Inorganic environment derived from the sol–gel route does not improve the thermal or oxidative stability of 2,4-dinitroaniline in coatings

Carol L. Schutte*†, Kevin W. Williams* and George M. Whitesides*‡

*Department of Chemistry, Harvard University, Cambridge, MA 02138, USA
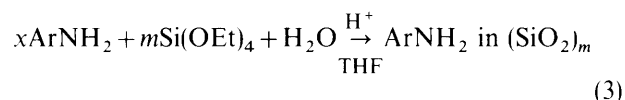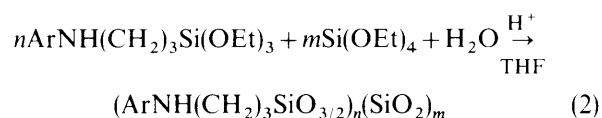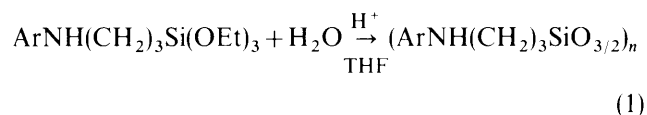†Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

The relative thermal and oxidative stabilities of N-[3-(triethoxysilyl)propyl]2,4-dinitroaniline (1), incorporated covalently into sol–gel coatings and of 2,4-dinitroaniline, incorporated non-covalently into similar coatings, showed no significant difference in relative thermal stability in sol–gel derived films under a variety of conditions: with no overcoat of SiO_2; with a dense sol–gel-derived overcoat of SiO_2; with a porous overcoat of SiO_2; over a porous, high surface area coating of SiO_2; and copolymerized with or physically incorporated into dense and porous SiO_2 films derived from tetraethylorthosilicate.
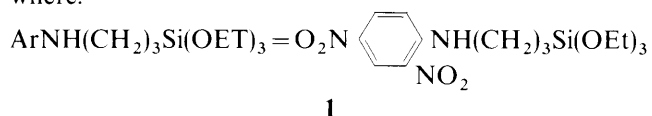
INTRODUCTION

Modification of materials derived from the sol–gel route, by covalently incorporating or physically mixing organic components into the inorganic network, results in useful materials with properties that combine those of the organic and the inorganic precursors[1–8]. Organics, thus, can modify the properties of these inorganic networks while being provided with a hard, chemically resistant matrix.

The purpose of this work was to evaluate the capability of a sol–gel-derived inorganic network (SiO_2) to improve the thermal or oxidative stability of organic components included covalently and non-covalently in it. The diffusion coefficient of oxygen through fully densified sol–gel-derived SiO_2 coatings on Si and on SiC ($D_{O_2} < 10^{-14}$ cm^2 s^{-1} at 750°C)[9] is indistinguishable from that through thermally grown SiO_2. Oxidation of silicon or of silicon carbide coated with a sol–gel-derived SiO_2 film is limited by the diffusion of oxygen through this film[10,11]. If mass transport of oxygen through the matrix similarly limits oxidative degradation of organic molecules included in sol–gel matrices, then a coating of SiO_2 should retard degradation of the organic dopants by serving as a barrier to diffusion of oxygen. Here, we have incorporated the representative organic chromophore 2,4-dinitroaniline into sol–gel-derived matrices by three procedures (Figure 1): first, by hydrolysing the derivatized chromophore 1 alone, to form arylsiloxane polymers (equation (1)); second, by copolymerizing it into a matrix by hydrolysing a mixture of 1 with TEOS (equation (2)); third, by physically mixing 2,4-dinitroaniline with hydrolysed tetraethylorthosilicate (TEOS) (equation (3)).

