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Stimuli-responsive self-assembled multilayer azo thin films: Photo-switchable absorbance and morphological characteristics

Haseeb Shaikh, Mohsin Hassan, Nasir M. Ahmad *

Polymer and Surface Engineering Laboratory, Department of Materials Engineering, School of Chemical and Materials Engineering, National University of Sciences and Technology, Sector H-12, Islamabad, Pakistan

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Abstract

Light has been employed as a source of energy for surface modulation, tuning and control in photo-responsive azo-incorporating self-assembled polyelectrolyte multilayer thin films. A custom built setup for controlled exposure enabled successful photo-switching. Spectral changes were characterized through UV–vis spectroscopy, while scanning electron microscopy technique was employed to study structural properties and response of the films. The effects of chromophore aggregation and dispersion on thin film photo-responsiveness have been studied, with significant contributions made to a recently proposed model correlating structural and spectral properties of the azo thin films. Structural and optical photo-responses have been acquired for surface tuning and modulation, while photo-reversibility is also achieved to control surface properties cyclically.

Keywords: Azobenzene; Methyl orange; Morphology; Photo-switchable; Self-assembled thin films

1. Introduction

The recent advancements in the field of materials science have made ''smart materials'' the buzz of the technological world. Organic photo-responsive materials fall into this category, owing to a variety of property modulations generated through optical stimulus. Such materials have been now actively explored with applications proposed in the field of electronics, biomedical technology and nanomaterials, among many others. Azobenzene has been one of the materials on the forefront of these investigations due to its well established, ultra-fast and clean photo-isomerization [1]. Incorporation of azobenzene into dyes, such as methyl orange (MO), is commercially very common, owing to spectral absorbance in the visible region shown by the –N=N– bond in the azo-structure.

Significant research has been carried out for exploration of further uses of azobenzene for electronic switching [2], photo-motion [3], sensory [4,5], and biological applications [6]. Different fabrication techniques have been employed over the years, with a promising one emerged in the shape of molecular self-assembly through polyelectrolyte multilayer (PEM) fabrication. The PEM fabrication technique offers highly controllable film deposition, in terms of film architecture [7–9], porosity [10], permeability [11] and number of layers coated [12,13]. The technique involves adsorption of oppositely charged layers of polyelectrolytes, producing films that are inherently stable, resulting from irreversible adsorption [14]. Incorporation of different

* Corresponding author. Tel.: +92 5190855213.
E-mail addresses: nasir.ahmad@scme.nust.edu.pk, nasirmahmad@live.com (N.M. Ahmad).

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polymers is possible within the layers without any restriction in properties. The effect of polyelectrolytes on film structure, such as aggregation and orientational order, has also been reported [15], which may lead to changes in spectral properties.

Azobenzene incorporating self-assembled multilayers (SAMUs) have been fabricated through this method for study and characterization. Recent studies have shown presence of H-type aggregation in film structure, leading to spectral peak splitting and shifting from original absorbance ranges [16]. The aggregation phenomenon has been documented previously with regards to Langmuir–Blodgett films as well [17]. Similar results have been obtained with MO incorporation SAMUs. Aggregation in both cases is a consequence of different factors. While Langmuir–Blodgett film properties are a result of the chemistry of the starting materials with azobenzene incorporation through covalent bonding, SAMU films involve physical adsorption, which causes local environment to be a major factor in determining film properties and leaves open the possibility of re-arrangement after deposition. In evidence, presence of cationic polymers and surfactants in self-assembly process has been shown to be responsible for aggregation [18], with the effect of chromophore interaction also being well documented [19,20].

The studies mentioned have been restricted to characterization of the PEM fabrication technique and its bearing on the spectral properties of as-fabricated MO SAMUs, while spectral characteristics have been used to infer morphological traits as well. However, morphological study of the dynamics of sub-molecular chemistry as a result of photo-exposure and its correlation with spectral properties for the given system has not been explored previously in the context of this fabrication technique, to the best of the authors' knowledge. This is vital in terms of utilization of the photo-responsive properties of the thin films. Therefore, the focus of this study is to investigate the photo-kinetic response of MO incorporating thin films, fabricated through PEM formation, in terms of spectroscopic and structural changes in the system by conducting near in situ characterization through UV–vis spectroscopy and scanning electron microscopy (SEM). The changes observed in both are theoretically analyzed and correlated, with dye aggregation and dispersion observed in the system. Through statistical morphological analysis, it is found that absorbance wavelengths are independent of aggregate size, while chemical composition and aggregation type are responsible for determining them. A model presented recently [16] attempted to highlight correlation between structural and spectral properties, primarily looking at effect of aggregation on peak shifting in azo-incorporating SAMU thin films. This study presents a morphological characterization of the system to validate and improve the previous model by incorporating the results of this study. Present work, thus, presents contributions to the science behind MO-SAMUs formed through PEM fabrication technique, enabling informed assessment and exploitation of the potential of such organic photo-responsive systems.

2. Experimentation

2.1. Materials and fabrication of thin films

Methyl orange (Fisher Scientific; >99%), and poly-diallydimethylammonium chloride (PDAC; MW = 180 K; 35% water) (Aldrich) were used as anion and cation with solution concentration of 10^{-4} M to prepare thin films through polyelectrolyte multilayer fabrication technique. Previous work described the typical protocol adopted to prepare the glass microslides (25.4 mm × 76.2 mm × 1 mm) (Fischer) for deposition [16]. The fabrication procedure is depicted in Fig. 1. Different numbers of bi-layers (BL) were fabricated on the glass slides for study. Fig. 2 illustrates the adsorption sequence expected through the mechanism adopted.

2.2. Characterization techniques employed

The absorbance characteristics of the fabricated SAMU thin films were investigated by measuring the UV–vis absorbance spectra using BMS UV-2800 UV–vis spectrophotometer. Morphology and the micro-structure of the prepared films were also studied with the aid of scanning electron microscope (SEM), Jeol JSM 6490A. A custom made sputtering setup was

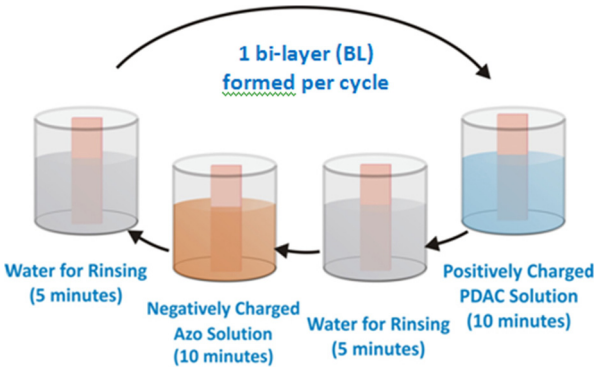

Fig. 1. Film fabrication procedure adopted, depicting the method for alternate adsorption of cationic and anionic polyelectrolytes on glass slide.

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