Langmuir
Article
pubs.acs.org/Langmuir

Polymer−Metal Complexes in Polyelectrolyte Multilayer Films as Catalysts for Oxidation of Toluene

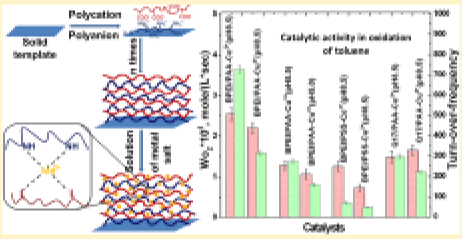
Almagul Mentbayeva,[†] Alyiya Ospanova,[†] Zheneta Tashmuhambetova,[†] Valeria Sokolova,[†] and Svetlana Sukhishvili*,[‡]

[†]Department of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty, 050038, Kazakhstan

[‡]Department of Chemistry, Chemical Biology and Biomedical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030, United States

Supporting Information

ABSTRACT: We report on the binding of metal ions (Me^{2+}; Co^{2+} and Cu^{2+}) with weak polyelectrolyte multilayers (PEMs), as well as on catalytic activity of PEM−Me^{2+} films for oxidation of toluene. Using several types of PEM films constructed using branched polyethyleneimine (BPEI) or quaterinized poly-4-vinylpyridines (QPVPs) as polycations and poly(acrylic acid) (PAA) or poly(styrene sulfonate) (PSS) as polyanions, we found that binding of Co^{2+} and Cu^{2+} ions with a PEM matrix can occur both through coordination to polycationic amino groups and/or ionic binding to polyacid groups. The amount of metal ions loaded within the film increased linearly with film thickness and was strongly dependent on polyelectrolyte type, film assembly pH, and fraction of permanent charge in polymer chains. Among various PEM−Me^{2+} systems, BPEI/PAA−Co^{2+} films assembled at pH 8.5 show the best catalytic performance, probably because of the preservation of high mobility of Co^{2+} ions coordinated to amino groups of BPEI in these films. With BPEI/PAA−Co^{2+} films, we demonstrated that films were highly permeable to reagents and reaction products within hundreds of nanometers of the film bulk; i.e., film catalytic activity increased linearly with layer number up to 30 bilayers and slowed for thicker films.



INTRODUCTION

The alternating layer-by-layer (LbL) deposition of polycations and polyanions at solid substrates is an attractive technique for preparation of nanostructured surface coatings of controlled thickness. As in the majority of cases, LbL films are composed of ionized or ionizable polymers, and such films are able to controllably interact with small ions of various valency. This important property has been used to regulate polymer deposition within films, as well as to construct novel types of polyelectrolyte multilayers (PEMs) acting as ion-selective membranes[1−3] useful in water softening and seawater desalination. Multivalent ions were also used in LbL deposition as polymer "cross-linkers", enabling construction of fluorescent coatings with metal ion sensing capabilities[4] or development of inorganic ion/polymer assemblies for tunable release of biological molecules.[5] Metal ions infiltrated within PEMs can also serve as precursors for synthesis of film-embedded metal or metal oxide nanoparticles useful in optical and electronic applications.[6−9] Recently, this latter approach has also been used to engineer catalytically active PEMs.[10]

Catalyst-carrying PEM films share several common features with more traditional heterogeneous catalysts immobilized at insoluble supports,[11] including ease of catalyst separation, recovery, and reuse. In the case when a catalyst is a multivalent metal ion, immobilization of these ions at/within an insoluble matrix through strong metal ion−polymer binding also prevents contamination of the product with trace amounts of metal ions.[12,13] In addition, earlier approaches to immobilization of metal complexes via covalent attachment to functionalized polymers demonstrated another advantage of polymer-bound metal catalysts, rooted in the unique microenvironments created for the reactants within the polymer support. In particular, improved catalyst stability[14] and increased selectivity for intramolecular reactions[15] have been reported for polymer-matrix-embedded catalytic systems.

