Sol−Gel Materials for Second-Order Nonlinear Optics

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Sol−gel processing of new materials for second-order nonlinear optics promises to be a simple and highly versatile synthetic route among those that have been evaluated to achieve large and stable second-harmonic generation. Introduction to various types of organic chromophore−inorganic matrix hybrid materials that have been fabricated via sol−gel methodology and a survey of the recent efforts in optimizing their nonlinear optical efficiencies are presented. It is incurred that main-chain chromophore-embedded processable hybrids with high glass transition temperatures and thermal stabilites offer great potential in the quest for building a device based on second-order nonlinear optical efficiency of synthetic materials.

Introduction

Second-order nonlinear optics continues to be a topical area of research because of its tremendous potential in the design of photon-based new materials for optical switching, data manipulation, and information processing.[1] The fabrication of efficient photonic devices is a challenging task because such systems need to meet stringent requirements for high optical quality and large and sustainable second-harmonic generation (d_{33}, $\chi^{(2)}$). It is a multifaceted problem that initially involved resolving several issues both at the molecular as well as the bulk levels. Much has now been done to establish structure−property relationships[2] and isolate organic chromophores (for example, the azo-dye, 2,2′-[4-[(4-nitrophenyl)azo]phenyl]iminobisethanol) with high molecular hyperpolarizability (β). The incorporation of these dipolar molecules into bulk components has been the focus of much activity in the past decade.[3]

Functionalized polymers have been at the forefront among the methodologies that have been extensively studied to incorporate nonlinear optical (NLO) chromophores into macromolecular systems.[4] For an optimization of the second-order nonlinear optical response in an assembly of NLO-active molecules, a high degree of noncentrosymmetric order of the dipoles needs to be achieved. It can be attained by either electric field[5] or optical[6] poling of a microscopically oriented medium. Light-induced alignment of chromophores is an area of substantial significance especially for media containing nondipolar molecules. It has been recently demonstrated that such a guest−host hybrid system containing an octupolar dye (Ethyl Violet) in a silica matrix can be successfully optically poled yielding a quasi-permanent light-induced noncentrosymmetry of molecules.[6b] Electric-field-induced chromophore alignment has been a widely used technique to obtain preferred polar orientations in macromolecules containing dipolar chromophores. However, an ordered state of NLO-active molecules obtained by the latter process would normally decay to an equilibrium isotropic state when the poling electric field is removed. The most probable candidate in which efficient poling of an adequate number density of NLO-active chromophores can be achieved and the relaxation of chromophore orientation is minimized must exhibit inherent properties that include: (i) high thermal stability to withstand heating during poling and (ii) high glass transition temperature (T_g) to lock the chromophores in their acentric order after poling. In addition, optical transparency of the medium to minimize optical loss and high temporal stability of the second-order NLO signal constitute significant issues. Most of the polymeric materials have either low T_g or exhibit poor reproducibility of optical quality including high optical loss which limit their applications as optical devices. Such problems can be alleviated by either doping or incorporating NLO-active organic chromophores into an inorganic matrix yielding organic−inorganic hybrid materials via sol−gel processing.[7] The latter has been rightfully described as a highly promising alternative and versatile synthetic approach to the fabrication of amorphous three-dimensional optical networks.[8] The use of sol−gel methodology in building useful materials is not limited to optics and their applications in the field of catalysis and selective separation of trace metals has recently been reviewed.[8b]

Sol−Gel Materials

The so-called sol−gel methodology for the processing of glassy materials has evolved from the original research efforts on thin film dielectric coatings.[9] It allows low-temperature fabrication of networks facilitating the introduction of organic chromophores, and the resulting hybrids possess high T_g, low beam propagation loss and are more stable because of the greater rigidity and higher thermal stability of silica than organic polymers.[10] These hybrid materials capitalize on the unique properties offered by the two components to generate novel materials with desired characteristics. The NLO-active chromophores modify physical properties to facilitate processing, control porosity, and adjust the hydrophobic/hydrophilic balance, and the inorganic

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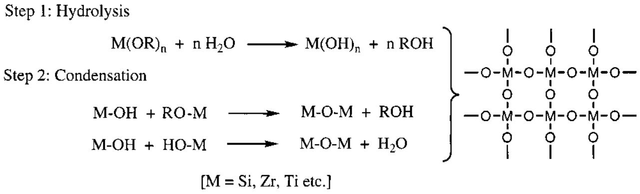
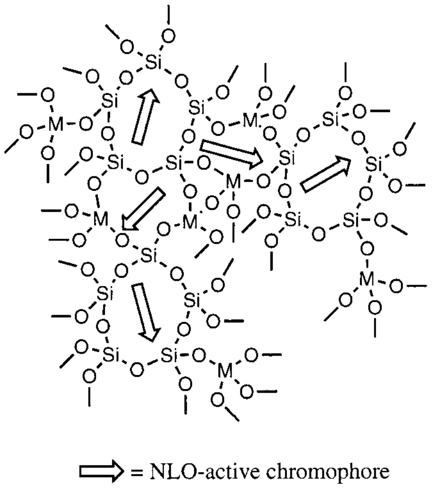
Scheme 1. Traditional Sol–Gel Methodology



