Effect of additives on the photostability of sol–gel-derived organic–inorganic photochromic coatings

LISONG HOU
Shanghai Institute of Optics and Fine Mechanics, Academia Sinica, PO Box 800–211, Shanghai 201 800, People's Republic of China

H. SCHMIDT
Institut für Neue Materialien, Geb. 43 Im Stadtwald, D-66123 Saarbrücken, Germany

Organic–inorganic hybrid materials (OIHMs) prepared by sol–gel processing have been the subject of extensive research activities for various purposes since they were reported by Schmidt and Philipp [1] in 1984. The low-temperature processing method provides a unique opportunity for organic dyes to enter solid matrices, which are especially favourable to the improvement of the dispersion degree and the thermal stability of photochromic dyes. The porous structure of the sol–gel-derived OIHMs offers free spaces for photochromic dyes such as spiropyran (SP) and spirooxazine (SO) to undergo reversible structural changes during photochromic transformation. The rigidity of OIHMs can be tailored by adjusting the composition, employing proper precursors and introducing appropriate additives, in order that the native structure and properties of the photochromic dye can survive the shrinkage of the gels during drying and moderate heat treatment and can survive ultraviolet (UV) irradiation during application.

Previous studies on sol–gel-derived solid matrices for photochromic dyes have shown that the OIHMs provided excellent cages for SO [2–4], SP [5] and 2,3-diphenylindenone [6], but for practical applications the photostability needs to be further improved. In order to achieve high photostability, it is advisable to maximize the initial photochromic intensity and to minimize the UV-induced photodegradation during application. In this connection, appropriate additives may work besides optimizing both matrix materials and photochromic dyes. In this letter, the effect of additives such as NaF, NaAc, fluoroalkylsilane (FAS), bisphynol-A (BPA) and 1-methylimidazole (MI) on the photostability of SO-doped OIHM coatings is reported. The results show a great improvement in the photostability by rational employment of BPA, MI and FAS.

For the preparation of organic–inorganic photochromic coatings, sols were firstly synthesized via a sonogel process using ethyltriethoxysilane (ETES) and 3-glycidoxypropyltrimethoxysilane (GPTMS) as starting precursors at a molar ratio (MR) of 3:7. They were mixed under stirring for 10 min, followed by the addition of water in the form of 0.1 N HNO_3 at MR of 1.5 to the total silanes. After stirring for another 10 min, the sol was subjected to sonication under 20 kHz ultrasonic radiation at a power of 20 W and cycle duty of 70% for 20 min. Additives were then introduced into the sol followed by stirring for 3 h. For fostering monomeric dispersion of the spirooxazine dye, 1,3-dihydro-1,3,3-trimethylspiro [2 H-indole-2,3-(3 H)-naphth(2,1-b)(1,4)oxazine] and enhancing adhesion of the coatings to the glass substrates, a non-ionic surface active agent, Triton X-100, was added into the sol at 8 wt% prior to the introduction of the photochromic dye. Concentrations of the dye and all the additives are expressed in their MRs to the total silanes. The dip-coating method was used to prepare coatings on microscopic glass slides at a withdrawal speed of 1.1 mm s^{-1}. The coatings were naturally dried in air for a couple of hours and then heated in an electric oven at 120 °C for 2 h. The thickness of the coatings is about 10 μm.

The photochromic intensity, ΔA_0, which is expressed in the absorbance of the sample at the photostationary state under UV irradiation from a Hg lamp, was deduced from the colouring–decolouring curve recorded with a computer-controlled apparatus [7]. For the evaluation of photostability, the coatings were exposed to UV irradiation at the intensity of 60 mW cm^{-2} in a Suntest apparatus. The variation in ΔA_0 with UV irradiation time, τ, was monitored and the half-lifetime, $\tau_{0.5}$, against UV irradiation, which is defined as the irradiation hours needed to halve the initial ΔA_0, was used as a measure of the photostability.

Table I lists values of $\tau_{0.5}$ for the coatings containing different additives at their respective optimal concentrations. It is clear that the photostability has been markedly improved by the introduction of additives. $\tau_{0.5}$ of the dye in ethanol solution is shorter than 1 h while that of the organic–inorganic coatings without any additives is

TABLE I Half-lifetime, $\tau_{0.5}$ against UV irradiation of the coating samples with different additives

Sample	Additives	$\tau_{0.5}$ (h)
1	None	5.0
2	NaF	6.8
3	NaAc	7.7
4	MI	13.9
5	MI+FAS	29.4
6	MI+FAS+BPA	55.2

longer than 5 h. The addition of NaF or NaAc led to only a slight increase in $\tau_{0.5}$ while the introduction of MI, FAS and BPA resulted in great enhancement of the photostability. $\tau_{0.5}$ increases in the order BPA > FAS > MI by factor of about 2.

