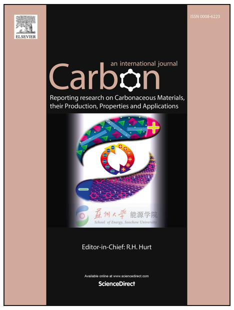

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Stability and dye inclusion of graphene oxide/polyelectrolyte layer-by-layer self-assembled films in saline, acidic and basic aqueous solutions

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Abstract

We demonstrate that a simple spectrophotometric method can be efficiently applied for the characterization of structural and chemical stability and adsorption properties of composite graphene oxide (GO) films in various solutions. The immersion stability of GO layer-by-layer (LbL) self-assembled with a polycation into ultrathin multilayered films was studied in water and in concentrated salty, acidic and basic solutions by UV-visible spectroscopy. These films were found to retain both their chemical stability and physical integrity in water, salt and HCl solutions with a slight rearrangement of the nanoscale structure as shown by the change in their visible spectrum. However, immersion into NaOH solutions above molar concentration led to the deconstruction of the multilayer structure by base-induced deoxygenation of GO. The adsorption of methylene blue on polymer/GO LbL films of various thicknesses revealed that the multilayers are largely impermeable towards this cationic dye.

1. Introduction

Ultrathin multilayers composed of polyelectrolytes and graphene oxide (GO) have been prepared and studied already before the advent of „graphene era" [1,2]. The primary application of these materials was to create electrically conductive graphitic coatings on solid supports [3]. Recently, however, the beneficial properties of GO layer-by-layer (LbL) incorporated into polymeric films have been exploited for a wide variety of potential applications [4]. For example, they have been consistently reported to exhibit enhanced barrier properties towards common gases such as oxygen [5,6] and hydrogen [7,8], while

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maintaining superior transmission towards water vapor [5]. As part of the anode interfacial layer of an organic solar cell, it improved the work function of the ITO anode by providing better contact with the active layer [9]. GO/polymer films were proposed as well for electromagnetic shielding [10], humidity sensing [11] or drug delivery [12,13], both on macroscopic and on microscopic supports, such as cotton fabrics [14] or erythrocyte cells [13].

Most of these applications require that the LbL film is in direct contact with a liquid phase, most often water or an aqueous solution. Obviously, the integrity of the multilayer in a given solution and temperature interval must be ensured in order to be practically useful for e.g. water-solute separation. Although the mechanical stability has been characterized by both macro and microtribological test methods in dry state [15,16], there has been much less emphasis on the investigation of chemical stability of polymer/graphene oxide composite nanofilms in contact with water and in solutions of potentially reactive chemical substances. Low stability of LbL films in certain solutions (e.g. due to disintegration or chemical modification) is one of the possible limiting factors for their potential applications. It is known that multilayered GO membranes dissolve in certain solutions of high pH [17,18] or may transform into jelly-like state, e.g. when cooled in liquid acetonitrile [18]. It is likely also that the stability of GO multilayers depends also on the particular method of their deposition and processing.

Up to date, the stability of the multilayered structure has only been investigated in solutions of very few kinds of compounds. The most notable is sodium hypochlorite [13,19], since this agent is of general use for the oxidative cleaning (removal of fouling) of nanofiltration membranes, and its effect is a major factor in determining the membrane lifetime. LbL-deposited graphene-based nanofilms cross-linked with glutaraldehyde were also immersed in simple inorganic compounds and they were shown to resist the attack of H_2SO_4 even at 5 M concentration [20]. However, the application of composite GO multilayers could be much easier if they were stable in strongly acidic or salty solutions without the need of additional chemical cross-linking.

Another rather scarcely investigated but important issue related with immersion stability of LbL films is the penetration of molecules into and through the multilayered structure. Dye molecules such as acridine orange, rhodamine or methylene blue are readily chosen as test molecules owing to the ease of their detection. Dye-containing GO films have been fabricated previously and their photophysical and morphological properties were investigated [21,22]. However, they contained the photoactive organic molecules by direct incorporation upon the layer-by-layer build-up, and it is an open question whether their indirect inclusion (by adsorption from aqueous dye solutions) into already prepared GO/polymer films is possible.

This paper reports on the immersion stability of graphene oxide/cationic polyelectrolyte (polydiallyldimethylammonium chloride) layer-by-layer self-assembled ultrathin films revealed by rapid and precise spectrophotometric investigation under relevant solution conditions (acidic, alkaline and saline). The incorporation of a common and well-studied dye, methylene blue (MB), into the multilayers by diffusion from the contacting liquid phase was also studied, giving important information on the permeability and internal structure of the polymer/GO nanofilm.

