A facile room temperature layer-by-layer deposition process for the fabrication of ultrathin films with noncentrosymmetrically oriented azobenzene chromophores†

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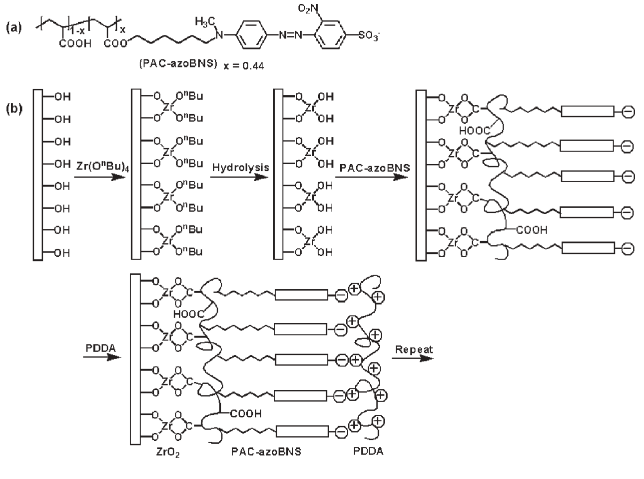
Received (in Cambridge, UK) 16th May 2006, Accepted 21st August 2006
First published as an Advance Article on the web 5th September 2006
DOI: 10.1039/b606927d

Ultrathin films with noncentrosymmetrically orientated azobenzene chromophores were constructed using a combination of layer-by-layer adsorption of polyelectrolytes and the surface sol–gel process.

Noncentrosymmetric structure is critical for the preparation of second-order nonlinear optical (NLO) film materials as second-order NLO processes are forbidden in centrosymmetric media. Currently, organic films with noncentrosymmetric structures for second-order NLO properties have been prepared using a variety of methods, including electric field poling,[1] Langmuir–Blodgett (LB) films,[2] covalent self-assembly,[3] modified metal–bis(phosphonate) self-assembly,[4] hydrogen-bonding-directed self-assembly during physical vapor deposition,[5] and so on. The layer-by-layer (LbL) assembly technique, which utilizes polyelectrolytes or oligo-charged organic molecules, holds great potential because of its simplicity in film preparation, the independence of film deposition from substrate type, size and morphology, and easy integration with the existing nanofabrication techniques.[6] The study of the use of these films in second-order NLO film materials was a hot topic in the middle of the 1990s, but interest has gradually diminished in the recent years. This is because the structure of polyelectrolyte multilayer films fabricated by the LbL assembly technique is generally centrosymmetric, as linear deposition behavior of the polyelectrolyte layers is usually observed with increasing numbers of deposition cycles. Kunitake *et al.*[7] and Tripathy *et al.*[8] reported separately that the SHG signal in LbL assembled azobenzene-containing polymeric films increased quadratically only in the first few layers, but leveled off or even decreased with further increase in the deposition layers.[7,8] Although Roberts *et al.* prepared a kind of polyelectrolyte film with a quadratic increase in the SHG signal up to 36 deposition cycles,[9] such an encouraging result was not found in other kinds of polyelectrolyte films. Strategies adopted to achieve noncentrosymmetric orientation of chromophores in LbL assembled polyelectrolyte/oligo-charge organic molecules include the combination of LbL assembly with a special interfacial reaction[10] and electric-field-induced LbL assembly.[11] The limitations are obvious for the above-mentioned strategies because the chemical reaction is tedious and the reaction yield is not always 100%, while electric field methodology restricts the preparation of films on nonconductive substrates.

Herein, using the combination of LbL assembly of polyelectrolytes and the surface sol–gel process,[12] we report a facile room temperature LbL process to prepare layered ultrathin films with noncentrosymmetric structures. A NLO-active azobenzene polymer (PAC-azoBNS) was employed as a model material to demonstrate the feasibility of this method. PAC-azoBNS, with a molecular weight (M_n) of 104 351 and graft ratio of 44%, is shown in Scheme 1(a). A detailed synthesis of PAC-azoBNS has been reported elsewhere.[13] The NLO-inactive deposition partner species are poly(diallyldimethylammonium chloride) (PDDA, M_n: 100 000–200 000, Aldrich) and zirconium *n*-butoxide ($Zr(O^nBu)_4$, Aldrich). The surface sol–gel process using $Zr(O^nBu)_4$ as the starting material produces thin layers of ZrO_2.[12] The film deposition process is illuminated in Scheme 1(b) and carried out as follows: first, a freshly cleaned silica wafer was immersed in a $Zr(O^nBu)_4$ solution (10 mM in 1 : 1 (v/v) toluene–ethanol) for 5 min, followed by rinsing with ethanol solvent and hydrolysis in water. In this case, a thin layer of amorphous zirconia was deposited on the substrate.[12] Then, the substrate was immersed in an aqueous solution of PAC-azoBNS (0.5 mg ml^{-1}, pH 3.0 adjusted with HCl) for 10 min to adsorb a layer of the NLO-active species. The deposition of the PAC-azoBNS layer was achieved



Scheme 1 (a) Chemical structure of PAC-azoBNS. (b) Layer-by-layer process for the construction of noncentrosymmetric multilayer films of ZrO_2/PAC-azoBNS/PDDA.

