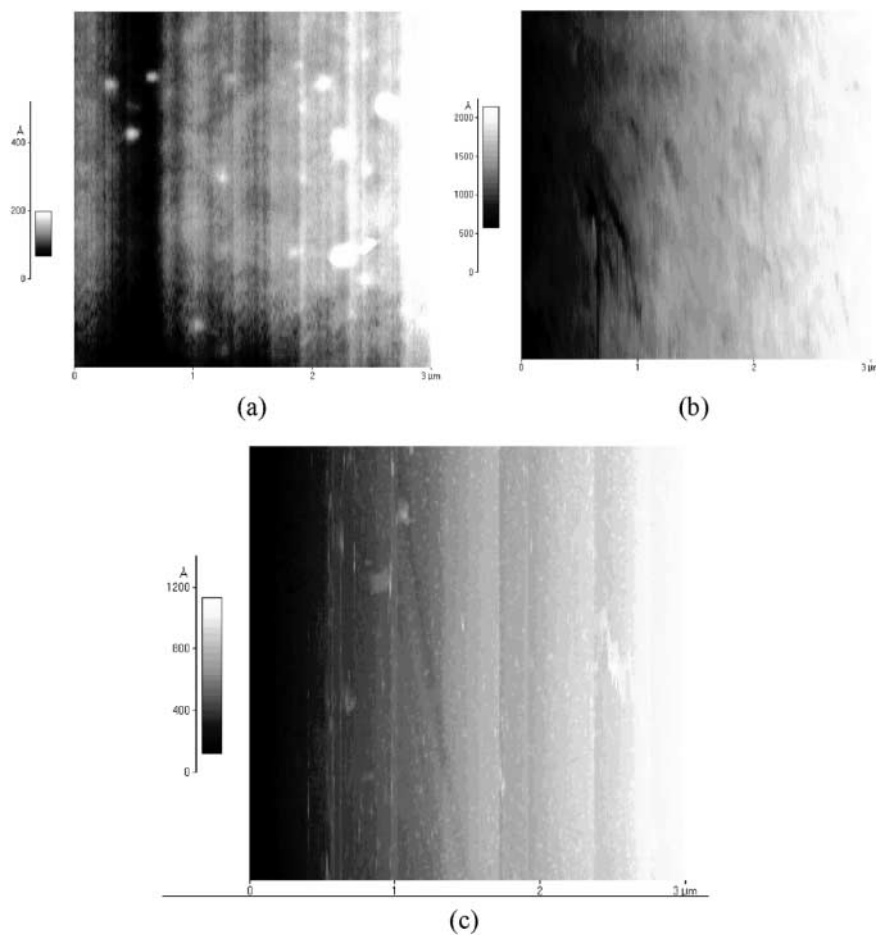


**Figure 6.** UV-VIS absorption spectra of 20 ( $\text{TiO}_2/\text{PTAA}$ ) bilayers.





**Figure 7.** UV-VIS absorption of 20 ( $\text{TiO}_2/\text{PTAA}$ ) bilayers at 420 nm.



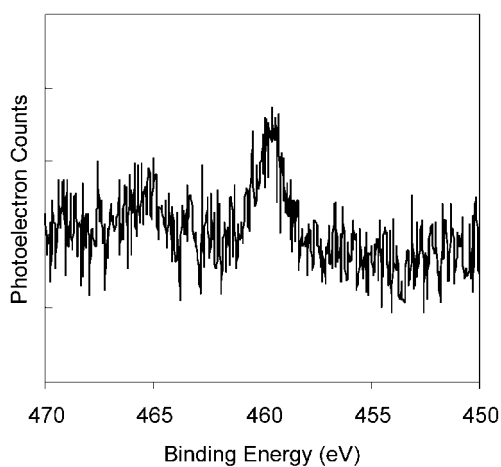
**Figure 8.** Atomic force microscopic images of APS, PTAA, and  $\text{TiO}_2$ , (a) APS/Glass (ave. roughness: 2.4 nm); (b) PTAA/APS/Glass (ave. roughness: 3.3 nm); and (c)  $\text{TiO}_2/\text{PTAA}/\text{APS}/\text{Glass}$  (ave. roughness: 3–12 nm).



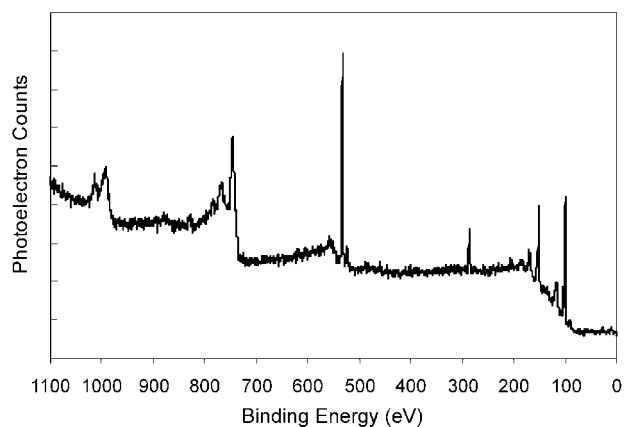


Fig. 8(a)–(c) shows the surface of APS, PTAA on APS, and  $\text{TiO}_2$  on PTAA. The roughness of each layer of APS, PTAA, and  $\text{TiO}_2$  is 2.4, 3.3, and 3–12 nm. Atomic force microscopic images verify that the alternating layers of PTAA and nanoparticle  $\text{TiO}_2$  have been sequentially assembled (Fig. 8).

The presence of  $\text{TiO}_2$  on PTAA layer was confirmed using XPS as shown in Fig. 9. Peaks at 460 and 465 eV were assigned to Ti 2p binding energy [Fig. 9(a)]. The integration of these instrumental analyses strongly supports the feasibility of the ELBL molecular assembly of organic/inorganic materials at nanometer scale.



(a)



(b)

**Figure 9.** X-ray photoelectron spectroscopy of  $\text{TiO}_2$  layer on PTAA/APS.



### CONCLUSION

Synthesis of nanocrystalline TiO<sub>2</sub> particles has been carried out. Size and composition of cationic nanocrystalline TiO<sub>2</sub> particles were analyzed by using TEM and EDXS, respectively. Multilayers of cationic TiO<sub>2</sub> particles and PTAA were fabricated using ionic adsorption and characterized using UV-VIS spectroscopy and XPS. Atomic force microscopy was also used to investigate the structure of the alternating layers and determining surface roughness. Electrostatic layer-by-layer technique could be a useful tool for understanding the mechanism of photoinduced charge transfer in solar cells.

### ACKNOWLEDGMENT

We thank Drs. Ravi Mosurkal and A. K. Jain for helpful discussions and corrections in the paper. The late Professor Sukant K. Tripathy is remembered for his great inspiration to this work.

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