$$ArNH(CH_2)_3Si(OEt)_3 + H_2O \xrightarrow[\text{THF}]{H^+} (ArNH(CH_2)_3SiO_{3/2})_n \tag{1}$$

$$nArNH(CH_2)_3Si(OEt)_3 + mSi(OEt)_4 + H_2O \xrightarrow[\text{THF}]{H^+}$$
$$(ArNH(CH_2)_3SiO_{3/2})_n(SiO_2)_m \tag{2}$$

$$xArNH_2 + mSi(OEt)_4 + H_2O \xrightarrow[\text{THF}]{H^+} ArNH_2 \text{ in } (SiO_2)_m \tag{3}$$

where:

$$ArNH(CH_2)_3Si(OET)_3 = O_2N \bigcirc \substack{NH(CH_2)_3Si(OEt)_3 \\ NO_2}$$

1

Monitoring the u.v.–vis absorption of the chromophore at 350 nm measured the relative stability of the 2,4-dinitroaniline moiety in these environments.

We prepared samples of the types illustrated schematically in Figure 1 and examined the stability, at high temperature, of the chromophore included in them, both under both argon and air.

The thermal stability of $(ArNH(CH_2)_3SiO_{3/2})_n$ alone (Figure 1A, the condition with the highest organic content and the lowest expected thermal/oxidative stability) served as a standard against which to test the other structures. We hypothesized that the placement of a barrier to oxygen diffusion – the coating of dense and of porous* SiO_2 (Figures 1B and C)[12–14] over

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‡ To whom correspondence should be addressed

*These preparations for dense and porous SiO_2 result in SiO_2 coatings with reported indices of refraction of 1.42–1.43 and 1.21–1.24 respectively, when made by dip-coating[12,13]

A   Chromophore-modified coating on sapphire: alone,

B   under a dense SiO₂ coating,

C   under a porous SiO₂ coating,

D   over a porous, high surface area coating,

E   copolymerized or physically incorporated into a dense SiO₂ coating,

F   and copolymerized or physically incorporated into a porous SiO₂ coating.
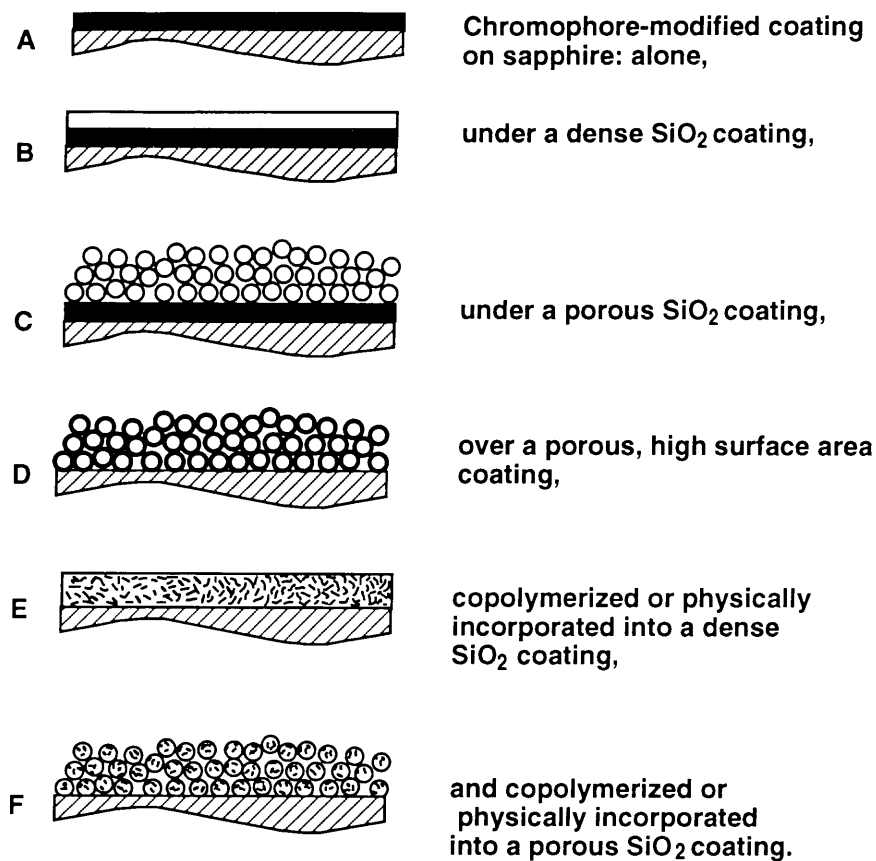
Figure 1 Schematic illustrations of structures that incorporate the arylsiloxane moiety into (or onto) a silicate matrix. ■, Material prepared by hydrolysis of 1; ▣, material prepared by cohydrolysis of 1 and TEOS or by physically mixing 2,4-dinitroaniline with previously hydrolysed TEOS (molar ratio 1:144 for formulations forming dense SiO_2, 1:31 for porous SiO_2); □, unmodified SiO_2, prepared from TEOS alone; ▨, sapphire substrate (crystalline Al_2O_3). The porous coating of SiO_2 consists of spherical silica particles[14]