2. Experimental

2.1. Materials

Graphite oxide was synthesized by Brodie’s method from a sieved fraction (250-500 µm) of natural graphite flakes (Graphitwerk, Kropfmühl AG, Germany). It was the moderately oxidized sample with $C_2O_{0.77}H_{0.29}$ chemical formula denoted as “GO1’ in a previous publication [23]. This sample has a basal spacing of 0.69 nm at 70% relative humidity content of ambient atmosphere, and an average number of 35 graphene oxide layers in the unexfoliated particles as shown by X-ray diffraction. As a cationic polymer, polydiallyldimethylammonium chloride was used which will be abbreviated here as PDDA. It was obtained as a 20 wt% aqueous solution from Aldrich Chemicals (MW = 100,000-200,000). The inorganic compounds used as solutes for the chemical stability tests and for pH and ionic strength settling, along with methylene blue (MB), were of analytic grade purchased from Molar Chemicals and were used as such in the experimental work. Ultrapure water obtained by membrane filtration (Millipore) was used for all experiments.

2.2. Layer-by-layer deposition

For the controlled and reproducible deposition of LbL films, precautions were taken to (i) clean all glassware and quartz supports (25×40 mm) with chromic acid immediately before use and (ii) to set the ionic strength of the graphene oxide suspensions to 0.01 M by a more concentrated NaCl solution.

The graphene oxide (GO) dispersion was prepared from graphite oxide by wet-grinding a 1 g/L aqueous slurry for 7 hours in a vibration ball mill. This stock was diluted to a concentration of 0.05 g/L including droplets of NaOH solutions by which the pH was set to 9 ± 0.1 after sonication for 5 minutes and stirring for 1 hour. The polyelectrolyte solution of 1 g/L concentration was also used at pH = 9 during the film deposition.

PDDA/GO multilayers were assembled over hydrophilic quartz (Q) supports by the already common LbL procedure with the following specific details. The first layer to be deposited was PDDA, created by dipping the substrate into the polymer solution for 5 minutes and subsequent rinsing with water and drying in N_2 stream. The next layer consisting of oppositely charged GO platelets were deposited on top of the PDDA monolayer by immersion into the GO suspension for 5 minutes (here, the liquid phase was gently but continuously stirred) and applying the same cleaning/drying step. Further bilayers were then assembled over the first one until the desired number of bilayers (n) was reached.

2.3. Immersion experiments

Substrates coated with the PDDA/GO nanolayers were immersed into different aqueous solutions at room temperature unless otherwise stated. Stirring was not applied for any of these cases. For the chemical stability tests, nanofilms containing 5 PDDA/GO repeating units were used. They were dipped into the test solutions rapidly using tweezers, and were removed similarly followed by washing with water and drying. For MB inclusion tests, nanofilms of different bilayer numbers were used. In this case, immersion steps were carried out by a home-made automated dipping apparatus with programmable cycle parameters. The set dipping rate (2 mm/min) enabled for a more controlled immersion and withdrawal, due to which it was unnecessary to remove the excess liquid by washing and drying.

2.4. Characterization

The layer-by-layer build-up and changes in the structure of GO films were characterized by UV-visible spectrophotometry. A dual-beam spectrophotometer was used (Uvikon 930, Kontron Instruments, Switzerland). First, baseline was recorded with two empty cell holders, and spectra were then taken with samples fixed perpendicular to the beam path. Since the as-recorded spectra contain the contribution from the quartz support (Supporting Figure S1), the respective cleaned slides were also subjected to measurements and their spectra were subtracted from the ones containing the nanofilms to obtain spectra that are only characteristic for the “support-free” LbL structures. This approach is validated by the fact that the absorbances of quartz were less than 0.1 within the whole spectral range investigated. However, we must note here that if very thick or less transparent supports (e.g. glass in the UV range) were used, photometry could not be used for the quantitative characterization of multilayer structure.

The atomic force microscopy (AFM) image of a self-assembled polymer/graphene oxide bilayer was recorded by a Digital Instruments Nanoscope III Multimode atomic force microscope operating in tapping mode. A small piece (ca 1 × 1 cm) of dry quartz slide, onto which a bilayer was previously deposited, was fixed to the sample holder, and a 5 µm × 5 µm area was scanned by etched silicon tapping mode tip (125 µm length) purchased from Veeco GmbH.

3. Results

3.1. Layer-by-layer build-up

Figure 1 shows the UV-visible spectra of PDDA/GO films upon their progressive multilayer construction. Independently of the number of deposition steps, two characteristic absorption bands were observed; one at 235 nm, and a weaker one appearing at about 300 nm. The first one is commonly attributed to the π-π^* transition of the aromatic carbon-carbon bond of the GO structure [24,25]. The other one refers to the excitation (involving nonbonding and π^* orbitals) of C=O groups, which usually appears as a shoulder but for these films they give rise to a definite band even for a monolayer of graphene oxide. PDDA was found to be practically transparent in the whole spectral range.

