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COMMUNICATION

Kinetic Approach to Hyper Doped Optical Quality Thin Films

33Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Efficient and benign doping of thin films is key for materials applications and sensor development. Herein, an alternative method of doping is presented where R6G is loaded to an evolving silica thin film. Dopant loading is markedly enhanced and doping can be carried out under relatively benign conditions. The film exhibits outstanding optical quality while its mechanical strength is well-preserved. Early results show diffusion and encapsulation can be tuneable.

The development of new materials and sensors through the sol-gel method has garnered considerable interest in academia and industry. The broad interest in the sol-gel method stems from the multitude of properties the resultant materials may afford. Among the many are optical transparency, chemical robustness, and mild processing conditions.¹ The materials scaffold so produced has superior versatility yielding many different classes of materials with perhaps the largest interest in thin films.² Chemical functionality and optical properties of these thin films are often tuned through the addition of dopants. This has been primarily performed in two manners commonly known as pre- and post-doping. In pre-doping, a dopant is first added to a liquid sol, which is then brought to gelation subsequently. This was first demonstrated by Avnir and co-workers where rhodamine 6G, R6G, was loaded into a silica film prepared from a tetraethoxysilane, TEOS, precursor.³ In post-doping, the dopant is allowed to infiltrate inside porous substrates like Vycor glass via adsorption onto inner pore surfaces.⁴ Herein we present an unorthodox approach utilizing the slow reaction kinetics associated with the sol-gel process by doping to an evolving sol-gel thin film, henceforth termed kinetic doping for distinction. The relatively low cost, high doping efficiency, benign conditions, and ease of implementation make this method enticing in general, but perhaps one of the most promising aspects will be development of sensors with biomolecules. By doping to an evolving sol-gel thin film, the exposure of dopant to denaturing alcohols encountered in pre-doping can be dramatically reduced. The use of a phosphate buffer during

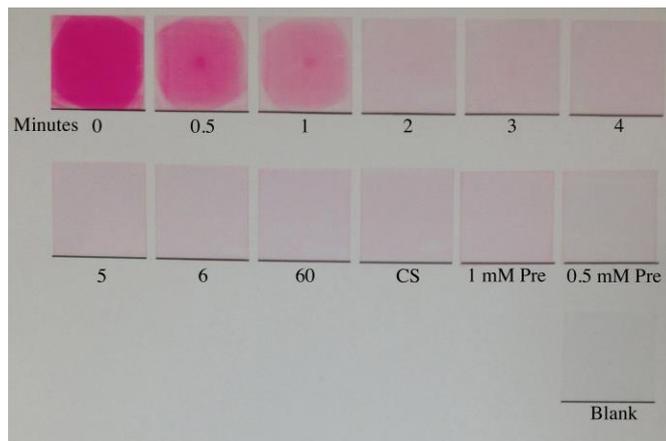


Fig. 1 The kinetically doped thin films are displayed with variable post spin coating delay (minutes). A post-doped cover slip (CS) and two pre-doped thin films (with 1 mM and 0.5 mM R6G) are presented for comparison. A thin film submerged only in 10 mM phosphate buffer (pH 7) is used as a “Blank” reference and to verify optical quality.

doping is expected to be amenable to a wide range of sensitive biomolecule dopants as well.

Utilizing the alkoxide hydrolysis pathway, a TEOS/ ethanol/ water/ 1% H₃PO₄ sol was prepared and allowed to age for 18-20 hours.⁵ During the aging time the sol undergoes simultaneous hydrolysis and poly-condensation. The properly aged sol was then spin coated into thin films. During the spin coating process, physical properties of the resultant films are rapidly evolving and are critically influenced by alcohol evaporation, reaction with air moisture (relative humidity), airflow dynamics, and spin chuck specifications. In contrast to pre- and post-doping, R6G in the kinetically doped approach was incorporated inside rapidly evolving pristine thin films by submerging the films into a dopant solution