As compared with noble metal catalysts used for oxidative conversion of toluene to benzaldehyde, benzyl alcohol, and benzoic acid,[16,17] polymer-supported transition metal complexes (such as those based on Co^{2+}, Cu^{2+}, and Fe^{3+}) present a cheap and efficient alternative enabling oxidation under mild conditions.[18] Usually, complexes of these metals are supported on zeolitic imidazolate frameworks,[19] polystyrene resin,[12] or immobilized by covalent grafting on polymer substrates.[20] Specific examples of polymer/transition metal catalytic complexes used in homogeneous oxidation of organic compounds include complexes of a temperature-responsive

Received: June 22, 2012
Revised: July 18, 2012
Published: July 20, 2012

polymer [poly(*N*-isopropylacrylamide)] with Co^{2+} ions[21] or coordination of Cu^{2+} ions within a cross-linked poly(4-vinylpyridine) matrix.[22]

PEMs have been previously explored as matrices for in situ synthesis of zero-charge noble metal nanoparticles (NPs), such as Pt, Pd, or Au, with an intention to generate large surface area heterogeneous catalyst. One interesting approach has been proposed by Wang and Lee, who synthesized nanosized Pd within PEMs deposited on magnetic nanoparticles and tested these nanocomposite catalysts in the hydrogenation reaction of olefinic alchohols.[10] In this example, however, deposition of multiple layers did not result in enhanced catalytic activity of the nanocomposite, as only Pd NPs within the outermost film layer retained their activity, with PEM-embedded NPs remaining catalytically inactive.[10] In another example, the LbL approach has been used in surface modification of hollow fiber microfiltration membranes through depositing a couple of polyelectrolyte layers, followed by in situ growth of polymer-supported Pd NPs,[23] but thicker, i.e., multilayer, films have not been studied.

Here, we explore the construction of PEM-based catalytic coatings that involves the use of transition metal ions such as Co^{2+} and Cu^{2+} rather than zero-charge noble metal nanoparticles as catalytic centers. Similar to Au and Pd nanoparticles, salts of transition metals are resistant to oxidation, but when compared with noble metal NPs, they present cheaper alternative catalysts for oxidation reactions of organic compounds. We study interactions of transition metal salts with several types of PEMs constructed using weak polyelectrolytes and show that both film assembly conditions and polyelectrolyte type strongly affect a film's capacity to absorb Co^{2+} and Cu^{2+}, as well as the catalytic activity of immobilized ions. We demonstrate that PEM−Me^{2+} (where Me^{2+} represents metal ion) films are highly permeable to reactants and reaction products and are catalytically active within hundreds of nanometers film thickness. The latter is in contrast with earlier reported PEMs with embedded NPs of noble metals, whose catalytic activity was restricted to the outer film surface.

■ EXPERIMENTAL SECTION

Materials. Branched poly(ethyleneimine) (BPEI; M_w 65 kDa), poly(4-vinylpyridine) (P4VP; M_w 160 kDa), 1-propyl bromide, acetonitrile, toluene, Trizma hydrochloride, hydrochloric acid, sodium hydroxide, nitric acid, cobalt(II) chloride, copper(II) chloride, and toluene were purchased from Sigma Aldrich. Acetic acid was received from Fluka. Poly(acrylic acid) (PAA; M_w 450 kDa) and polystyrene sulfonate sodium salt (PSS; M_w 500 kDa) were purchased from Scientific Polymer Products, Inc. All chemicals were used without any further purification. Millipore (Milli-Q system) filtered water with a resistivity of 18.2 MΩ was used in all experiments. Silicon (110) wafers (prime grade, p-type with boron dopant, 525 ± 25 μm thick, with native oxide layer of ~2 nm thick) were bought from Cemat Silicon S.A.

On the basis of the parent P4VP polymer, a series of quaternized products (Q*X* polymers, where *X* denotes a molar percentage of quaternized units) were synthesized by reacting poly(4-vinylpyridine) with 1-propyl bromide in DMSO solution using a procedure described earlier.[24] A typical synthesis procedure included placing a solution of 1 g of P4VP in 16 mL of DMSO in a double-neck flask, freezing the solution in liquid nitrogen, and adding different amounts of 1-propyl bromide to achieve various quaternization degrees. After reaction completion, solutions were purged with nitrogen for 15 min until melted. The flask was sealed and placed in an oil bath at 40 °C for 24 h. Polymer solutions were then precipitated in cold diethyl ether, and the precipitate was filtered, dissolved in water, and dialyzed using a 25 kDa cutoff dialysis membrane. Quaternization degrees of Q*X* polymers were determined using FTIR as described elsewhere.[25] Q*X* polycations with $X < 15$ were not soluble in aqueous solutions at basic pH because of insufficiently small charge density. Therefore, polycations soluble at basic pH values having percentages of quaternized units higher than 15 (Q17, Q25, Q45, and Q65, synthesized with molar ratios of P4VP to C_3H_7Br of 1:0.23, 1:0.5, 1:1, and 1:3.33, respectively) were used in this study.

