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Covalently attached multilayer assemblies of diazo-resins and binuclear cobalt phthalocyanines

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Abstract

By using the ionic self-assembly technique, ordered multilayer thin films composed of diazo-resin (DAR) as polycation and water-soluble binuclear cobalt phthalocyaninehexasulfonate (Bi-CoPc) as polyanion were alternately fabricated on quartz, CaF_2 and glassy carbon electrodes (GCEs). Upon ultraviolet irradiation, the adjacent interface of the multilayer films reacted to form a covalently cross-linking structure. The obtained thin films were characterized by ultraviolet (UV)-vis, Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD), atomic force microscope (AFM), surface photovoltage spectra (SPS), and cyclic voltammetry. The results show that the uniform, highly stable and ordered multilayer thin films were formed. The linkage nature between the adjacent interface of the multilayer films converts from ionic to covalent, and, as a result, the stability of the multilayer thin films dramatically improved. The multilayer thin films on GCEs also exhibited excellent electrochemical behavior.

Keywords: Binuclear cobalt phthalocyaninehexasulfonate ammonium salt; Diazo-resin; Ionic self-assembly; Covalently attached multilayer films

1. Introduction

The quest for novel materials for molecular electronics and optoelectronics has prompted scientists to focus their attention on chemically versatile organic molecules that could be easily synthesized, modified, and handled. Recently, small dye molecules, such as porphyrins and phthalocyanines, and their related compounds have aroused great interest due to their potential application in the field of nonlinear optics [1–4], photoelectrochemistry [5–8], molecular metals [9], catalysis [10,11], sensor [12–17], and so on. Although the parent dye molecules have a number of useful properties, to synthesize novel structures for advanced materials preparation is still a challenge. In this respect, many binuclear phthalocyanines have been synthesized and their properties have been reported in the last years [18–22]. These properties of binuclear phthalocyanines were different from the mononuclear species. In addition, much attention has been paid on the formation of ordered thin film assemblies, such as Langmuir–Blodgett (LB) films [23–33] that have their applications as molecular devices. More than 10 years ago, Decher et al. [35–37] extended Iler's pioneering work [34] to fabricate the layer-by-layer organized ultrathin films by alternating deposition of bipolar cationic and anionic compounds (or polyelectrolytes). This layer-by-layer self-assembly as a simple, fast, and versatile technique has become an efficient procedure that made possible fabrication of thin films with the systematic control of both their thicknesses and structures. Ariga et al. [38], Lütt et al. [39], Yoo et al. [40], and Linford et al. [41] reported the incorporation of different dyes into such layered structures by using this method. However, the main defect of the multilayer films from electrostatic force is less stability toward polar solvents or electrolyte aqueous solution. Recently, Sun et al. [42] have reported a new method to fabricate covalently attached multilayer films by the photolysis of the layer-by-layer ionic self-assembled

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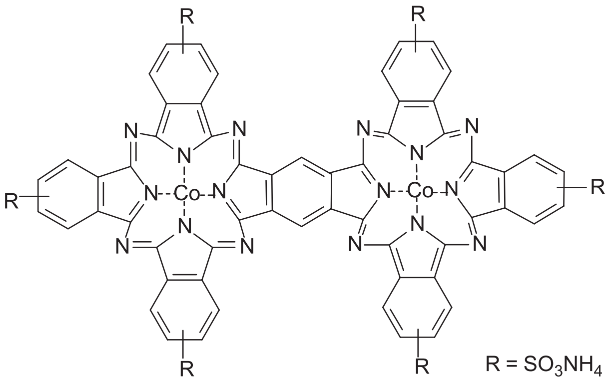
multilayer films containing diazo-resins (DAR). This method combines the simplicity of the ionic self-assembly technique and high stability of the covalently attached multilayer films.

In this paper, we described the preparation of covalently attached multilayer thin films formed by alternating deposition of water-soluble binuclear cobalt phthalocyaninehexasulfonate (Bi-CoPc) and diazo-resins (DAR). The films were fabricated by sequential deposition of Bi-CoPc and DAR on quartz, CaF_2, and glassy carbon electrodes (GCEs). Under ultraviolet (UV) irradiation, the linkage between layers of the multilayer films has been converted from ionic to covalent. The resulting films were thoroughly characterized by UV-vis, Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD), atomic force microscope (AFM), surface photovoltage spectra (SPS), and cyclic voltammetry. The results showed that the formed thin films were uniform and stable, and when deposited on GCEs, they had good electrochemical behavior.