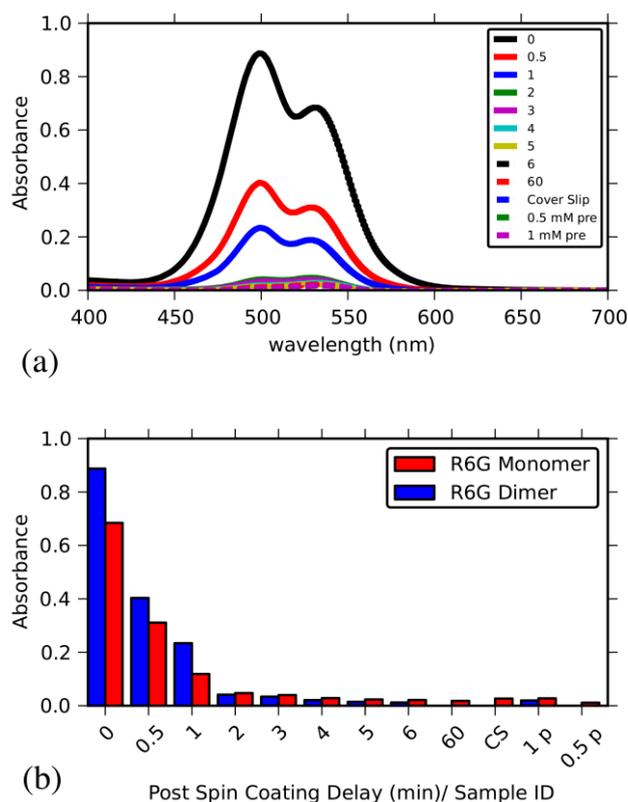


Fig. 2 In Figure 2 (a) the visible absorption spectrum from 400 nm to 700 nm is plotted for each thin film and control. In Figure 2 (b) the maximum absorption of the monomer and dimer forms of R6G is plotted for each kinetically doped thin film and control.

consisting of 0.5 mM R6G in 10 mM phosphate buffer (pH 7). The films stayed submerged for one hour; subsequently removed from solution, rinsed with deionized water, and blown dry. R6G uptake by the resultant films was found to vary systematically with the post spin coating delay time (PSCD) prior to submersion to the dopant solution as shown in Figure 1.

In Figure 1 the kinetically doped thin films are shown with varying PSCD (minutes). For comparison, a clean cover slip was post-doped with the same R6G buffer solution for the same amount of time as the kinetically doped films were. Also shown are 1 mM and 0.5 mM R6G pre-doped controls where R6G was added to the sol and mixed immediately before spin coating. It is obvious from visual inspection of the pink R6G colour that the kinetically doped film with zero minute PSCD leads to significantly more R6G uptake. The loading of these kinetically doped films quickly diminished and plateaued shortly after two minutes PSCD. Doping with 2 minutes PSCD or longer appears to be comparable to that of the pre-doped 1 mM and post-doped coverslip controls. It is worth pointing out that thin films with long PSCD are expected to be more alcogel-like, hence exhibiting a similar R6G doping level to that of a plain glass coverslip. Besides high doping efficiency, another key advantage of the kinetically doped thin films is their ability to maintain a high degree of structural integrity as they did not crack or display surface imperfections significant enough to degrade the optical quality of the thin films. This allowed the doping efficiency to be quantified by absorption spectroscopy.

Absorption spectra were recorded from 400 nm to 700 nm by simply placing the R6G-doped thin films in the sample path of a dual beam spectrophotometer. We note in Figure 2 (a) that the absorption spectra of the thin films exhibit characteristic absorption