the $(ArNH(CH_2)_3SiO_{3/2})_n$ layer — might improve the oxidative stability by limiting the diffusion of oxygen to the chromophore (see Introduction).

Coating a layer of high surface area SiO_2 with $(ArNH(CH_2)_3SiO_{3/2})_n$ allowed us to test whether the increased surface area at the $(ArNH(CH_2)_3SiO_{3/2})_n$/air interface affected the stability of the chromophore (*Figure 1D*), which it should if oxidation is the mechanism of degradation.

Studying the stability of the chromophore in the gel matrix, made by copolymerizing $(ArNH(CH_2)_3SiO_{3/2})_n$ with TEOS (*Figures 1E* and *F*), reflected both the effects of reduced oxygen diffusion to the chromophore and of intimate incorporation with restricted mobility of the chromophore with the inorganic matrix.

Physically mixing 2,4-dinitroaniline with TEOS formed non-covalently incorporated chromophore-containing precursors for both dense and porous coatings (*Figures 1E* and *F*). Comparing the differences in stability of covalently *versus* non-covalently incorporated chromophore, tested whether covalent incorporation had any effect on the dye's stability.
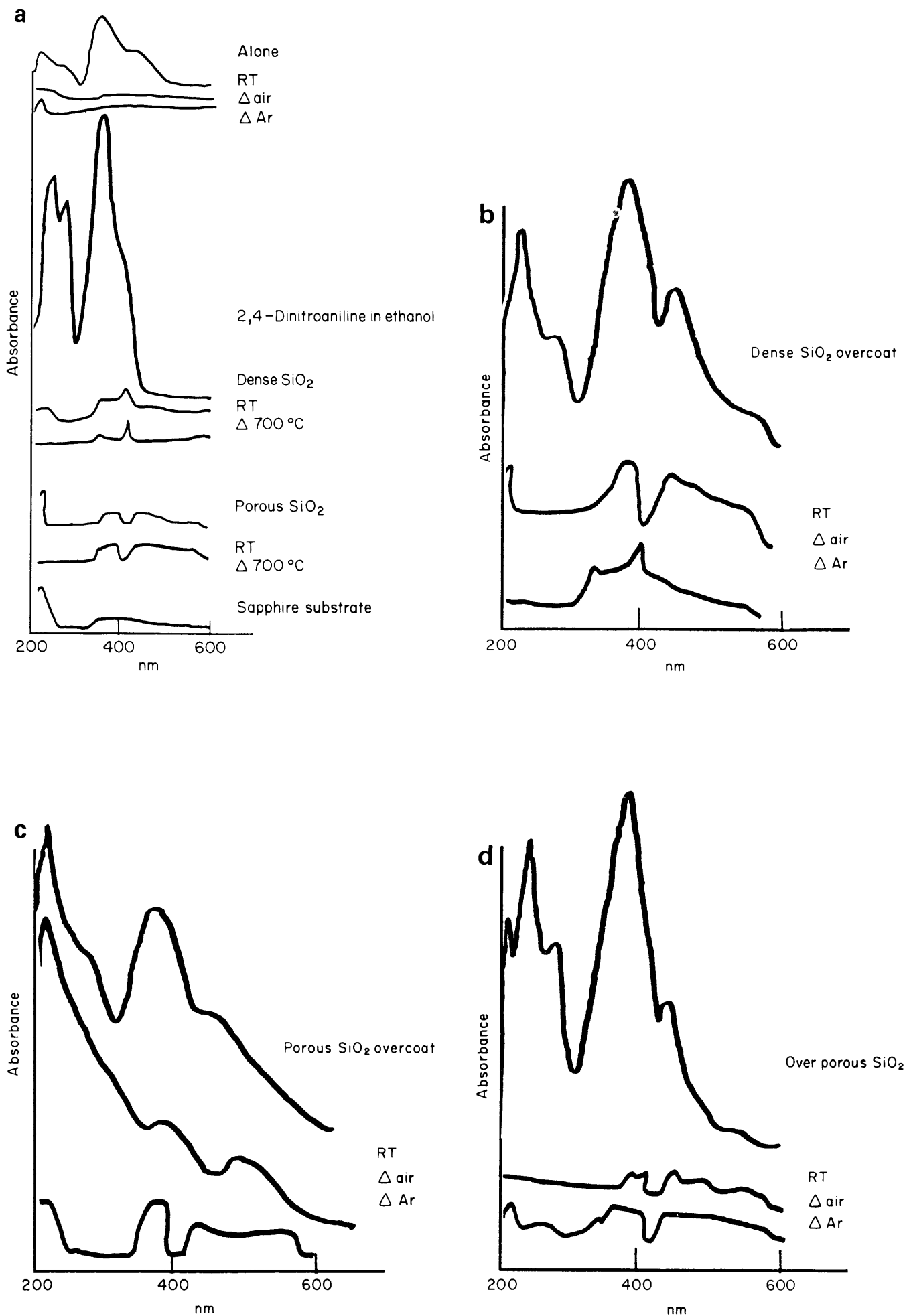
EXPERIMENTAL

Materials

N-[3-(triethoxysilyl)propyl]2,4-dinitroaniline   (1) (Petrarch), 2,4-dinitroaniline (Aldrich), tetraethylortho-silicate (Alfa), ammonium hydroxide (Mallinckrodt)

and absolute ethanol (USI) were used as received. Hydrochloric acid (Mallinckrodt) was diluted with doubly distilled water. The sapphire substrates were optical quality single crystals $(2.00 \pm 0.02$ in long × 0.500 ± 0.015 in wide × 0.018 ± 0.003 in thick; ≈ 5 cm × 1.25 cm × 0.45 cm), purchased from Saphikon, Milford, NH.

General procedure

Treatment of 1 with acidified water in THF and stirring overnight converted it to a yellow sol of $(ArNH(CH_2)_3SiO_{3/2})_n$. The sapphire substrate was dip-coated in the solution, air dried, heated to 100°C for 5 min, placed directly into the spectrophotometer with the dip-coated side in the bottom end of the sample holder, and its u.v.–vis spectrum was measured directly in transmission mode. These samples were heated without further modification and served as controls in studies of stability (*Figure 1A*).

