Applied Surface Science 277 (2013) 111–120

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Photoactive layer-by-layer films of cellulose phosphate and titanium dioxide containing phosphotungstic acid

Sajjad Ullah[a], José Javier Sáez Acuña[b], André Avelino Pasa[c], Sara A. Bilmes[d], Maria Elena Vela[e], Guillermo Benitez[e], Ubirajara Pereira Rodrigues-Filho[a,*]

[a] Instituto de Química de São Carlos, Universidade de São Paulo, PO Box 780, São Carlos, São Paulo 13564-970, Brazil
[b] Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo Andre, Sao Paulo, 09210-170, Brazil
[c] Surface and Thin Film Laboratory, Physics Department, Federal University of Santa Catarina, PO Box 476, Florianópolis, SC 88040-900, Brazil
[d] Universidad de Buenos Aires, Facultad Ciencias Exactas y Naturales, Instituto de Química Física de los Materiales, Medio Ambiente y Energía – INQUIMAE, Ciudad Universitaria, Pab. 2, Buenos Aires C1428EHA, Argentina
[e] Laboratorio de Nanoscopías y Fisicoquímica de Superficies, Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Universidad Nacional de La Plata – CONICET, diagonal 113 esquina 64. C.C.16.Suc.4, 1900 La Plata, Argentina

ARTICLE INFO

*Article history:*
Received 5 February 2013
Received in revised form 14 March 2013
Accepted 3 April 2013
Available online 12 April 2013

*Keywords:*
Cellulose phosphate
Layer-by-Layer
Titania
Phosphotungstic acid
Photocatalysis
Photochromism

ABSTRACT

A versatile layer-by-layer (LbL) procedure for the preparation of highly dispersed, adherent and porous multilayer films of $TiO_2$ nanoparticles (NPs) and phosphotungstic acid (HPW) on a variety of substrates at room temperature was developed based on the use of cellulose phosphate (CP) as an efficient and non-conventional polyelectrolyte. UV/vis absorption spectroscopy confirmed the linear and regular growth of the films with the number of immersion cycles and a strong adsorption ability of CP towards $TiO_2$ NPs. FTIR spectroscopy showed that HPW binds to the surface of $TiO_2$ through the oxygen atom at the corner of the Keggin structure. XPS results showed that the interaction between $TiO_2$ and CP is through Ti–O–P linkage. A model is proposed for the $TiO_2$–HPW interaction based on XPS and FTIR results. FEG/SEM study of the surface morphology revealed a porous film structure with a homogenous distribution of the $TiO_2$ NPs induced by CP. HRTEM studies showed that the resulting composite films consist of crystalline anatase and rutile phases and poly-nano-crystalline HPW with a semi-crystalline $TiO_2$–HPW interface. These CP/$TiO_2$ and CP/$TiO_2$/HPW LbL films showed good photoactivity against both saturated and unsaturated species, for instance, stearic acid (SA), crystal violet (CV) and methylene blue (MB) under UV irradiation. The CP/HPW films formed on bacterial cellulose (BC) showed good photochromic response which is enhanced in presence of $TiO_2$ due to an interfacial electron transfer from $TiO_2$ to HPW. This simple and environmentally safe method can be used to form coatings on a variety of surfaces with photoactive $TiO_2$ and $TiO_2$/HPW films.



## 1. Introduction

$TiO_2$ is a wide band-gap semiconductor with extensive use in pollutants remediation as a photocatalyst [1] and other applications such as self-cleaning devices [2], superhydrophilic coatings [3], nanoparticles-coated facemasks to protect against infectious agents [4] and antibacterial coatings on medical devices [5]. Another important use of $TiO_2$ layers is in energy generation; two energy generation devices based on $TiO_2$ have attracted the attention: (a) dye sensitized photovoltaic devices [6] and (b) bio-photo-fuel cells based on biomass degradation [7].