bands of R6G and its dimer. In the zero minute PSCD kinetically doped thin film, the R6G monomer maximum absorbance is 0.68 at 531 nm and the dimer is 0.89 at 500 nm. The λ_{\max} of R6G monomer absorbance has been reported to vary from 526 nm to 534 nm.⁶ The dimer spectrum is an aggregation of bands, but the blue shifted maximum at 500 nm is its most notable peak.⁷ The maxima in kinetically doped thin films are close to these values indicating that R6G monomer and its low-order aggregates are the predominant forms in the kinetically doped films and that there is no significant change in their electronic structures. The slight discrepancies are likely attributed to variations in local environment and the different extents of aggregation. This suggests that R6G loading in the kinetically doped thin films is a combined result of simple entrapment and adsorption. Meanwhile, as the absorption of the kinetically doped films decrease, the spectra also display a shift in the relative population of R6G monomer and dimers. The population of the dimer decreases with increasing PSCD, and after four minutes of PSCD little dimer absorbance remained. No trace of dimer absorbance was observed when PSCD reached 60 minutes. The decrease in R6G dimer population could be a direct result of shrinking pore volume and decreasing water content in the resultant film as PSCD increases.⁸ Further studies are underway to provide more insight into how PSCD influences film morphology.

The rapid decrease in kinetic doping results in many spectra overlapping in Figure 2 (a).[†] For clarity, the absorbance values for the monomer and dimer, when present, are plotted vs. PSCD in Figure 2 (b). In accordance with visual inspection, the kinetic doping decays rapidly until it plateaus at a relatively constant monomer absorbance of ~ 0.02 . This represents the minimum value for kinetic doping which is actually quite comparable to the absorbance of ~ 0.03 from the 1 mM pre- and 0.5 mM post-doped controls. In comparison, both monomer and dimer absorption from the zero minute PSCD sample are more than one order of magnitude greater than the pre- and post-doped controls! Unfortunately, R6G aggregation makes a quantitative comparison using absorbance measurements from thin films unreliable. The presence of dimer absorption at zero PSCD suggests an even greater R6G loading differential between zero minute PSCD and the pre- and post-doping doping. An approximation of the relative amount of R6G doped can be made using the pre-doped 0.5 mM thin film to calculate a film thickness since no dimer absorbance is observed in this thin film. While this thickness undoubtedly shrinks as the film ages, the total number of moles of R6G trapped should remain unchanged. Using the relative absorbance values in this manner with the known extinction coefficients for the R6G monomer and dimer yields a 175-fold increase in R6G doping in the zero minute PSCD kinetically doped thin films.⁶⁻⁷ Assuming a typical thickness of 200 nm for an aged alcogel film, this would translate to concentrations as high as 1200 mM for the kinetically doped films!^{††} This hyper doped technique may find its way to applications like dye-sensitized solar cells. A recent study found that the dimeric form of R6G also participates in electron injection in titania based films, thus making our technique ideal when a very concentrated layer of dye in a thin film can significantly enhance energy absorption efficiency.⁹ Further work is under way exploring this avenue.

When exploring the reproducibility of kinetic doping, we found that the technique is sensitive to several parameters. The key variables found were: PSCD, relative humidity, and heat flow on coverslip during spin coating. These parameters are critical to maximizing doping and thus rigorous control is necessary for consistent reproducibility. Under strict control of experimental conditions (zero minute PSCD, 50-51% relative humidity, 74 °F) optical quality thin films hyper-doped with R6G were prepared,

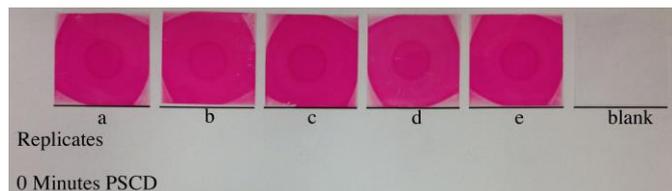


Fig. 3 The reproducibility of the method is verified by producing several hyper-doped thin films under controlled conditions and zero minute post spin coating delay.

Figure 3. The loading is precise as indicated by the average absorbance values for the R6G monomer and dimer, 0.67 ± 0.04 and 0.85 ± 0.06 respectively. The effect of varying these parameters will be reported in a subsequent full publication.

