Applied Surface Science 428 (2018) 566–578

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

# Polyacrylic acid polymer brushes as substrates for the incorporation of anthraquinone derivatives. Unprecedented application of decorated polymer brushes on organocatalysis

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ARTICLE INFO

*Article history:*
Received 24 February 2017
Received in revised form
14 September 2017
Accepted 19 September 2017
Available online 23 September 2017

*Keywords:*
Polymer brushes
Organocatalysis
Functional coatings

ABSTRACT

The synthesis of amino-terminated anthraquinone derivatives and their incorporation onto polymer brushes for the fabrication of silicon-based nanometric functional coatings are described for the first time. The general process involves the covalent grafting of anthraquinone **1** onto two different polymer-brushes by amidation reactions. They are composed by amino- and carboxy-terminated poly(acrylic acid) chains (PAA-$NH_2$- and PAA-COOH, respectively) tethered by one end to an underlying silicon oxide ($SiO_2$) substrate in a polymer brush configuration. A third substrate is fabricated by UV induced hydrosilylation reaction using undecenoic acid as adsorbate on hydrogen-terminated Si(111) surfaces. One- and two-dimensional nuclear magnetic resonance (NMR), FT-IR, MS and X-ray diffraction (XRD) were used to characterize anthraquinone **1**. Ellipsometric and X-ray photoelectron spectroscopy (XPS) measurements demonstrated the presence of the polymer brushes on the silicon wafers, and atomic force microscopy (AFM) was used to study its surface morphology. The covalent linkage between anthraquinone and polymer brushes was proven by XPS and confocal fluorescence microscopy. The resulting surfaces were assayed in the heterogenous organocatalytic transformation of (1*H*)-indole into 3-benzyl indole with moderate yields but with high recyclability.

## 1. Introduction

Polymer brushes are defined as an array of macromolecular chains attached to a surface in certain proximity in which the anchor distance (defined as the space between grafted chains, D) is smaller than twice the radius of gyration (*Rg*) [1,2]. Interestingly, from the early 1990s [3,4] polymer brushes have turned in an important and promising alternative for the immobilization of different specimens and moieties as macromolecules, proteins and nanoparticles on macroscopic surfaces [5–7]. Compared with other methodologies used for the chemical grafting of different specimens on silicon substrates; among others, electron-beam lithography [8], block copolymer micelle nanolithography (BCML) [9], in situ nucleation and growth [10], layer by layer deposition [11], or self-assembled monolayers (SAMs) [12], the incorporation of polymer brushes possesses a great number of advantages. For example, they can be grown on a variety of functional surfaces by exploiting two methodologies, “grafting to” or “grafting from” approaches [13,14]. Moreover, polymer brushes resist hard operational conditions of solvent and temperature. The length, grafting density and the terminal functional group of the polymer brushes can be conveniently modified [15,16]. Additionally, polymer brushes are capable of responding to external stimuli, generally by reversible swelling/deswelling [17]. Consequently, the grafting of polymer brushes on a solid substrate is currently used to control important surface features such as adhesion [18], lubrication [19], wettability [20], friction [21], biocompatibility [22], and colloidal stabilization [23] with the principal aim to be implemented in different technological applications. As was previously mentioned,

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http://dx.doi.org/10.1016/j.apsusc.2017.09.150
0169-4332/

polymer brushes can be fabricated containing different functional groups in their repetitive structure (COOH, $NH_2$, SH, terminal double or triple bonds). This rich functional group diversity has been extensively exploited for the incorporation of different structures via covalent bond, thus serving as a perfect template for the preparation, immobilization, and stabilization of molecules and particles for applications in different areas. For example, Liu et al. deposited gold nanocrystals avoiding particle aggregation on a thin film composed by polymer chains tethered by one end to an underlying substrate, resulting in elongated particle rich domains which was applied sensing purposes [24]. Gupta et al. [25] immobilized silver nanoparticles onto pH-responsive poly(2-vinylpyridine) (P2VP) brushes towards the fabrication of pH nanosensors in aqueous media. Yang et al. used thermo-responsive polymer brushes to immobilized proteins on the surface of silica particles, where the activity of the immobilized proteins could be controlled by the thermo-responsive brushes [26]. More recently, Zheng et al. have used a novel approach based on cylindrical polymer brushes (CPBs) for the incorporation of rare-earth metal cations ($Ln^{3+}$) to be introduced into silica hybrid nanoparticles. These templates resulted in multicomponent systems which possess both visible photoluminescence and T1 contrast enhancement, showing applications as multimodal bioimaging probes [27]. Of particular interest here is the use of polymer brushes as scaffolds for the immobilization of catalysts molecules, always with the perspective of considerably simplifying separation and recycling steps. In this sense, polymer brushes of diverse nature and supported over different solid matrices, have been widely introduced as supports for the covalent grafting of catalysts [28].

In this work, we have covalently attached amino- and carboxy-terminated polyacrylic acid polymer brushes (here denoted as PAA-$NH_2$ and PAA-COOH, respectively), on silicon wafers substrates for the subsequent chemical incorporation of anthraquinone derivatives for organocatalytic applications. In addition, an alternative route based on the photo-induced hydrosilylation reaction of undecenoic acid, yielded the synthesis of hydrocarbonated monolayers with just one molecule of anthraquinone per chain. As far as we know, these new redox-active surfaces represent the first example where high local concentrations of anthraquinone within the brush framework have been fabricated and used in organocatalysis, a process that has lately attracted a great interest in the context of environmentally benign processes, and that has never been catalyzed through this type of nanometric entities.

