



Layer-by-layer assembled highly absorbing hundred-layer films containing a phthalocyanine dye: Fabrication and photosensibilization by thermal treatment



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ABSTRACT

Highly absorbing hundred-layer films based on poly(diallyldimethylammonium chloride) (PDADMAC) of various molecular weights and on sulfonated copper phthalocyanine (CuPcTs) were prepared using layer-by-layer assembly. The multilayer films grew linearly up to 54 bilayers, indicating that the same amount of CuPcTs was adsorbed at each deposition step. This amount, however, was dependent on the molecular weight of PDADMAC in the range 100–500 kDa: the higher the molecular weight, the more CuPcTs molecules were adsorbed. This can be explained by the larger surface charge number density specific to longer polymer chains. Domains of pure PDADMAC and of the PDADMAC/CuPcTs complex were formed in the films during the assembly. Uniform distribution of CuPcTs over the films could be achieved by thermal treatment, leading to an $\alpha \rightarrow \beta$ phase transition in phthalocyanine at 300 °C. Annealing caused changes in the film absorbance spectra, resulting in a 30-nm red shift of the peak maxima and in a strong (up to 62%) decrease in optical density. Thermogravimetric analysis revealed thermodegradation of PDADMAC during annealing above 270 °C, giving rise to micrometer-sized cracks within the films, as evidenced by scanning electron microscopy.

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1. Introduction

Nano- and microstructured thin films containing organic materials (such as phthalocyanine dyes) serve as components of highly integrated devices in different fields of science and technology, including optoelectronics [1–7]. A wide variety of methods can be used to fabricate such coatings. Layer-by-layer (LbL) assembly is one of the simplest techniques to design multilayer films with controlled thickness and chemical composition [8]. This approach makes it possible to use substrates of various shapes and dimensions (up to the micro- and nano-scale) for the fabrication of planar and curved nanomaterials with required properties [9–16]. The LbL technique has been employed to pattern surfaces with various particles, including microcapsules, micelles, and nanoparticles [17–22]. The nature of the polyelectrolytes used in LbL assembly is important, owing to the strong influence of interpolyelectrolyte complexation [23,24]. The thickness of deposited layers

depends strongly on polyelectrolyte molecular weight (MW), surface charge density, and polymer transport to the film surface [25–28]. The formation of domains or phase separation can take place during layer deposition [27,29,30] or as a result of some post-treatment [31–33], leading to film microstructurization. In the case of phthalocyanine-polymer films, thermal treatment can cause both phase separation and formation of a homogeneous phase [29].

LbL films containing conductive polymers, carbon nanostructures (single- or multiwall tubes, fullerenes), and dyes can serve as electrodes or photoactive layers in multilayer photovoltaic converters [7,34–40]. Indeed, the hybrid photoelement structure can be fabricated only by all-solution processes [7,34–40]. The main advantages of such multilayer organic elements are that they are cheap, easy to process, and ecologically safe; however, the photovoltaic characteristics are not satisfactory. Therefore, the next promising direction in optoelectronics (apart from the creation of thin-film hybrid solar cells) is the development of unconventionally constructed photoelements [41–46]. Modern approaches to modifying photovoltaic converters are based on the use of textured templates [41], nanowire arrays [42], plasmonic nanoparticles [45], spherically shaped elements [43], and photonic crystal structures [44]. Alternative constructions with the abovementioned changes in design can provide enhanced photovoltaic converter efficiency. The performance improvement can be achieved both by

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optimizing absorbance spectra and by enlarging the space-charge region (increasing the photogenerated charge separation area). Surface patterning reduces the reflection and increases the number of adsorbed photons [41–44], leading to enhanced efficiency.

A nonconventional design for a thin-film photovoltaic converter was suggested recently by Regan et al. [46]. The proposed construction is a screening-engineered field-effect photoelement based on a single-doped inorganic semiconductor [46]. The multilayer architecture is similar to the metal–insulator–semiconductor structure and consists of a bottom contact on a solid substrate, a single-doped semiconductor layer, an ultrathin top contact, and two transparent layers: a gate contact and a gate insulator. This unconventional construction shows acceptable characteristics, which can be additionally improved by applying an external voltage to the gate contact and blocking the recombination current [46].

Regan et al.'s [46] work inspired us and became a starting point for this research. Si and Cu₂O films can be replaced with an organic layer (such as a sulfonated phthalocyanine complex acting as a single-doped semiconductor), so that the described construction [46] could be fabricated using an all-solution process. One challenge is to obtain the LbL photoactive organic layers with a proper thickness of about 30–200 nm [1–3] in general for hybrid solar cells based on fullerene–phthalocyanine evaporated films. Thus, to prepare sufficiently thick phthalocyanine films by LbL assembly, one should use an acceptable cationic polyelectrolyte [e.g., poly(diallyldimethylammonium chloride) (PDADMAC), poly(ethyleneimine) (PEI), poly(allyl amine hydrochloride) (PAH), or polyaniline] coupled to an anionic phthalocyanine to consecutively deposit the necessary number of layers. For a single LbL bilayer, a thickness of 0.8–1.2 nm has been reported for MPCts/PDADMAC and MPCts/PAH structures [47–49] (here, MPCts is sulfonated phthalocyanine of a certain metal). Thus, it is important to fabricate hundred-layer structures to achieve a proper thickness for a photoactive semiconductor film. Note that CuPcTs/PDADMAC multilayers possess electrochromic as well as photovoltaic properties [49].