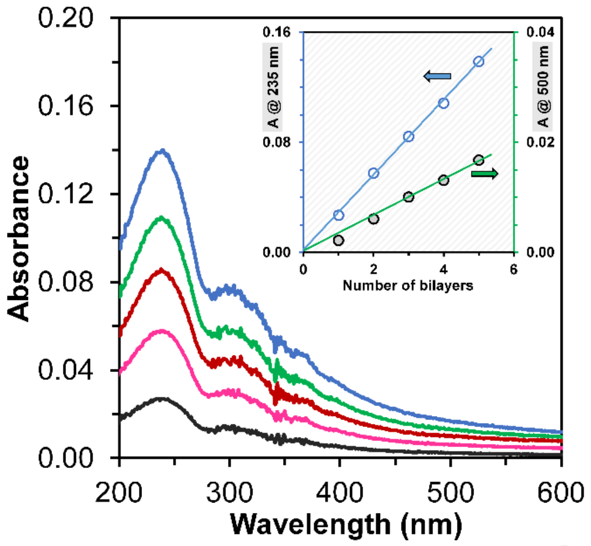

Fig. 1 – UV-visible spectra of (PDDA/GO)$_n$ films of different bilayer numbers (n = 1-5). The inset shows the build-up functions at 235 and 500 nm.

The construction of films are well characterized by the build-up functions (Figure 1 inset) showing their absorbances at two distinct wavelengths (one in the UV and one in the visible region) as a function of the bilayer number. Apparently, at both wavelengths, the build-up functions are linear, showing that the layer-by-layer construction is uniform. Thicker films up to n = 15 (data not shown for clarity) exhibited the same characteristics. This implies that the deposited amount of GO per immersion cycle is constant and the charge-regulated build-up proceeds without a significant change in the nanoscale ordering of film-forming building blocks in the dry state. Upon comparison with the build-up functions of PDDA/GO films published in our earlier study [3], one may reveal that they are much steeper, indicating that the present nanostructures are much thinner than those assembled from the same GO samples at identical polymer concentrations. Although the differences in the molecular weight of the cationic polymer samples could have a slight influence on the thickness, we think that other factors such as the deposition time and the GO suspension concentration could have more related effect. However, more noteworthy, the pH was not set in [3], and the original, acidic suspension (pH = 4) of higher concentration (1 g/L) must have contained a large proportion of multilayered GO particles (samples prepared by Brodie method do not completely exfoliate at pH = 4). On the other hand, the present dispersion of lower concentration used for GO deposition contained unilamellar platelets at pH = 9, leading to significantly thinner LbL sandwich structures.

The nanostructure of a one-bilayer composite nanofilm has been characterized by atomic force microscopy. Topographic and cantilever deflection micrographs from a 5 µm × µm area are shown in Figure 2. They reveal irregularly shaped, partially overlapping graphene oxide nanosheets (yellow areas) on top of the polymer-coated quartz surface (red/orange areas). Some of these sheets are wrinkled, but the majority of them are flat unilamellar graphene oxide particles with typical length scales of several tens to several hundreds of nanometers. Area analysis of the image of the bare support (not shown) afforded root-mean-square roughness of 0.3 nm. This is clearly lower than the roughness found for the bilayer-modified surface (1 nm) which is induced by the partial surface coverage of GO.

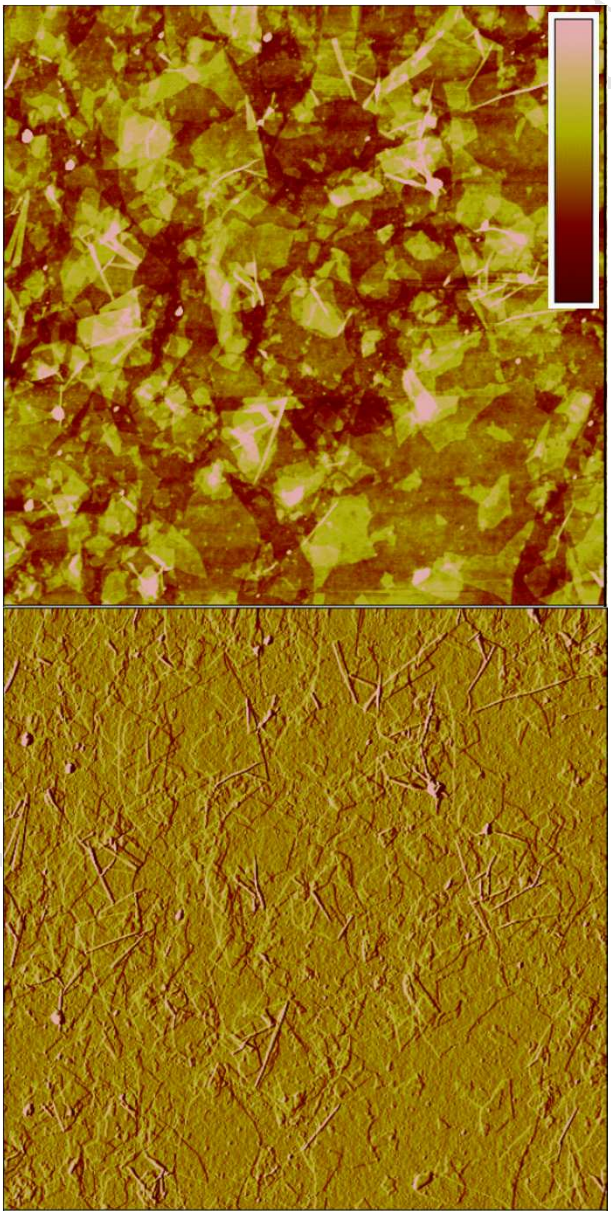

Fig. 2 – AFM images of a (PDDA/GO) bilayer with 5 × 5 µm lateral dimensions. Top: topographic image with scale bar of 6 nm, bottom: cantilever deflection image of the same area.

