ChemComm

ROYAL SOCIETY
OF CHEMISTRY

Kinetic approach to hyper-doped optical quality thin films†

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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 tunable.

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 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% H_3PO_4 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 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 Fig. 1.

In Fig. 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

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† Electronic supplementary information (ESI) available: Expanded view of Fig. 2, Fig. S2(c). Details of relative loading, film concentration, and images of the leaching test are also provided, Fig. S6. See DOI: 10.1039/c4cc01746c
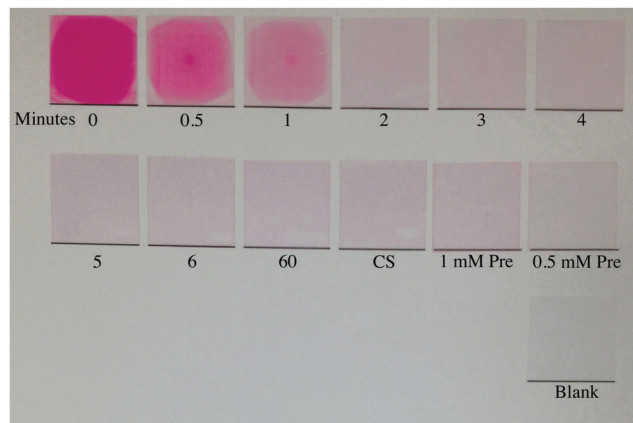
Fig. 1 The kinetically doped thin films are displayed with variable post spin coating delay (minutes). A post-doped cover slip (CS) and two pre-doped thin films (with 1 mM and 0.5 mM R6G) are presented for comparison. A thin film submerged only in 10 mM phosphate buffer (pH 7) is used as a "Blank" reference and to verify optical quality.

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

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 Fig. 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 Fig. 2(a).‡ For clarity, the absorbance values for the monomer and dimer, when present, are plotted *vs.* PSCD in Fig. 2(b). In accordance with visual inspection, the kinetic
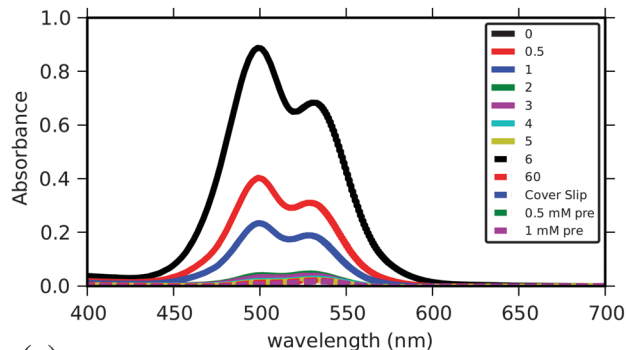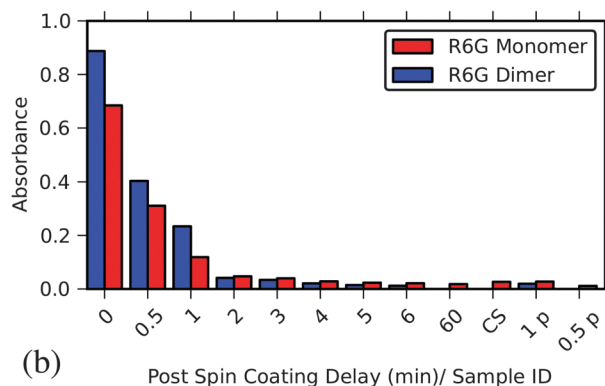
doping decays rapidly until it plateaus at a relatively constant monomer absorbance of ∼0.02. This represents the minimum value for kinetic doping which is actually quite comparable to the absorbance of ∼0.03 from the 1 mM pre- and 0.5 mM post-doped controls. In comparison, both monomer and dimer absorption from the zero minute PSCD sample are more than one order of magnitude greater than the pre- and post-doped controls! 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 controls, which only lends more to the merit of kinetic controlled doping.

An approximation of the relative increase in R6G loading can be made using the ratio of total monomer units in the kinetic-doped film verse the pre-doped 0.5 mM control. This method is advantageous in that the calculation is simplified since no dimer absorbance is observed in the 0.5 mM pre-doped control, and thus only aggregation in the kinetically doped films must be taken into account. Furthermore, while the thickness undoubtedly shrinks as the films age, the ratio of loading should depend only on the absolute amount of R6G trapped. As no leaching is possible once the films were removed from the R6G loading buffer, the relative amount of R6G loading should remain static. Using the relative absorbance values in this manner with the estimated extinction coefficients for the R6G monomer and dimer in aqueous solution yields a 146-fold increase in R6G doping in the zero minute PSCD kinetically doped thin films.[6,7]† This large increase in

doping appears to be consistent with the more qualitative visual inspection of Fig. 1. During the evolution of the thin films to the eventual alcogel product, the concentration is expected to vary significantly as the volume of the films decrease with decreasing film thickness. Given sufficient time to mature, however, thin film thickness and volume should stabilize. Characterization of the film thickness at this stage allows the determination of R6G concentrations *via* absorbance measurements using the estimated extinction coefficient values.[7]