To improve wetting and adhesion of subsequent overcoatings, samples (*Figure 1A*) prepared by this procedure were treated briefly with an oxygen plasma. These surface-oxidized samples, when dipped into the appropriate hydrolysed solution of TEOS, formed a dense[12] or porous[13] SiO_2 coating over the chromophore-containing layer (*Figures 1B* and *C*) after being heated to 100°C for 5 min. As an alternative method of preparing a sample with high surface area, the sapphire substrate was first dip-coated with a suspension that formed a
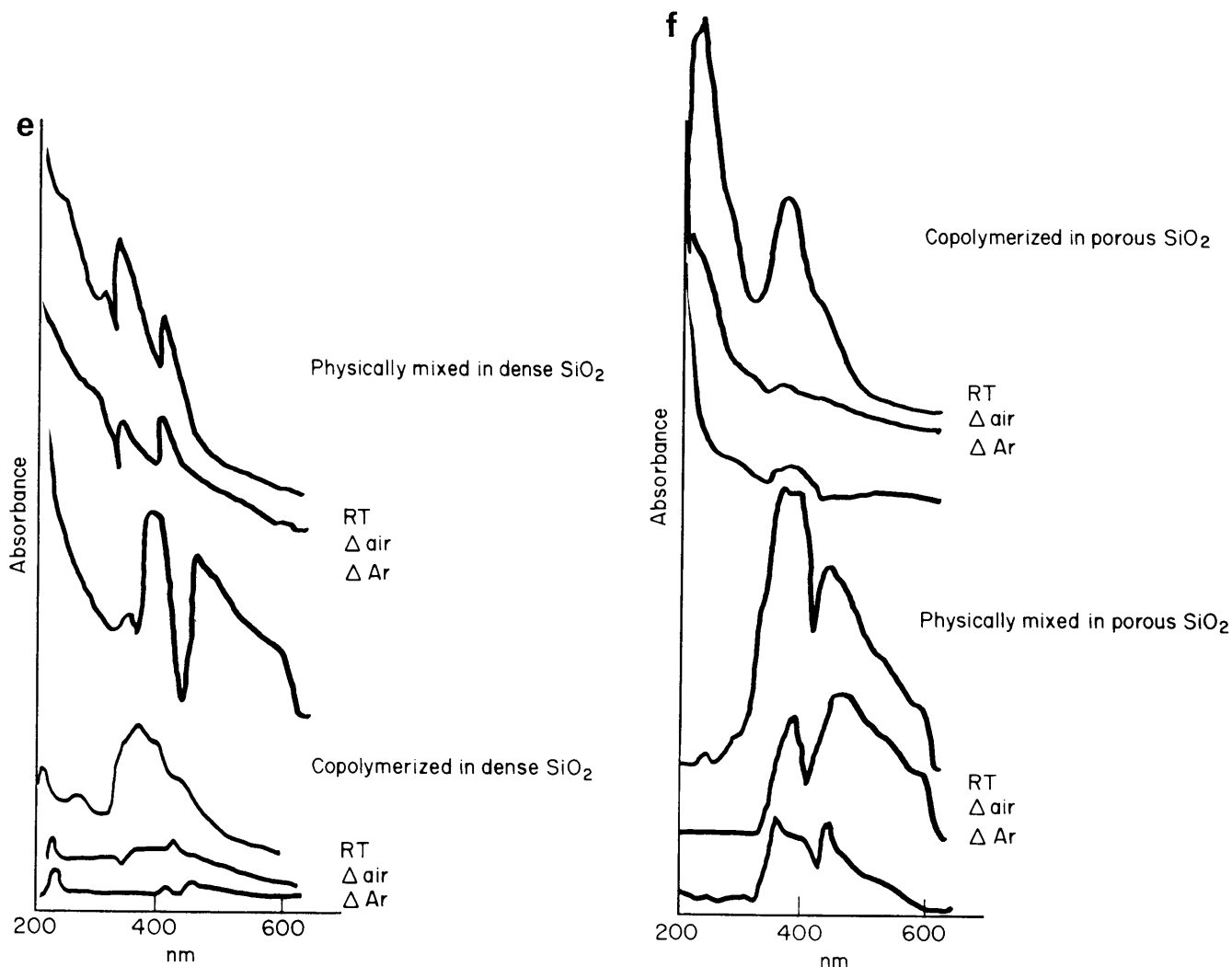
a