3.2. Immersion stability at ambient temperature

UV-visible spectroscopy provides sufficient detail on the structure of the present nanoscale coatings because only graphene oxide particles absorb light in both wavelength regions allowing for selective assessment of their deposited amount. However, a change in the nanoscale structure brought by structural reorganization (e.g. interdigitation of polymer chains or partial restacking of GO nanosheets) or disintegration of the alternating monolayers would lead to spectral changes and a concomitant variation in the ratio of the absorbances in the UV and visible region. Therefore, to obtain meaningful information on the immersion stability of the multilayers, one must monitor the absorbances simultaneously at least at two chosen (UV and visible) wavelengths. This is firstly demonstrated in Figure 3 and its inset comparing the spectral changes of $(PDDA/GO)_5$ films before and after dipping into water for one hour.

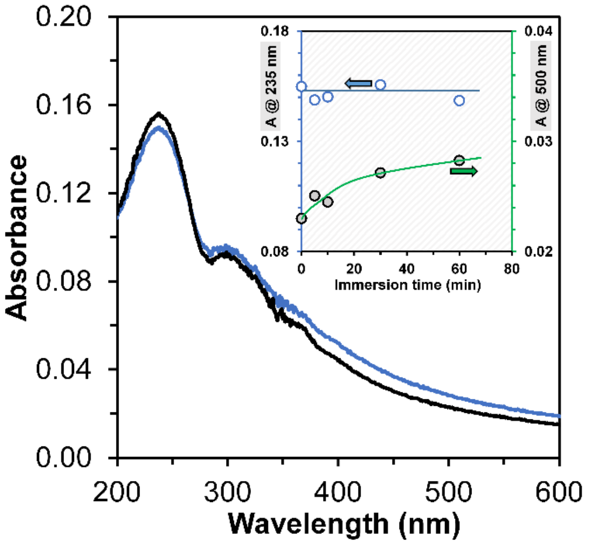

Fig. 3 – UV-visible spectra of $(PDDA/GO)_5$ films immersed into water for 0 min (black) and 60 min (blue). The inset shows the change of absorbances at 235 and 500 nm with the dipping time.

While the light absorption have not changed much in the UV region, it has clearly shown a total of ca. 20% increase at 500 nm after 60 minutes. This implies that the GO content of $(PDDA/GO)_5$ remained practically the same, but its nanostructure was affected simply by wetting with pure water for times longer than the rinsing time of several or several tens of seconds normally used during LbL deposition. Very likely, the rehydration of the multilayered structure is a relatively slow process even for films containing only a few bilayers. When these films gradually reach the equilibrium hydration state, the GO particles may be able to move laterally in the swollen polyelectrolyte matrix and partially restack, leading to an increased light scattering. However, hydration cannot overbalance the strong attractive forces holding together the adjacent layers, so neither the polymer molecules, nor GO platelets can be desorbed from the quartz surface.

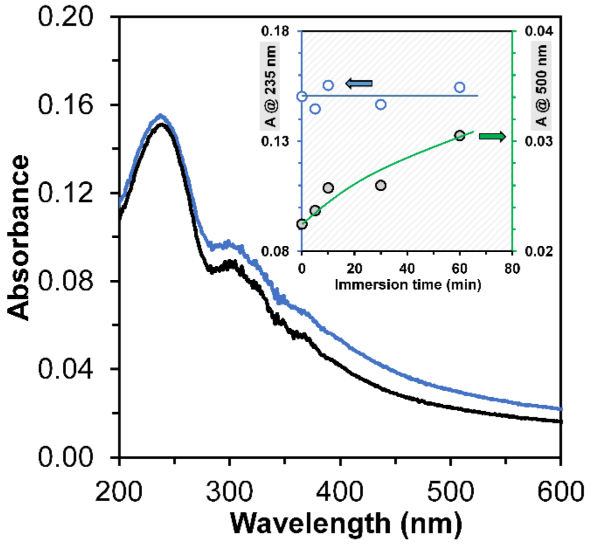

Fig. 4 – UV-visible spectra of (PDDA/GO)$_5$ films immersed into 2 M NaCl solution for 0 min (black) and 60 min (blue). The inset shows the change of the absorbances at 235 and 500 nm with the dipping time.