Fig. 1 shows that $\tau_{0.5}$ increases monotonically with increasing BPA content. This is because the OH and aromatic groups in BPA help to stabilize effectively the coloured form of SO and thus to maintain a higher photochromic intensity. The reason for the improvement in the photostability by FAS is the prevention of some detrimental compounds, which cause the dye to denature, from entering the coatings by the enrichment of fluorine atoms at the surface layer. The role of MI is to adjust the rigidity of the organic–inorganic matrix via participating in the reactions between GPTMS, ETES and BPA. These reactions resulted in the complicated effect of MI on $\tau_{0.5}$ as shown in Fig. 2. Although a more rigid matrix is favourable to the protection of the dye by the matrix, it always suppresses ΔA_0 greatly. It is advisable, therefore, to optimize the matrix rigidity by adjusting the concentration of MI. One can see from Fig. 2 that the optimal concentration of MI is about 0.05.

Fig. 3 shows the variation in ΔA_0 of the coating sample 6 with colouring–decolouring cycle number. It can be seen that the photochromic intensity remains constant within almost 1000 cycles. More than 10 000 cycles is needed to halve the initial photochromic intensity.

In conclusion, great improvement in the photostability of SO in organic–inorganic coatings has been achieved by rational employment of the additives BPA, FAS and MI.
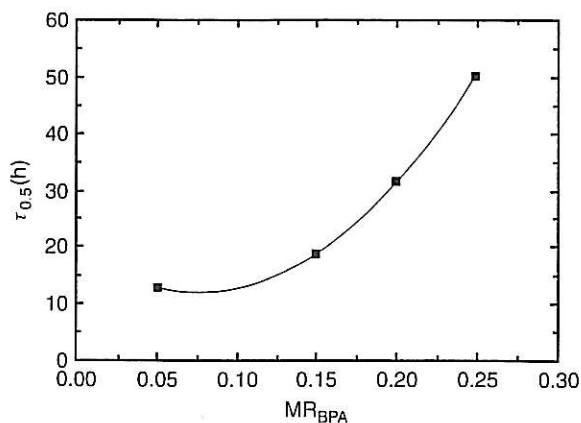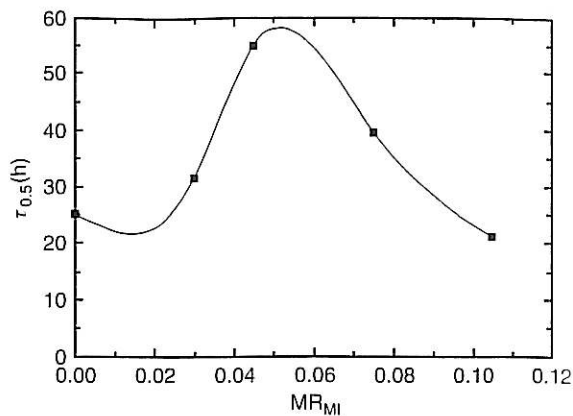
Figure 2 Half-lifetime, $\tau_{0.5}$, against UV irradiation as a function of MI concentration.
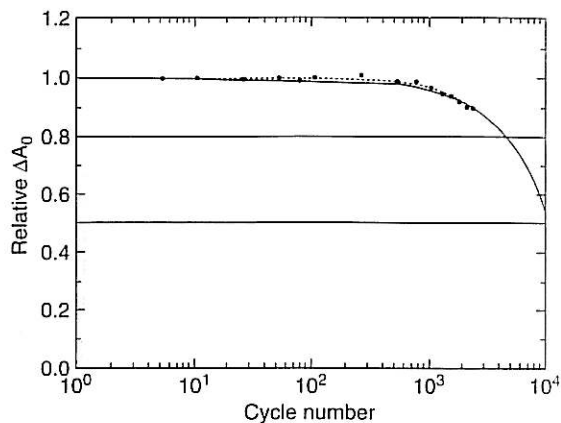
Figure 3 Relative photochromic intensity, relative ΔA_0, as a function of colouring–decolouring cycle number.

Figure 1 Half-lifetime, $\tau_{0.5}$, against UV irradiation as a function of BPA content.

References

1. H. SCHMIDT and G. PHILIPP, J. Non-Cryst. Solids 63 (1984) 283.
2. L. HOU, B. HOFFMANN, M. MENNIG and H. SCHMIDT, J. Sol–Gel Sci. Technol. 2 (1994) 635.
3. L. HOU, M. MENNIG and H. SCHMIDT, Chim. Chronica, New Ser. 23 (1994) 175.
4. L. HOU, M. MENNIG and H. SCHMIDT, Proc. Soc. Photo-Opt. Instrum. Engrs 2255 (1994) 26.
5. D. LEVY, S. EINHORN and D. AVNIR, J. Non-Cryst. Solids 113 (1989) 137.
6. S. A. YAMANAKA, J. I. ZINK and B. DUNN, Proc. Soc. Photo-Opt. Instrum. Engrs 1758 (1992) 372.
7. L. HOU, M. MENNIG and H. SCHMIDT, ibid. 2288 (1994) 328.