## 2. Experimental

### 2.1. Materials

Amino-terminated poly(acrylic acid) (PAA-$NH_2$, Mn = 6000 g/mol), carboxy terminated poly (tert-butylacrylate) (PBA–COOH, Mn = 42000 g/mol), and poly(glycidyl methacrylate) (PGMA, Mn = 17500 g/mol) used as an adhesion promoter, were purchased from Polymer Source, Inc. (Canada). N-(3-Dimethylaminopropyl)-N-9-ethylcarbodiimide hydrochloride (EDC), N-hydroxy succinimide (NHS), phosphate buffered saline (PBS) and 10-undecenoic acid (98%) were purchased from Aldrich and used as received. Highly polished single-crystal silicon wafers of {111} orientation with a native $SiO_2$ layer thickness of about 2 nm were obtained from WRS Materials (US). Chloroform, methanol and ethanol were used as received. Millipore water was employed throughout the experiments. The reagents employed in the catalytic runs whether in homogeneous or heterogeneous phase, such as benzylamine, potassium carbonate and (1*H*)-indole were commercially available and used without further purification.

### 2.2. Characterization methods

The thicknesses of the grafted polymers brushes and the 10-undecenoic acid were measured using a SENTECH-402 (Sentech, Germany) at $\lambda = 632$ nm, and an incidence angle of 70°. The ellipsometric box model was used to follow the different preparation steps. The measurements were performed (with an accuracy of ±0.1 nm) for each sample after each step of the modification. The refractive indices used for the box model calculations were 3.858–0.018i, 1.4598, 1.525, 1.527, and 1449 for silicon substrate, native silica layer, PGMA layer, PAA brushes and 10-undecenoic acid, respectively. Thicknesses reported are the average of measurements made from at least three spots on the polymer-modified wafer. XPS was performed with a PHI 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al Kα X-ray source (1486.7 eV) at a takeoff angle (TOA) of 45° from the film surface. The spectrometer was operated at both high and low resolution with windows pass energies of 23.5 and 187.85 eV, respectively. Electron binging energies were calibrated with respect to the C1s line at 284.6 eV (C—C). The atomic concentrations were estimated by the PHI Multipak 5.0 software (Physical Electronics) using the standard procedure including the Shirley background subtraction and correction with the corresponding Scofield atomic sensitivity factors, assuming a homogeneous distribution of the atoms to a depth of a few nanometers. Signal deconvolution was performed first by Shirley background subtraction, followed by nonlinear fitting to mixed Gaussian–Lorentzian function with 80% Gaussian and 20% Lorentzian character.

AFM images and roughness of samples were obtained using an atomic-force microscopy (NX20, Park Systems). We used the tapping mode to study the surface morphology of the films in ambient air. ACTA cantilevers were used for all the measurements. Imaging was done at scan rates ranging from 1.5 to 2.0 Hz. The root mean square roughness of our samples was evaluated from the AFM images recorded.

Fluorescence images were taken at ambient temperature on a Leica TCS SP5 Confocal (Leica). We characterized the localized emission fluorescence from surfaces between 550 and 650 nm, excited with a laser at 458 nm using 20 x objective.

NMR spectra were measured on a Bruker Avance 300 ($^{1}H$, 300.13 MHz; $^{13}C$, 75.47 MHz) using a 5 mm SmartProbe (BBFO $^{1}H$/BB-$^{19}F$). Two-dimensional (gHMQC and gHMBC) correlation spectra were measured on a Bruker Avance 500 spectrometer ($^{1}H$, 500 MHz; $^{13}C$, 125.7 MHz and $^{15}N$, 50.7 MHz) using an inverse TBI $^{1}H$/$^{31}P$/BB. Chemical shifts are given relative to TMS for $^{1}H$ and $^{13}C$, $NH_3$ for $^{15}N$. Unless otherwise stated, standard Bruker software routines (TOPSPIN) were used for the 1D and 2D NMR measurements. The $^{1}H$,$^{15}N$-gHMQC measurements were carried out using the standard sequence with a delay adjusted to a coupling of 7 Hz (71.4 ms), with 32 scans for each of the 160-$t_1$ increments recorded. The delay between increments was set to 1 s.

Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded using a Bruker Optics Vertex 70 spectrometer. The Raman spectra were acquired using a near-infrared (NIR) diode laser at 514 nm (Renishaw inVia Raman spectroscope). The apparatus was equipped with a 100× objective (numerical aperture of 0.90). For the Raman measurements, each spectrum was acquired using 100% of the maximum laser power (12 mW) and co-adding 5 scans of 10 s exposure. The resolution was set at 4 $cm^{-1}$ and the geometry of micro-Raman measurements was 180°.

High resolution mass spectra were recorded on Agilent Technologies LC/MSD TOF and HP 1100 MSD equipment with electrospray ionization. Melting points were recorded on Büchi B-540 capillary melting point apparatus and are uncorrected.

Prismatic red crystals of compound **1** suitable for X-ray experiments were obtained. A crystal was resin epoxy coated and