Absorbance

Alone
RT
△ air
△ Ar

2,4–Dinitroaniline in ethanol

Dense SiO₂
RT
△ 700 °C

Porous SiO₂
RT
△ 700 °C

Sapphire substrate

200   400   600
nm

b

Absorbance

Dense SiO₂ overcoat

RT
△ air
△ Ar

200   400   600
nm

c

Absorbance

Porous SiO₂ overcoat

RT
△ air
△ Ar

200   400   600
nm

d

Absorbance

Over porous SiO₂

RT
△ air
△ Ar

200   400   600
nm

Figure 2 Survey transmission u.v.–vis spectra of the alumina substrate. the alumina substrate with SiO₂ coatings not containing chromophore, and alumina substrates bearing the chromophore in the configurations shown in *Figure 1*. The spectra were recorded at different gains. Chromophore-modified coating on sapphire: (a) alone: (b) under a dense SiO₂ coating: (c) under a porous SiO₂ coating: (d) over a porous, high surface area coating: (e) copolymerized or physically incorporated into a dense SiO₂ coating: (f) copolymerized or physically incorporated into a porous SiO₂ coating

porous silica[13]. Heating this sample to 200 C for 5 min consolidated the porous SiO₂ coating (*Figure 1D*).

Cohydrolysis of **1** with TEOS (molar ratio of 1:TEOS, 1:144 and 1:31 for the dense and porous formulations, respectively) and addition of 2,4-dinitroaniline (same ratios as for 1:TEOS) formed 'composite' materials with the dyes covalently and non-covalently incorporated, respectively (*Figures 1E* and *F*).

Procedure for thermal treatment

Samples were initially heated to 100 C for 5 min, measured in the u.v.–vis in transmission mode, heated in air or argon to 100 C for 2 h, and cooled to 25 C. The samples were reheated to a higher temperature (200 to 700 C in 100 C intervals) using the same thermal cycle and rate, 1 C min⁻¹.

Conditions of hydrolysis of sol–gel monomers

Solutions forming dense SiO₂ coatings were prepared according to literature procedures[12-14]. All sol–gel mixtures were stirred overnight at room temperature (24 C) and stored in a freezer (−8 C).

Hydrolysis of 1. To a solution of **1** (0.1 g, 0.26 mmol) in tetrahydrofuran (THF) (20 ml) was added HCl (0.02 ml of a 1 M solution, 1.1 mmol H₂O).

1 with TEOS for dense coatings. To a solution containing previously hydrolysed TEOS[12] (10 ml, 18.6 mmol) and ethanol (90 ml) was added **1** (0.05 g, 0.13 mM).

1 with TEOS for porous coatings. To a solution in a 25 ml round-bottomed flask containing ethanol (13.6 ml), ammonium hydroxide (0.44 ml, 29.9 wt%), and **1** (0.08 g, 0.2 mmol) was added TEOS (1.4 ml, 6.3 mmol) dropwise while the solution was stirred vigorously.

2,4-Dinitroaniline and TEOS for dense coatings. To a solution of ethanol (10 ml) and previously hydrolysed TEOS[12] (10 ml, 18.6 mmol) was added 2,4-dinitroaniline (0.02 g, 0.13 mmol).