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† Electronic supplementary information (ESI) available: Fabrication of (PAC-azoBNS/PDDA)**n* films, characterization of the films, cross-sectional SEM image of ZrO_2/PAC-azoBNS/PDDA film, UV-vis absorption spectra of PAC-azoBNS/PDDA films, and SHG measurements. See DOI: 10.1039/b606927d

using the coordination interaction between zirconia and carboxylic acid groups.[14] Because of the strong repulsion between negatively charged zirconia and sulfonate groups, the NLO-active azobenzene, which is substituted with a sulfonate group, cannot bind to zirconia and should protrude outside.[15] In this way, noncentrosymmetric orientation of the NLO-active azobenzene chromophores was realized. After the deposition of the PAC-azoBNS layer, the film surface contains mainly sulfonate groups because the carboxylic acid groups in PAC-azoBNS either interact with zirconia or are buried within azobenzene side chains. Finally, the substrate was immersed into a 1 mg ml^{-1} aqueous solution of PDDA to adsorb a layer of PDDA. In this way, one cycle of a ternary film of ZrO_2/PAC-azoBNS/PDDA was prepared. The positively charged PDDA layer allows the deposition of the next layer of zirconia. The process for the deposition of ZrO_2 onto the PDDA layer is the same for that onto the cleaned silica wafer. By repeating the above steps, ternary (ZrO_2/PAC-azoBNS/PDDA)*n (herein n refers to the number of deposition cycles) films can be prepared.

UV-vis absorption spectra of different deposition cycles of ZrO_2/PAC-azoBNS/PDDA films are shown in Fig. 1(a). All spectra have an absorption peaking at 482 nm, which is attributed to the absorption of *trans*-azobenzene in PAC-azoBNS. The absorption peak in the films is 18 nm red-shifted compared with the absorption of PAC-azoBNS in diluted aqueous solution, indicating the possible formation of J-aggregates of azobenzene chromophores in solid films.[7] The linear increase in the absorbance at 482 nm with the increase in the number of deposition cycles confirms that equal amounts of PAC-azoBNS were deposited in each deposition cycle (shown in the inset of Fig. 1(a)). Because ZrO_2 and PDDA show almost no absorbance in the tested range of UV-vis spectroscopy, quartz crystal microbalance (QCM) measurements were conducted to further prove the successful LbL deposition of ZrO_2/PAC-azoBNS/PDDA films. QCM measurements (Fig. 1(b)) show a linear deposition process, with frequency decreases of 25.5 ± 1.7 Hz, 319.4 ± 59.3 Hz and 238.7 ± 92.5 Hz for one deposition cycle of ZrO_2, PAC-azoBNS and PDDA, respectively.

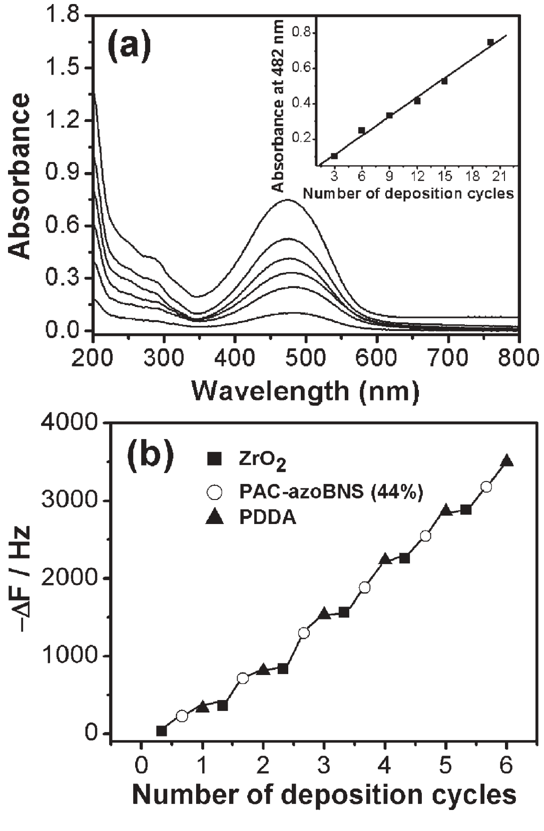

Fig. 1 (a) UV-vis absorption spectra of (ZrO_2/PAC-azoBNS/PDDA)*n films with a different number of deposition cycles. The numbers of deposition cycles are 3, 6, 9, 12, 15 and 20 from the bottom to the top. (b) QCM frequency decreases ($-\Delta F$) in successive depositions of (ZrO_2/PAC-azoBNS/PDDA)*n films.