Most of these applications demand the formation of uniform and porous $TiO_2$ layers. Therefore, the study of methodologies to form homogenous layers of $TiO_2$ on different substrates under soft conditions is of great interest. The aim of this work was to study the viability of the use of LbL approach [8] as a soft and affordable procedure to form the mixed anatase/rutile NPs thin films on a variety of substrates using CP as a promising polyelectrolyte. Though the LbL method has the advantages of simplicity, flexibility, low-cost instrumentation and low temperature deposition, it usually requires modification of the substrate's surface to improve adherence of NPs and a longer film deposition time since the amount of the NPs adsorption per deposition cycle is usually low. To overcome the problem of low adsorption, we need a polyelectrolyte or some molecular binder to bind $TiO_2$ NPs together and at the same time to the substrate on which the film is grown. Many binders, both molecular and polymeric, have been used for this purpose such as poly(diallyldimethylammonium chloride), PDDAC [9], poly(acrylic acid), PAA [10], titanium (IV) bis(ammonium lactato) dihydroxide, TALH [11] and phytic acid, PA [12]. However,

* Corresponding author. Tel.: +55 1633739439; fax: +55 1633739982.
*E-mail addresses:* uprf@iqsc.usp.br, biraprfilho@yahoo.fr (U.P. Rodrigues-Filho).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.04.011

the use of most of these polyelectrolytes either requires a strict pH-control of both polyelectrolyte solution and nanoparticles suspension or lack universality with respect to the type of substrates being used. For example, PDDAC, a cationic polyelectrolyte, can be used to form $(PDDAC/TiO_2)_n$ LbL films on quartz by adjusting pH of PDDAC solution to 6.4 and $TiO_2$ dispersed in a pH 10 carbonate–hydrogencarbonate buffer solution [9]. Similarly, poly (acrylic acid) (PAA), a weak anionic polyelectrolyte has been used to form LbL films of $TiO_2$ on cellulose acetate nanofibers but again such deposition require pH-adjustment of both PAA and $TiO_2$ to 2.5 [10]. Kim et al. observed that the thickness and roughness of $(TiO_2/TALH)_n$ LbL films were highly sensitive to a change in pH of TALH [11]. Phytate, an inositol poly-phosphate, has also been used as a molecular binder to build nanostructured $TiO_2$ films by LbL method on ITO [12] and thiol-modified gold electrodes at pH 3 [13]. However, the use of phytate as a binder lacks universality. Thus a best binder is one which reduces the deposition time and/or number of steps involved and can be applied on a variety of substrates. In this study, the polyelectrolyte chosen was CP, a phosphoric ester of cellulose which can act as chelate [14] toward transition metals in a similar fashion as phytate [15]. However, unlike phytate, the use of aqueous suspension of CP does not require any pH-adjustment and rapid deposition of $TiO_2$ NPs occurs into films formed on CP-modified substrates. Moreover, cellulose is a polymer, so it can fold all over the nanoparticles improving their dispersion on different substrates. We are going to demonstrate the ability of CP as a binding and dispersing agent for mounting photoactive $TiO_2$ LbL films on glass, quartz, silicon and bacterial cellulose. Furthermore, polyoxometalates such as HPW find wide application in preparation of photochromic and photocatalytic materials [16–18]. They accept electrons without significant structural changes to yield mixed valence coloured species (heteropolyblues or heteropolybrowns) useful for photochromic application while the generation of OH radical from the reaction of the excited catalyst (HPW) with $H_2O$ upon UV illumination make them important photocatalyst [19,20]. Since, the combined use of HPW and $TiO_2$ is advocated to improve the quantum yield of the $TiO_2$ photoactivity [21] and photochromic response of HPW [22–24], based on the fact that the transfer of electron form the conduction band of $TiO_2$ to HPW is thermodynamically favourable [21], which on one hand can decrease the electron–hole ($e^-$–$h^+$) recombination in $TiO_2$ and on the other hand can assist in the photoreduction of HPW. Thus photochromism and photoactivity of $TiO_2$/HPW system has close connection. Here, we also report the formation of nanocomposite LbL films of HPW and $TiO_2$, $(CP/TiO_2)_n$/HPW, with photocatalytic and photochromic properties using CP as binder. The method for the preparation of such multilayers nanocomposite films based on the use of CP as a binder offers the greater advantages of generality, versatility and practicality since it can be used to form multilayer films of the desired thickness on almost all substrates in a very short time and involves the use of more environmentally safe reagents.

## 2. Materials and methods

### 2.1. Chemicals

Phosphotungstic acid hydrate ($H_3PW_{12}O_{40}\cdot nH_2O$), cellulose phosphate (fine mesh), and Titanium dioxide (10% (wt/vol.) dispersion in water) were purchased from Sigma–Aldrich (USA) and used without any modification or purification. Crystal violet ($C_{25}N_3H_{30}Cl$) was supplied by QHEMIS (SP, Brazil) and stearic acid (SA) was obtained from Labsynth (SP, Brazil). Bacterial cellulose (BC) membranes were from BioFill (Curitiba, Brazil) and cotton quantitative filter paper (MN 640 m) was obtained from Macherey–Nagel (Germany).