2,4-Dinitroaniline and TEOS for porous coatings. To a solution in a 25 ml round-bottomed flask containing
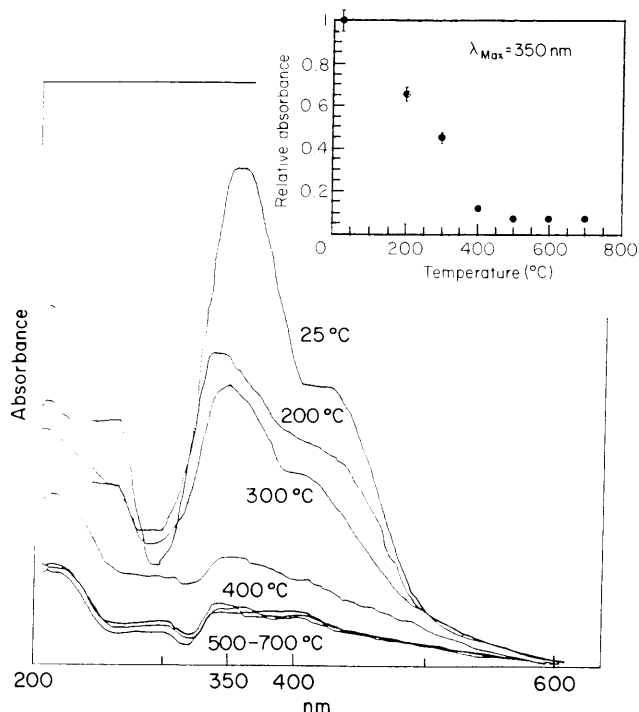
Figure 3 U.v.–vis spectra and (inset) a plot of relative absorbance of 1 (*Figure 1A*) as a function of temperature of thermal treatment in air

ethanol (13.6 ml), ammonium hydroxide (0.44 ml, 29.9 wt%), and 2,4-dinitroaniline (0.035 g, 0.19 mmol) was added TEOS (1.4 ml, 6.3 mmol) dropwise while the solution was stirred vigorously.

Rutherford backscattering spectroscopy analysis. The depth profile of oxygen in the coating on a Si substrate was obtained using a 2 MeV He$^+$ beam.

RESULTS AND DISCUSSION

Characterization of the chromophore-modified coatings and SiO$_2$ overcoats

Sample characterization consisted of measuring the thicknesses of coatings, by Rutherford backscattering spectroscopy (RBS), and the u.v.–vis spectra of the chromophore.

Measurement of coating thicknesses. The thickness of the chromophore-modified coatings on a $\langle 100 \rangle$ silicon substrate increased from 300 ± 200 Å to 7000 ± 200 Å after application of the dense SiO$_2$ coating, and to 4500 ± 200 Å after application of the porous SiO$_2$ coating.

U.v.–vis spectra of the chromophores in sol–gel-derived coatings. Figures 2a–f show survey transmission u.v.–vis spectra of the alumina substrate, the alumina substrate with SiO$_2$ coatings not containing chromophore, and alumina substrates bearing the chromophore in the configurations shown in *Figure 1*. These spectra include 'initial' spectra taken before significant heating and after heating to the highest temperatures used (700°C), both in air and under argon. We chose the λ_{max} at 350 nm to monitor the absorbance of the chromophore because there is no significant interference at this wavelength from either the substrate or the SiO$_2$ coatings. These

survey spectra, although they vary in total content of chromophore, illustrate the decrease in the intensity of the absorption at 350 nm as a function of thermal treatment under both air and argon.

Figure 3 presents the u.v.–vis spectra and a plot of relative absorbance at 350 nm of a film derived from **1** alone (*Figure 1A*) as a function of temperature of thermal treatment in air up to 700°C. The relative absorbance is the ratio of the measured absorbance to that after an initial treatment at 100°C for 5 min.