The dependence of the SHG signal on the number of deposition cycles is the direct means to characterize the noncentrosymmetric structure of the ZrO_2/PAC-azoBNS/PDDA films. Transmission SHG measurements were performed using the 800 nm output of a regeneratively amplified Ti:sapphire laser operating at 1000 Hz. The SHG signal at 400 nm was collected by spectrograph (Chromex precision: 0.1 nm) and CCD. The nearly destructive interference pattern observed for a quartz substrate deposited on both sides with ZrO_2/PAC-azoBNS/PDDA multilayer films demonstrates that the quality and uniformity of the films on both sides are nearly identical. Fig. 2(a) shows that the square root of the SHG signal ($I_{2\omega}{}^{1/2}$) increases linearly with the increase in the number of film deposition cycles for (ZrO_2/PAC-azoBNS/PDDA)*n films. A cross-sectional SEM image shows that a (ZrO_2/PAC-azoBNS/PDDA)*10 film has a thickness of 66.0 ± 3.0 nm, corresponding to an average thickness of *ca.* 6.6 nm for one deposition cycle of ZrO_2/PAC-azoBNS/PDDA. The thicknesses of the ZrO_2/PAC-azoBNS/PDDA films examined are much less than the SHG coherence length (typically a few microns). Therefore, the quadratic dependence of the SHG signal affirmatively supports noncentrosymmetric orientations of the azobenzene groups in ZrO_2/PAC-azoBNS/PDDA films.[16] Calibrating the data *versus* quartz yields $\chi^{(2)}_{zzz} = 7.23 \times 10^{-7}$ esu and $\chi^{(2)}_{zxx} = 4.06 \times 10^{-7}$ esu. Here, an average chromophore orientation angle of 47° with respect to the substrate normal was confirmed by SHG analysis. Multilayer films of PAC-azoBNS/PDDA were prepared in a similar way to ZrO_2/PAC-azoBNS/PDDA films without the ZrO_2 deposition steps. As shown in Fig. 2(b), although a linear deposition process of PAC-azoBNS/PDDA multilayer films was

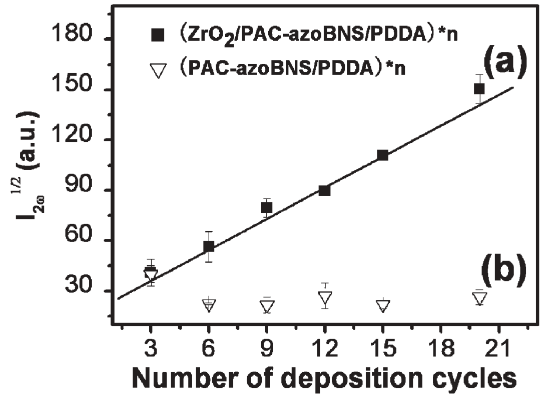

Fig. 2 Square root of the SHG signal *vs.* the number of film deposition cycles for (ZrO_2/PAC-azoBNS/PDDA)*n (a, ■) and (PAC-azoBNS/PDDA)*n (b, ▽) films.

confirmed by UV-vis absorption spectroscopy, the SHG signal increases with the number of deposition cycles up to 3, while further deposition reduces the signals. This result demonstrates that the ZrO_2/PAC-azoBNS/PDDA film composition is unique in achieving the noncentrosymmetric orientation of NLO-active chromophores in ultrathin films.

In summary, we have demonstrated that by using a combination of LbL assembly of polyelectrolytes and the surface sol–gel process, a new methodology has been developed for preparing hybrid organic/inorganic ultrathin films with noncentrosymmetric orientations of NLO-active chromophores in each triple layer. The present method has the advantages of simplicity in film fabrication, long-term stability of the SHG signal and easy integration with other kinds of optoelectronic elements. We are currently investigating the influence of the graft ratio on the detailed SHG properties of the corresponding ZrO_2/PAC-azoBNS/PDDA ultrathin films.

This work is supported by the National Natural Science Foundation of China (NSFC Grant No. 20304004, 60478015), the Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (FANEDD Grant No. 200323) and the Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT Grant No. IRT0422).

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