2. Experimental details

Binuclear cobalt phthalocyaninehexasulfonate ammonium salt was synthesized and characterized according to the Chinese Patent [43]. Its structure is shown as Scheme 1. Diazo-resins were synthesized according to the methods described in Refs. [44,45]. 4-Aminobenzoic acid (4-ABA) was purchased form Beijing Chemical (China) and the solution of 4-ABA was freshly prepared for each modification. Poly(dially dimethyl)ammonium chloride (PDDA; M_w: ~400,000–500,000) was obtained form Aldrich. Lithium perchlorate was dried at about 90 °C before use. The absolute ethanol was dried over 3-A molecular sieve before use. All of the other chemicals were analytical agents and used as received. The 0.1 M phosphate buffer solution was kept at a constant ionic strength of 0.1 M KCl. Deionized water was used throughout all experiments. All the glassy apparatus were boiled in 50% sulfuric acid, then washed with deionized water, and dried before use.



Scheme 1. Chemical structure of Bi-CoPc.

The characterization of the films used quartz, CaF_2, or silicon wafer as substrates. All substrates used for sampling were treated before film deposition in the following way: a sample (e.g., silicon wafer) was first immersed in a freshly prepared piranha solution (v/v=1:3, 30% H_2O_2/98% H_2SO_4) and slowly heated until no air bubbles were released from solution. Then, a sample was rinsed with ample water, dried with N_2, and transferred into an aqueous cationic solution of 0.9 vol.% PDDA for 25 min. This procedure yielded positively charged surfaces. The substrate was then successively rinsed with water and dried with N_2 to remove all physically adsorbed materials. The dried substrate was dipped alternately in aqueous solution of Bi-CoPc (1.5 mg ml^{-1}) and DAR (1.5 mg ml^{-1}) for 30 min, with intermediate water rinsing and again N_2 dried. The multilayer films could be formed by repeating the last two steps in a cyclic fashion. The deposition process was carried out in dark to avoid decomposition of the DAR. Finally, the multilayer films were irradiated with a 30-W medium-power mercury lamp at a distance of 15 cm for a given time to ensure that the photoreaction proceeded completely. The fabrication of multilayer films on GCEs was done as follows: a GCE was first polished with emery paper followed by polishing it with alumina (1.0, 0.5, and 0.3 μm), thoroughly washed with water and ethanol and finally dried in a N_2 flow. A clean GCE was then modified by 4-ABA via the C–N covalent bond in an absolute ethanol solution containing 3 mM 4-ABA and 0.1 M $LiClO_4$ by electro-oxidation between 0.0 and +0.9 V (vs. $Ag/Ag^+|0.01$ M $AgNO_3$ in ethanol). At about +0.7 V, 4-ABA was found to be sufficiently oxidized to form an amino cation radical at the GCE surface [46–50]. Thus, the GCE surface was modified with a carboxyl-terminated monolayer, forming a 4-ABA/GCE. After rinsing it with water and drying with N_2, the electrode was then alternately immersed in an aqueous solution of DAR (1.5 mg ml^{-1}) and Bi-CoPc (1.5 mg ml^{-1}) for 30 min, with intermediate water rinsing and N_2 drying. The following procedure was similar to that of fabrication of the multilayer films on quartz, CaF_2 or silicon wafers.

The UV absorbance of the films on quartz was recorded on a Shimadzu 3100 UV-vis near-IR recording spectrophotometer with the selected scan range from 200 to 800 nm. The UV measurement was employed in order to monitor both the self-assembly process and the conversion of ionic into covalent bonds and the stability of the films against their etching by sonicating them in water. Each sample was measured two to three times to ensure the reliability of the results.

The photoreaction between diazonium and sulfonate groups in multilayer films was further confirmed by IR spectroscopy. For the IR measurements, both unirradiated and irradiated 18-bilayer films were prepared on CaF_2 and measured before or after UV irradiation. The measurements were carried out in air at ambient temperature on a Nicolet 5DX FTIR spectrophotometer.

The SPS were used to study the electron transfer process. 4-Bilayer films on silicon (n-type) substrates were used for