Figure 4 shows the changes in the optical characteristics of the polymer/graphene oxide film in contact with 2 M NaCl solution. Quite surprisingly, the optical features were very similar to that found for the water-immersed sample, except for a slightly more pronounced absorbance increase at 500 nm. This indicates that the polymer-sandwiched GO assembly was not removed from the surface even at very high ionic strengths, in stark contrast to several studies reported earlier for oppositely charged polyelectrolytes [26,27]. For example, Dubas and Schlenoff have found that a 20-bilayer PDDA/Na-polyacrylate nanofilm is stable to salt concentrations up to ca. 0.4 M, above which its thickness gradually decreases and the system is completely removed from the support at 0.6 M forming loosely associated polyelectrolyte complexes in the rinsing solution [28].

The immersion stability was also monitored under acidic conditions (Figure 5). Although the spectra of the related films before and after dipping into 2 M HCl solution for an hour are almost completely overlapped, a closer inspection of the inset of Figure 5 points out that the absorbances both at 235 and 500 nm are dropped after 5 minutes and then start to increase gradually. To check whether this effect is not an artefact caused by in-plane variations of the optical film thickness, we have measured the spectra of all dry, 5-bilayer assemblies (shown in Figures 1 and 3-8) at eight different positions. It was found that while the total absorbances at 235 nm showed considerable sample-to-sample variations (from 0.102 to 0.155), there was only a negligible lateral heterogeneity in the film thickness (0.24%). Therefore, the spectral changes of solution-immersed films must have been caused by the aforementioned change in the nanostructure and/or partial dissolution. In HCl solution, it seems that both were effective. Soon after immersion, absorbances in the UV and visible decreased indicating a slight redispersion of GO sheets from the topmost part of nanofilms, but the associated decrease was compensated further on, by the successive increase of light scattering.

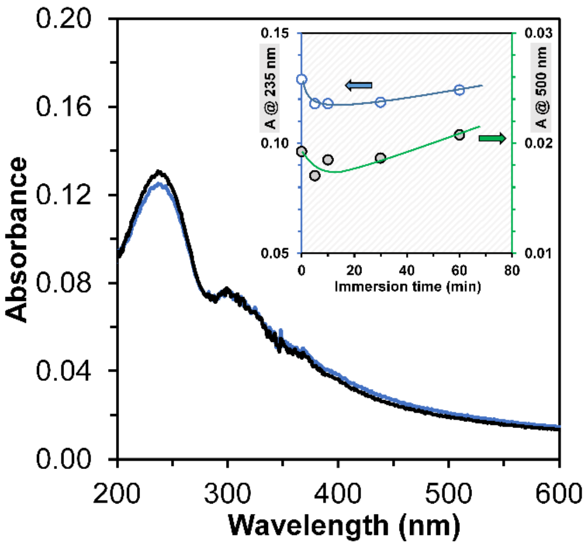

Fig. 5 – UV-visible spectra of (PDDA/GO)$_5$ films immersed into 2 M HCl solution for 0 min (black) and 60 min (blue). The inset shows the change of the absorbances at 235 and 500 nm with the dipping time.

Ambient-temperature stability was finally investigated in a concentrated NaOH solution (c = 2 M), see Figure 6. In contrast to the previous cases, an abrupt decrease of UV absorption was observed after 5 minutes dipping, which levelled off soon afterwards. The visible absorption changed in a different way, showing only a slight drop after 5 minutes, and then increased similarly to the above mentioned cases. The different magnitudes of absorbance changes after 5 minutes unequivocally signify that the base induced a rapid chemical transformation of the graphene oxide particles, and the contribution of their "leaching", that is, the loss of particles from the solid structure into the liquid phase is minor.

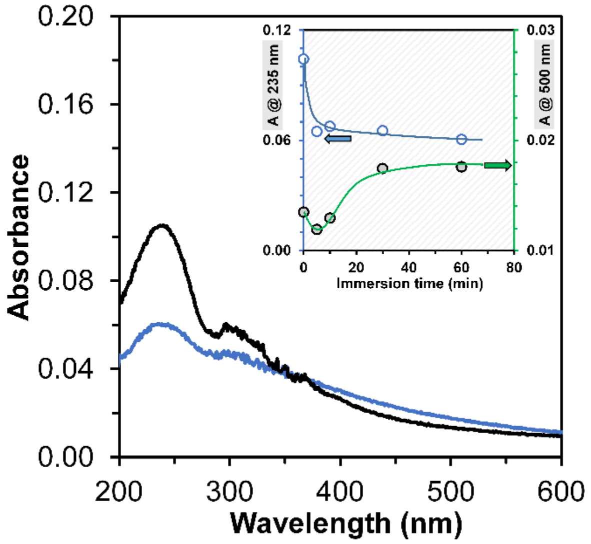

Fig. 6 – UV-visible spectra of (PDDA/GO)$_5$ films immersed into 2 M NaOH solution for 0 min (black) and 60 min (blue). The inset shows the change of the absorbances at 235 and 500 nm with the dipping time.

3.3. Immersion stability at 50 ºC

Stability tests in water and NaOH solution were performed also at 50 ± 2 ºC. Figure 7 shows the effect of water on the UV-visible spectra. The related absorbances were in line with those found for the five-bilayer nanofilm in contact with room temperature water and showed only very slight changes even after 5 hours. Thus, it is clear that the layer-by-layer GO/PDDA sandwich structure can retain its structural integrity in aqueous solutions unless the solute has a specific dissolution-inducing tendency.