### 2.2. Films preparation

The multilayer $(CP/TiO_2)_n$ and $(CP/TiO_2)_n$/HPW films were prepared using the versatile LbL assembly technique employing a disc elevator MA-765 Marconi (Piracicaba, SP, Brazil). The general procedure for all film preparations was to prepare a 0.1% (unless otherwise specified) suspension of $TiO_2$ and 0.1% suspension of CP separately, followed by sonication in an ultrasonic bath for 1 h at room temperature. Only the supernatant layer of CP was used for films preparation. The HPW solution was prepared by adding the weighed amount of HPW to an aqueous solution already adjusted to pH ~ 1 with $HClO_4$ to avoid decomposition of the polyanion into its lacunary compounds [25]. The substrates (quartz, glass plate, Si wafers) were cleaned before use by immersing in Piranha solution (2:1 mixture of $H_2SO_4$ and $H_2O_2$) and heating at 90 °C for 1.5 h followed by rinsing with copious amount of distilled water and drying in a stream of nitrogen. The whole film formation process consisted of (i) surface modification of the substrate and (ii) formation of the films on modified surface. Surface modification step consisted of two immersions, of 2 min each, of the substrate in CP suspension. The onward film formation procedure consisted of a sequence of immersion steps of the CP-modified substrates in (a) $TiO_2$ suspensions for 2 min and (b) CP suspension for 10 s, and the cycle repeated $n$-times to obtain multilayers $(CP/TiO_2)_n$ films. Finally a single immersion of the $(CP/TiO_2)_n$ films in HPW solution (40 mM, unless otherwise specified) was carried out to complete the film formation. The photochromic CP/HPW and CP/HPW/$TiO_2$ films formed on bacterial cellulose (BC), and discussed in Section 4, were prepared by two immersion of BC in CP, followed by one immersion of 2 min in HPW solution and one immersion in 0.05% $TiO_2$ suspension. In all cases, the immersion and withdrawal speed of the disc elevator was adjusted to 150 mm min$^{-1}$ and a drying interval of 90 s was used between each two immersions in $TiO_2$.

### 2.3. Characterisation techniques

UV/Vis Spectra of the films on quartz plates (UQG Optics, UK) were obtained using HP 8452A diode array single beam spectrophotometer (Hewlett Packard, USA). Absorption FTIR spectra in the range 400–4000 cm$^{-1}$ at a spectral resolution of 4 cm$^{-1}$ were acquired for the films on Si windows (UQG Optics, UK) with an MB-102 (Bomem, Canada) spectrometer. Raman spectra of the films formed on cotton quantitative filter paper and BC were collected with a LabRAM HR 800 model Raman Spectrophotometer (Horiba Jobin Yvon) equipped with a camera and CCD detector (model DU420A-OE-325) and using a He–Ne laser (632.81 nm). The spectra were taken between 100 and 4000 cm$^{-1}$ with acquisition time of 300 s, 3 cycles and slit size of 100 μm. SEM images were obtained using JEOL JSM-6701F Scanning Electron Microscope equipped with field emission gun (FEG-SEM) and ZEISS LEO 440 (Cambridge, England) Scanning Electron Microscope equipped with a tungsten filaments and SE Detector (model 7060, Oxford). For HRTEM study, films were formed by immersing the carbon-coated copper grid (CFC-200Cu, Electron Microscopy Sciences, USA) in respective suspensions. HRTEM images were obtained using a JEOL (JEM2100) transmission electron microscope operated at an accelerating voltage of 200 kV and equipped with a $LaB_6$ electron gun and an Energy-Dispersive X-ray (EDX) detector. The TEM image analysis was performed using the Gatan's Digital micrograph image processing programme. X-ray photoelectron spectroscopy (XPS) data were collected using a non-monochromatic Al Kα source (1486.6 eV) XR50, Specs GmbH and a hemispherical electron energy analyzer PHOIBOS 100, Specs GmbH operating at 40 eV pass energy for survey spectra and 20 eV for narrow scans. A two-point calibration of the energy scale was performed using sputtered cleaned gold (Au 4f7/2, binding energy (BE) = 84.00 eV) and copper (Cu 2p3/2,