Fabrication of thick micrometer-sized polyelectrolyte multilayers with large numbers of bilayers (tens or more) has been demonstrated previously for different polymers [8,50]. Such thick films usually serve as reservoirs for bioactive molecules and are utilized in various biological applications to load, store, and release biomolecules to biological cells [51–54], also upon external stimulation [55,56]. However, the literature describing the LbL fabrication of hundred-layer films, especially thick coatings containing phthalocyanines, is very limited [47,49].

LbL assembly was applied to fabricate highly absorbing hundred-layer organic semiconductor coatings from PDADMAC as a cationic component and from sulfonated copper phthalocyanine (CuPcTs) as an anionic single-doped organic semiconductor. PDADMACs of different MWs were used to examine the effect of the polymer MW on the thickness of deposited films [25,50,54,57–62].

The choice of phthalocyanine as an anion is driven by its photovoltaic properties and its strong optical absorbance between 550 and 750 nm [47,63–73]. In fact, phthalocyanine films can be in the amorphous α -phase or in the crystalline β -phase, depending on the fabrication approach. As both α - and β -phthalocyanines demonstrate photogeneration, both forms are used in photovoltaic devices. In both cases, the planar phthalocyanine macrocyclic molecules are arranged in one-dimensional stacks; however, the relative arrangement of these stacks and the stacking overlap of adjacent molecules differ between α - and β -phases. The main distinction between the two phases is the difference in the stacking axis of the phthalocyanine molecules and the normal to the surface plane of the dye molecule; this can be distinguished by using a strong diffractive peak near 6.9° in X-ray diffraction spectra of phthalocyanine films [69,70]. The overlap between the neighboring molecular stacks in the β -phase is smaller (0.38 nm), as compared with that for the α -phase (0.48 nm). The closer spacing of the molecular stacks and the orientation of molecules lying flat (face-down) on the substrate (in contrast to the standing-up (on-edge)

molecule arrangement) facilitate the electron transport that is of importance for photovoltaic converter efficiency. The usual way to obtain β -phase phthalocyanine films is to employ high-temperature evaporation techniques and special conditions (i.e., heating of substrates), resulting in high crystallinity and good electrical properties of the structures. Alternatively, a high-temperature postannealing is applied to amorphous phthalocyanine films (e.g., those prepared by wet chemical deposition techniques) to cause an $\alpha \rightarrow \beta$ phase transition accompanied by improvement of the molecular structure as well as spectral and electrical characteristics. The influence of annealing on evaporated pure phthalocyanine films has been studied [66–70]. For 30–150-nm-thick coatings prepared by vacuum evaporation, a phase transition was achieved if the temperatures from 240 to 250 °C [68,69] to 300 °C [66] were used. The minimum known phase transition temperature is 200 °C for 80-nm-thick vacuum-evaporated ZnPc films [70]. The phase transition point for phthalocyanine–polyelectrolyte multilayer films may differ from that for pure phthalocyanine owing to the presence of the polyelectrolyte matrix, which can lead to phase separation [27,29–33] and affect phthalocyanine thermostability [47].

In this work, we examine the high-temperature behavior of hundred-layer PEI/CuPcTs/(PDADMAC/CuPcTs)_n films, taking into account film composition and morphology.

2. Experimental details

The general definition of the LbL method, used to prepare multilayer thin-film structures on solid substrates, was first given by Decher and Hong [8]. A detailed description of this process in the context of this work is given below.

2.1. Materials

Poly(ethyleneimine) (MW 600–1000 kDa), poly(diallyldimethylammonium chloride) (MW <100 kDa, 35 wt.%), poly(diallyldimethylammonium chloride) (MWs 100–200 kDa, 200–350 kDa, and 400–500 kDa; 20 wt.%), and tetrasulfonated copper phthalocyanine (CuPcTs) were purchased from Sigma-Aldrich and used without further purification. Aqueous polymer solutions (2 mg mL⁻¹) and homogeneous dispersions of CuPcTs (0.25 mg mL⁻¹) were prepared in deionized water. Glass slides coated with fluorine-doped tin oxide (FTO) (20 × 30 × 3.2 mm³; surface resistance, 8 Ω square⁻¹; transmittance, 80–81.5% in the visible range; Sigma-Aldrich) were used as substrates to assemble the films.

2.2. Deposition of multilayer thin films

Thin films of polyelectrolytes and sulfonated copper phthalocyanine were prepared by LbL assembly [8] on ethanol-precleaned glass slides coated with conductive FTO [74,75]. Films were deposited onto the slides by vertical immersion of the glass substrate into PDADMAC and CuPcTs solutions at a controlled rate (5 mm min⁻¹) by using a dipping mechanism (part of the KSV Nima Langmuir–Blodgett Trough). The first layer was made by adsorption of the cationic polyelectrolyte (2 mg mL⁻¹ water solution), with subsequent three rinsing steps in deionized water. The second layer was prepared by adsorption of anionic copper phthalocyanine (0.25 mg mL⁻¹ water solution) followed by three rinsing steps. The fabricated multilayer structure was air dried during a variable period after each bilayer deposition. Either long-time drying (1 min for every layer and 20 min after every 3 bilayers) or short-time drying (1 min for every layer) was used during LbL deposition. The deposition procedure was repeated *n* times to assemble (PDADMAC/CuPcTs)_n films. In this way, glass/FTO/PEI/CuPcTs/(PDADMAC/CuPcTs)_n structures (*n*, 15–54) were obtained (Table 1).

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