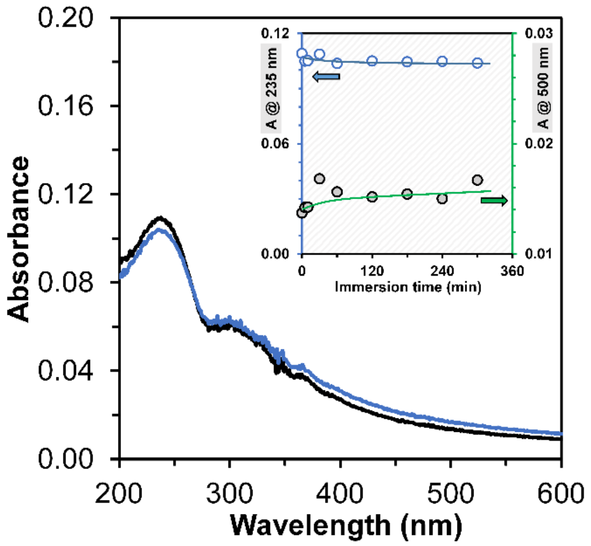

Fig. 7 – UV-visible spectra of (PDDA/GO)$_5$ films immersed into water for 0 min (black) and 300 min (blue) at 50 ^{0}C. The inset shows the change of the absorbances at 235 and 500 nm with the dipping time.

Spectral changes brought by the immersion of the polyelectrolyte/GO assembly into 2 M NaOH at 50 ºC are seen in Figure 8. These changes are more complex than those found for water. The visible absorption linearly increases with the immersion time, showing no saturation after 7 hours. Such a pronounced darkening of the multilayers cannot be attributed to enhanced light scattering, but it indicates that NaOH, at such high concentrations, catalyzes the decomposition of GO to chemically derived graphene. Accordingly, a gradual deoxygenation of GO particles was found by Fan et al. suspended in “strongly alkaline solutions” [29] of ca. 50 mM at the same temperature (50 ºC). While the concentration of base used in our study is much larger, we observed a less readily progressing reaction. Two possible explanations for this controversy involve (i) the hindered accessibility of the base to the underlying GO particles in the multilayered film and, more likely, (ii) the difference in the type of graphite oxide (i.e. Brodie vs. Hummers) applied [30].

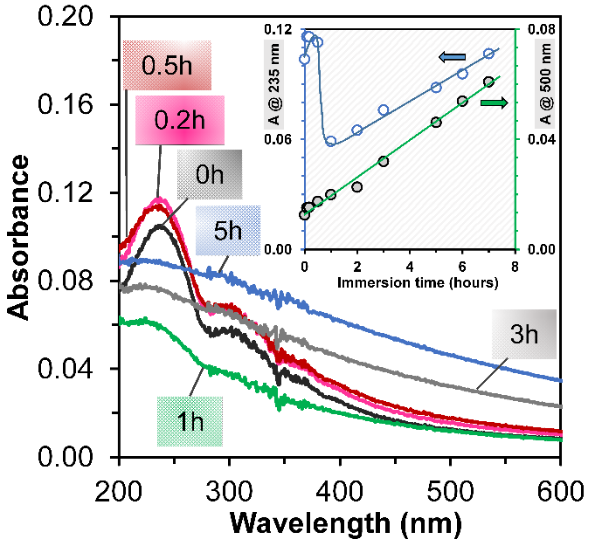

Fig. 8 – UV-visible spectra of (PDDA/GO)$_5$ films immersed into 2 M NaOH solution for different times at 50 ^{0}C. The inset shows the change of the absorbances at 235 and 500 nm with the dipping time.

The absorbance at 235 nm increases first, which would imply an increase in the GO content of the nanofilms, but this obviously cannot be true because the dipping solution does not contain graphene oxide. Instead, it is caused by the GO transformation, which gradually increases the absorbances in this region as well. However, after the initial slight increase, the film shows the same abrupt decrease in UV-absorption as that studied at room temperature, and the two characteristic GO bands are almost completely vanished here after one hour contact with the basic solution. This indicates that the oxygen removal is completed after this time, while the extension of the conjugation in the polyaromatic domains is continuously proceeding for several hours. Remarkably, the featureless spectrum is reminiscent to that of natural organic matter [31].

3.4. Dye inclusion into multilayers

The incorporation of dye molecules into the polycation/GO LbL nanostructures was studied by comparing the spectra of hybrid nanofilms of different thicknesses immersed into MB aqueous solution of 200 ppm concentration (pH = 5.9) for 30 minutes. We used an automated deposition device applying a programmed, slow upstroke. This enables that the wetting liquid flows down from the surface and rinsing with excess of water, which could have disturbed the absorption equilibrium, was efficiently avoided. Thus, the weakly bound MB could not leach out from the multilayer upon a cleaning process and the light absorption of as-obtained films must reflect the optical characteristics of dye molecules diffused into and/or adsorbed on the PDDA/GO nanostructure.