Multilayer Deposition. PEMs were deposited onto silicon wafers and glass slides. Silicon wafers and glass slides were precleaned under a quartz UV lamp for at least 2 h, soaked in concentrated sulfuric acid for 1 h, and then carefully rinsed with Milli-Q water. Then, the silicon wafers and glass slides were immersed in 0.25 M NaOH solution for 10 min, rinsed with water, and dried under a flow of nitrogen. Preparation of multilayers at the surface of substrates was performed using 0.3 mg/mL of polyelectrolyte solutions at pH 8.5 in 0.01 M Trizma buffer. Polycations and polyanions were allowed to sequentially adsorb for 10 min. Each deposition step was followed by rinsing with buffer solution at the same pH value. All films were then stabilized by thermal cross-linking in an oven at 125 °C for 1 h.

Incorporation of Metal Cations within the Films. To load a metal cation, multilayer films were exposed to 0.05 M solutions of $CoCl_2$ and $CuCl_2$ (in aqueous buffer at pH 5.0 or in ethanol) for 10 h to achieve complete absorption within the films, followed by rinsing with a solvent.

Leachability of Metal from the Films. To study the stability of catalysts within the film, glass slides with deposited metal-loaded films were immersed in 10 mL of acetonitrile at 75 °C and shaken for 2 h. Substrates with deposited films were then removed from the solvent, immersed in fresh acetonitrile, and the shaking cycle was repeated. Acetonitrile solutions were evaporated, and the residue was dissolved in 5 mL of 5% nitric acid solution. To determine the total amount of Co^{2+} or Cu^{2+} ions within the PEM films, samples were treated with UV radiation for 10 h and dissolved in 50 mL of 5% nitric acid. The solutions were then analyzed for Co^{2+} and Cu^{2+} by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Varian Vista MPX instrument. To determine cation concentrations, we used calibration curves obtained for Co^{2+} and Cu^{2+} ions at wavelengths 231.2 and 324.7 nm, respectively.

Scanning Electron Microscopy (SEM). SEM was performed using a Zeiss Auriga Dual-Beam FIB-SEM. Silicon wafers were glued to the SEM stage by a conductive tape. Prior to imaging, Au−Pt alloy was sputtered onto sample surfaces using an RF-plasma chamber for 10 s. The applied voltage was varied from 1 to 3 kV.

Atomic Force Microscopy (AFM). AFM measurements were performed in air at room temperature using a NSCRIPTOR dip pen nanolithography system (Nanoink) operating in ac (tapping) mode.

Phase-Modulated Ellipsometry Measurements of Dry Films. Ellipsometry measurements were performed using a home-built, single-wavelength, phase-modulated ellipsometer at 65° incidence. Optical properties of substrates and oxide layer thickness were determined prior to polymer deposition. In measurements of dry film thickness, the refractive index was fixed at a value of 1.5.

Catalytic Activity Measurements. Oxygen was used as an environmentally benign, readily available oxidant, which acquires selectivity when used with transition metal complexes.[26] Oxidation of toluene was carried out during 1 h at 348 K under an atmospheric pressure of O_2 in a fixed-bed U-shaped reactor (with the total volume of 350 mL) containing 10 mL of a mixture of toluene (0.95 mol/L) and acetonitrile (17.2 mol/L) used as a solvent. The mixture was shaken at 400 times per minute. Prior to the addition of a catalyst, the mixture was purged with oxygen in order to remove air from the system. Both the oxygen buret and the reactor were temperature controlled using a circulating water bath. Concentration of consumed oxygen (Q_{O_2}) (mol/L) was determined from consumption of oxygen using a gas buret (the data points were taken at a 1-min intervals during 1 h) and calculated as the ratio of the amount of consumed oxygen (in mol) to the volume of the reaction mixture (0.01 L).