Relative chromophore stability as a function of thermal treatment. *Figure 4* illustrates the absorbances of the 2,4-dinitroaniline group at 350 nm as a function of the
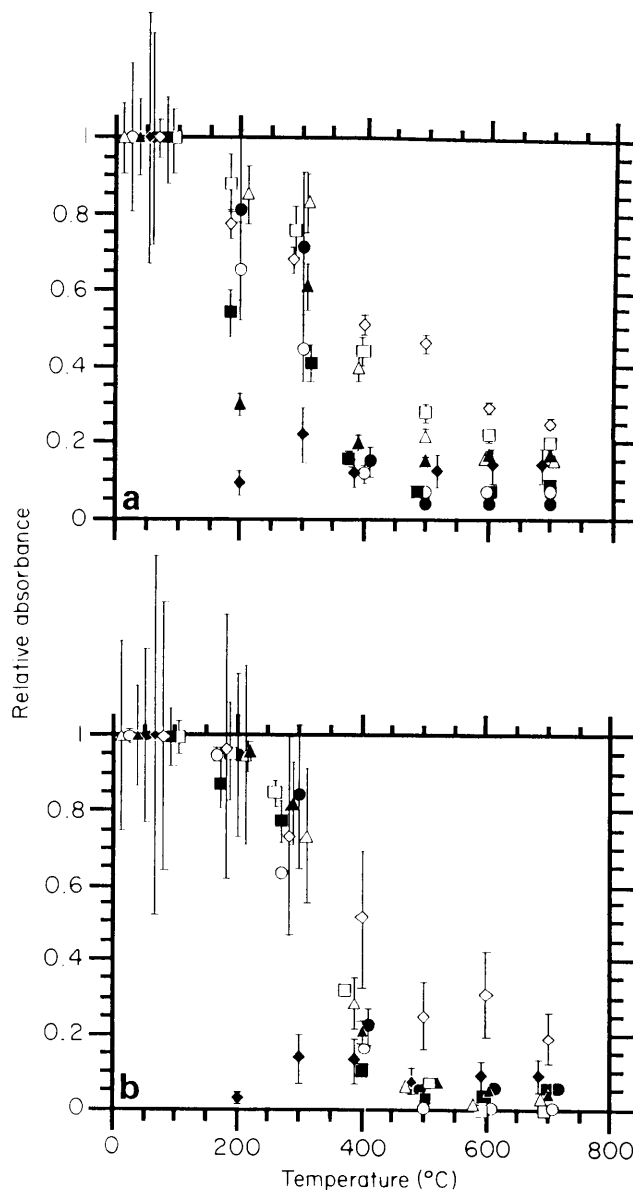

Figure 4 Relative absorbance at 350 nm of incorporated 2,4-dinitroaniline in sol–gel coatings as a function of temperature of thermal treatment (a) in air and (b) under argon. Samples were held at each temperature for 2 h. The relative absorbance is the ratio of the measured absorbance to that after an initial treatment at 100°C for 5 min. The symbols denote chromophore: (○) alone, (●) over porous SiO$_2$, (△) with a dense SiO$_2$ overcoat, (▲) with a porous SiO$_2$ overcoat, (□) copolymerized in dense SiO$_2$, (■) copolymerized in porous SiO$_2$, (◇) physically mixed in dense SiO$_2$, and (◆) physically mixed in porous SiO$_2$. The points are shown displaced from the nominal temperatures to avoid overlap. The data points represent the average measurement of two samples, the error bars their range

temperature of the most recent thermal treatment under air and under argon. The relative decrease of the absorbance at 350 nm is the same under treatments in air and in argon. Furthermore, the relative decrease in the signal is similar for all the conditions studied.

CONCLUSIONS

The relative oxidative and/or thermal stability of the organic group – the 2,4-dinitroaniline group – seems not to be significantly improved by inclusion in the sol–gel-derived matrix. The process that limits degradation of the chromophore appears to be thermal rather than oxidative, based on the observation that there is no increase in relative stability under the oxygen-free, argon environment relative to air. Adding a SiO_2 coating, which should serve as a barrier to diffusion of oxygen, had no effect on the stability of the chromophore; this result is also consistent with a thermal rather than an oxidative mechanism for degradation.

There was no significant difference between the relative rate of disappearance of the chromophore when it was covalently or non-covalently incorporated into the gel.

There appears to be no significant effect on the relative stability of the chromophores when coated on a high surface area silica compared with placement on the flat substrate.

The sol–gel lattice (at least for the delicate chromophore 2,4-dinitroaniline) does not provide any real thermal/ oxidative protection to organic chromophores incorporated in it.

ACKNOWLEDGEMENTS

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