Figure 9 shows the spectra of nanofilms in the visible range where only the dye exhibits significant light absorption. They are also compared to the spectrum of methylene blue adsorbed on the bare quartz support under identical conditions. The latter features two absorption bands at 615 nm and 678 nm. Schoonheydt and coworkers published in-depth studies on the spectral features of MB adsorbed on various smectite-type clay minerals suspended in water [32,33]. They assign the band at 670 nm to a single dye molecule, which is in direct contact with the silicate surface. The monomer also gives rise to absorption originating from the 0-1 vibronic transition, but this usually appears as a shoulder between 610 and 620 nm. For MB adsorbed on quartz, however, this band extends well beyond even that at 678 nm, indicating that dimeric aggregates in which the individual molecules are stacked face-to-face are also deposited on the substrate, in analogy to the processes taking place in MB solutions at higher concentrations [34]. Trimers, higher aggregates and protonated MB molecules were not observed.

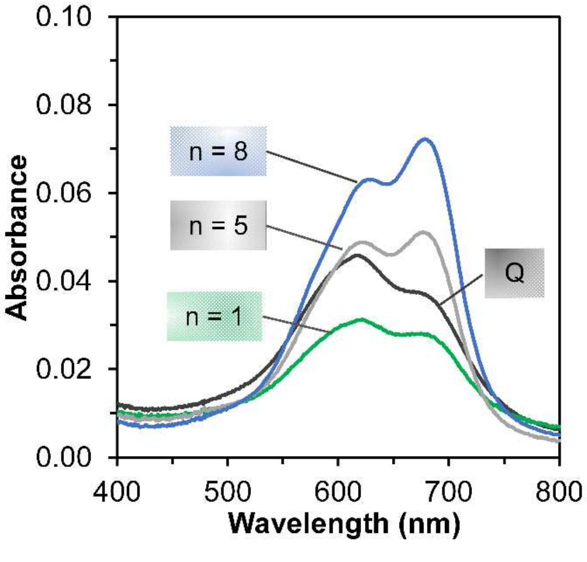

Fig. 9 – Visible spectra of (PDDA/GO)$_n$ films and that of bare quartz (Q) slide immersed into 200 ppm MB solution for 30 minutes.

MB molecules were found to change their spectra when they are adsorbed on the polycation/GO surface. Already when a single bilayered film is present (n =1), the contribution of the 615 nm peak is less pronounced. For a 5-bilayer film, the peak at higher energies has lower absorbance than that at 678 nm, while the deposition of further bilayers lead to the further progressive decrease in the relative absorbances of the two characteristic bands of the dye. These changes clearly show that the extent of dimerization is gradually decreasing with the film thickness, and at n > 8 mostly single MB molecules are incorporated into the film structure.

To obtain information on the dye content of the nanofilms, the integrated intensities of the band envelope of MB within the 400 to 800 nm range are used. They are plotted against the absorbances measured at 235 nm instead of using the bilayer numbers due to the aforementioned sample-to-sample variations, making the UV absorbance characteristic for GO more feasible to express the layer thickness. To our surprise, as shown in Figure 10, the amount of dye decreased first when the quartz was coated by the thinnest PDDA/GO films with bilayer numbers of 1 or 2. Upon successive increase of the layer thickness, the adsorbed amounts of MB start to increase until the GO-related absorbance reaches ca. 0.18 (5-6 bilayers) where the dye content becomes saturated.

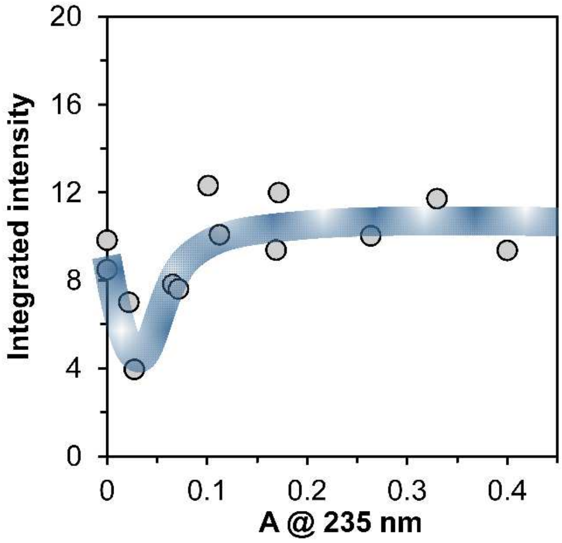

Fig. 10 – Integrated band intensities of MB (between 400 and 800 nm) upon inclusion into (PDDA/GO) films of different optical thicknesses (characterized by their absorbances at 235 nm).

4. Discussion

The ultrathin multilayer structure of LbL self-assembled PDDA/GO films are held together largely by Coulombic forces. The first layer (PDDA) is of crucial importance in determining the stability of the film. The cationic polyelectrolytes adsorb strongly on the negatively charged quartz surface, expelling the counterions off the surface with a concomitant release of their own counterions [35]. This has a great entropy production, resulting in a virtually irreversible adsorption. Thus, the polymer molecules are not removed by excessive dilution and the PDDA/GO LbL film remains intact during rinsing or wetting with water for prolonged times.