The thickness for similarly prepared samples with different PSCD, and thus different degrees of R6G doping was measured by profilometry. Fig. 3 illustrates that film thickness did not display any significant correlation with R6G absorbance, which is equivalent to the degree of doping, over one decade difference in loading efficiency. The average thickness for all samples was determined to be 190 ± 10 nm and is represented by the horizontal line in Fig. 3. The lack of significant variation supports the observation that these kinetically doped films are structurally very similar regardless of loading efficiency. As a reference, the thickness of an alcogel film was measured and determined to be 185 ± 3 nm. This thickness is within the standard deviation of the kinetically doped films thickness supporting the idea that all kinetically doped films eventually evolve into alcogel. The lack of a correlation between film thickness and doping suggests that the enhanced doping is not a result of a thicker film, but due to the nature of doping during the transient phase of thin film evolution.

Using the film thickness as the optical path length in an absorbance measurement, it is possible to estimate the concentration of R6G monomer units in a film. In the zero minutes PSCD kinetically doped film, which exhibited the highest doping, the concentration was determined to be 1100 mM.† Though the films may further shrink upon normal aging or subjecting to thermal treatment to accelerate aging, the enhanced doping from this method would not change. Being capable of producing large dopant concentrations may make the hyper-doped technique find its way into 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, heat flow on coverslip during spin coating, and the charge of a dopant. It is known that silica film favors cation encapsulation over that of anion because of electrostatic attraction. Indeed, despite similar molecular structures between cationic R6G and anionic fluorescein, we observed no kinetic controlled enhancement in fluorescein doping at all as opposed to the enhanced doping observed in R6G. All parameters mentioned above 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. 4. 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 publication in detail.

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, Fig. 5. 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
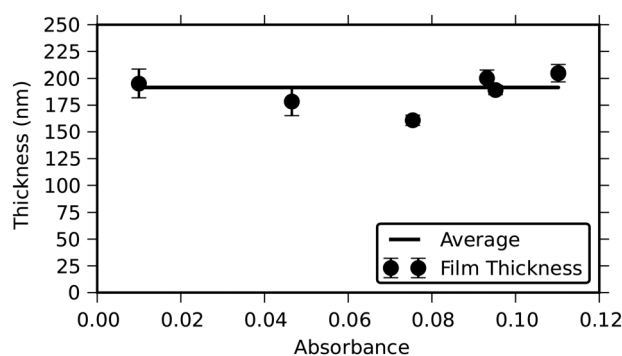
Fig. 3 The film thickness is plotted *versus* R6G absorbance of kinetically doped thin films. Individual points (circles) are average measurements from a single film. The horizontal line represents the average of all film thickness measurements.
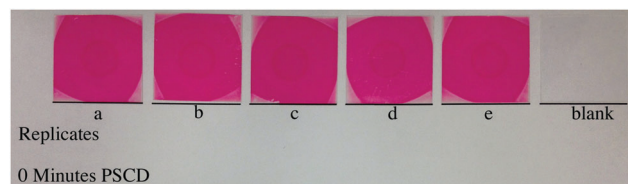
Fig. 4 The reproducibility of the method is verified by producing several hyper-doped thin films under controlled conditions and zero minute post spin coating delay.
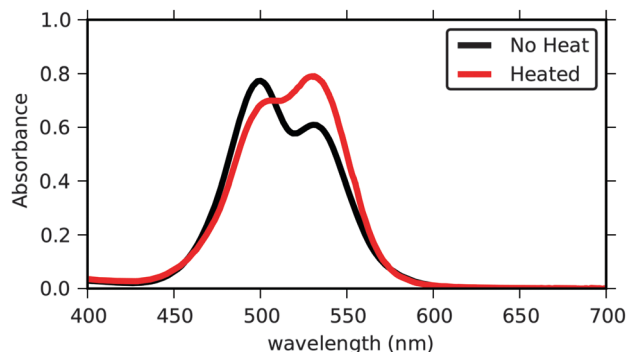
Fig. 5 Absorption spectrum of kinetically doped thin film prior and post heating at 65 °C for 5 days.

becomes permanently trapped. Images of this experiment are provided in the ESI.†

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-doping methods, the relative concentration of dopants is increased by as much as 146-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 TiO_2.

Notes and references

‡ 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.†

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