Development of materials for sensor application requires that loading of the sensing molecule be efficient and benign.² The ability to support diffusion is also critical for rapid sensor response. Initial tests show that kinetically doped films exhibit minimal R6G leaching when the films are submerged in water. After one hour of submersion little leaching is observed and the majority of R6G remains trapped. On the other hand, R6G can be efficiently extracted from the hyper-doped film by ethanol, which suggests that there is a network of channels throughout the entire film for molecules of appropriate size to diffuse readily in an appropriate solvent. Heating of a kinetically doped thin film at 65 °C for five days was performed to accelerate aging to the thermodynamically more stable alcogel film.³ Absorption measurements indicated that there was a significant conversion of the R6G dimer to the monomeric form in the heat-treated sample, Figure 4. This is likely due to losing water which is critical for dimer formation. Moreover, the shrinkage of pore volume in a heat-treated sample is expected to reduce space available to accommodate R6G dimers.⁸ Extraction with water was very slow and leaching was insignificant. Subsequent extraction with ethanol showed considerably more leaching, but much less than those from the non-heat treated films. Despite further attempts to extract, some R6G remained in the thin films. This observation is likely attributed to significant shrinkage of pore volume in the thin film, which renders a portion of R6G inaccessible and becomes permanently trapped. Images of this experiment are provided in the ESI.

Conclusions

In this work we have demonstrated that there is a window of opportunity to perform chemistry on a freshly spun-cast silica film before it evolves into a thermodynamically more stable alcogel film. This has enabled us to develop an alternative approach to doping utilizing a constantly evolving sol-gel thin film. Initial results demonstrate that the degree of loading is directly impacted by PSCD before submersion to a doping buffer. Kinetic doping appears to correlate strongly with the aging of a pristine film to an alcogel thin film, where shorter PSCDs result in higher R6G doping. Loading into a freshly preformed silica sol-gel film during its evolution stage allows a sensing molecule to be loaded under a more benign environment where alcohol is mostly absent, making the direct loading of biological molecules a reality. Since the structure of the preformed film is not significantly altered by the addition of a dopant, the desirable characteristics of the parent material can be preserved. This has allowed mechanically rigid thin films to be produced of optical quality. In contrast to pre- and post-

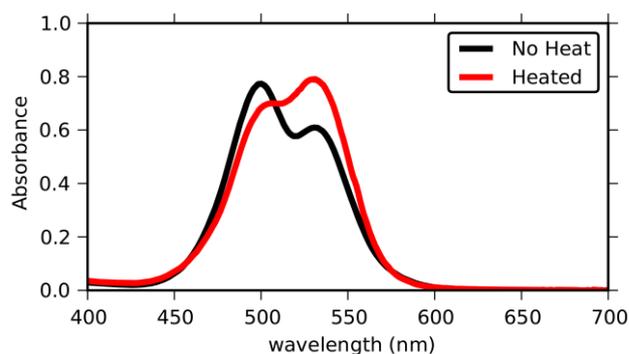


Fig. 4 Absorption spectrum of kinetically doped thin film prior and post heating at 65 °C for 5 days.

doping methods, the relative concentration of dopants is increased by as much as 175-fold. Achieving similar concentrations by pre-doping requires very high dopant concentration in the liquid sol, which would likely alter the thin film structure. Post-doping to such a high concentration would require a very porous glass that may result in loss of mechanical rigidity and optical quality of the thin films. We note that the use of TEOS as a precursor is not a necessity. We envision this doping approach to be applicable to a wide variety of inorganic precursors, making this a viable method of doping to a broad spectrum of thin film materials such as TiO₂.

This work was supported by Oklahoma Centre for the Advancement of Science and Technology (HR 03-144).

Notes and references

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† An expanded view of these spectra reveals that the Dimer/ Monomer ratio decreases in congruence with the idea that the pore size is decreasing in the maturing thin films. See ESI.

†† The absorbance value for the dimer only was approximated by subtracting out a scaled monomer bands absorbance at 500 nm.

Electronic Supplementary Information (ESI) available: Expanded view of Figure 2, Figure 2 (c). Images of the leaching test are also provided, Figure 5 (ESI). See DOI: 10.1039/c000000x/

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