Polyelectrolyte stability is greatly changed in saline solutions. The adsorbed amount normally increases with the solution ionic strength [36]. As the salt concentration is increased, the effective strength of Coulombic interactions is decreased. The polymer can gain conformational entropy by extending into the solution, as shown by the formation of more swollen layers [37] leading to higher adsorbed amounts. However, in concentrated electrolyte solutions the entropy effects ultimately reduce and the polymer may come off the surface. The same argumentation should stand for charged polyelectrolyte assemblies as well. Accordingly, Gui et al. found that a polyzwitterion/polyacrylic acid LbL film completely disintegrated at physiological conditions within 15 minutes [38]. In stark contrast, immersion of GO containing LbL films does not lead to disintegration in highly concentrated saline media.

The relative high stability of $(PDDA/GO)_n$ films in the studied strongly acidic HCl solution is also somewhat unexpected. GO completely loses its negative charge due to complete protonation of its anionic functional groups in the studied case of pH = -0.3 and the effective strength of electrostatic interactions is ultimately diminished. Indeed, Kharlampieva et al. found that films deposited from weakly acidic poly(methacrylic acid) and weakly basic quaternary poly(4-vinylpyridine) underwent deconstruction already at pH = 2 [39]. However, the loss of charge of the “polyanionic” graphene oxide does not result in disintegration of the hybrid PDDA/GO films. The retained layer adhesion in salt and acid must originate from interparticle hydrogen bonding and van der Waals interactions between the film constituents. These bonds are certainly much weaker than the electrostatic interactions, but they afford many linkage points between the GO particles and the polymer molecules, which is enough to hold together the adjacent layers. Wetting the films with basic solutions induces a relatively fast chemical transformation of the GO particles to chemically converted graphene. This reaction is, however, only partial at ambient temperature in 2 M NaOH. These films prepared from delaminated Brodie-GO are more stable chemically than Hummers-GO samples in suspension which are deoxygenated more rapidly at much lower base concentrations.

The common cationic dye, methylene blue, adsorbs on the surface of PDDA/GO multilayered films. However, the adsorbed amount surprisingly decreases for the first two bilayers as compared to the clean quartz support. This may be caused by several effects. As shown by spectral shifts, the dye is, to a large extent, present on the bare quartz as $(MB)_2$ dimers, and this mixed “monolayer” consisting of single and dimerised molecules thus contains higher amount of MB than that formed on $(PDDA/GO)_1$. Furthermore, as evidenced by the AFM image, the graphene oxide platelets cannot cover films completely. Consequently, even when enough time is left for the formation of a monoparticulate GO layer during film deposition, areas covered only by PDDA inevitably remain on the support. This effect decreases the total adsorbed amount, because MB molecules are positively charged and their adsorption on the polycation will be hindered. However, when the film is built further by the deposition of several more bilayers, the MB content starts to increase, and reaches a saturation plateau related to absorbances 15-20% higher than that found over bare quartz. Since MB molecules are found only as monomers in these multilayered films, the apparent surface coverage of the dye is larger when it is adsorbed on the LbL films. This can be envisioned either by the monomolecular adsorption on a rough external surface or by the diffusion of MB molecules into the nanostructured assembly. Given the present and the numerous reported cases (e.g. [40]) for enhanced surface roughness upon successive LbL deposition, the first hypothesis is not unlikely. The diffusion of MB molecules may also take place. Moreover, for a completely permeable, membrane-like surface structure, the adsorbed amount of dye should have linearly increased with the layer thickness, while for a completely impermeable one, it should be independent of the number of bilayers. Since the thicker PDDA/GO films show a saturation in the dye content, it is clear that the in-layer diffusion of MB is severely hindered and may only be restricted to the bilayer adjacent to the external surface.

5. Conclusions

The stability and degradation of polycation/GO LbL films in various aqueous solutions have been extensively studied using a simple spectrophotometric method. Most importantly we found that these assemblies retained both their chemical integrity and structural stability in water and under highly acidic and saline conditions, in contrast to reported examples of LbL films of oppositely charged macromolecules. This finding is relevant in light of various practical uses of polymer/GO films. Another important aspect is that immersion of films into a reactant or precursor solution can be often necessary for further functionalization or loading with inorganic nanoparticles e.g. to prepare photocatalytically or electrocatalytically active composites [41,42]. Since many of these precursors are only stable in acidic media or afford themselves high ionic strengths, it is important to emphasize that the GO-supported multilayers are able to resist the degradation in a wide range of solutions, not only in the salt-free rinse water. Finally, the inclusion of cationic methylene blue molecules into multilayered films was found to proceed mostly by adsorption onto the external surface of LbL films containing GO as the outermost particle layer. A small amount of the dye may be able to diffuse below the swollen topmost layer. This high degree of dye impermeation found for the present LbL films represents their potential use in nanofiltration applications.

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