Scheme 2. Guest–Host Organic–Inorganic Hybrids [M = Si, Zr, Ti, etc.]



matrix helps to tune the mechanical and thermal strength and to modulate optical indices.[11]

A typical sol-to-gel process (Scheme 1) involves inorganic polymerization of metallo-organic compounds such as alkoxides, $M(OR)_4$ (M = Si, Ti, Zr, Al; R = alkyl), which act as cross-linkers by a sequence of hydrolysis and condensation steps. These reactions are normally carried out in an alcoholic solvent due to immiscibility of alkoxide compounds and water. The hydrolysis and condensation reactions can be optimized by the addition of acidic or basic catalysts.[12] To modify the network with the desired organic microstructures, alkoxysilanes such as $R'_xSi(OR)_{4-x}$ are generally added. The ultimate structure of these nanocomposites can be fine-tuned by varying the molar concentrations of the cross-linker and network modifier.

Sol–gel-based nonlinear optical materials can be divided into two classes, the guest–host matrixes and chromophore-linked hybrids. In the guest–host-doped systems (Class I), the NLO-active molecules are embedded in the inorganic network with weak interactions such as van der Waals or hydrogen bonds. The chromophore is strongly bound to the matrix by one or more covalent bonds in the main-chain inorganic–organic hybrids (Class II).

Guest–Host Matrixes Containing Trapped NLO Chromophores

Class I type of materials were the first to be investigated. In this methodology NLO-active molecules are mixed with the network-forming precursors. Upon sol–gel processing the chromophores become trapped in an inorganic matrix (Scheme 2), which can then be subjected to electric-field-induced chromophore alignment to achieve a noncentrosymmetric order. Examples of such hybrids include trapping of *N*-(4-nitrophenyl)-(s)-prolinol in the following: (i) a $CH_3SiO_{1.5}$–ZrO_2 matrix with a second-order NLO coefficient d_{33} of 0.16 pm V^{-1};[13a] (ii) a SiO_2–TiO_2 network ($d_{33} = 2$ pm V^{-1}),[13b] methylnitroaniline in an aluminum oxide matrix[13c] and Disperse Red 1 in a silica matrix ($d_{33} = 75$ pm V^{-1}).[13d] In the latter case, because the dye has a λ_{max} in the range of 450–497 nm (Table 1), strong absorption at second-harmonic wavelength of 532 nm was observed. In general, a maximum of only about 15–20% loading of the chromophore could be attained in such systems, and they depicted unstable nonlinear optical responses attributed to phase separation, sublimation at elevated temperatures during electric field poling, and thermal and environmental instability.

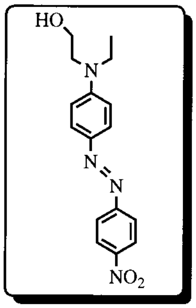
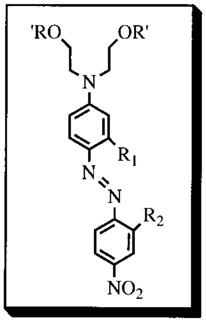
Attempts have been made to improve the properties of the guest–host systems by using a mixture of dye-doped polymer and silica.[14] Poly(methyl methacrylate) and tetraethoxysilane (TEOS) were mixed in THF and the hydrolysis of the inorganic network forming agent was affected by using an acid catalyst. The organic dye DR1 was then added to about a 5% doping level. The interaction of the doped polymer with the inorganic matrix led to a significant enhancement of the glass transition temperature which resulted in an increase in stability of the second-order nonlinear optical response of the material and its temporal stability. The other physical characteristics of the hybrid material such as thermal stability and phase separation were found to be dependent on the inorganic matrix content of the mixture. An increase in the molar percentage concentration of TEOS to higher than 70% gave translucent films due to phase separation. The optimal molar ratio of the doped polymer and inorganic matrix was found to be 2:1 or 1:1. The second-order nonlinear optical efficiency of the polymer-matrix hybrid ($\chi^{(2)} = \sim 4$ pm/V) was found to be lower than that of the pure polymer ($\chi^{(2)} = 10$ pm/V) at similar doping percentages.[14a] It may be attributed to the interaction of the dye with the inorganic matrix via hydrogen bonding or a decrease in orientational stability with the increasing amounts of silica.

An evaluation of the environment of NLO-active chromphores in the doped sol–gel network has also been carried out recently which might help in understanding the trapping efficiencies of matrixes.[15] However, because the chromophore is not efficiently locked in the inorganic matrix, fast reversal to random orientation takes place once the electric field is switched off, leading to a substantial reduction in their nonlinear optical response. The randomization process could be slowed by optimization of the curing temperature; however, it is limited by the low thermal stability of the guest–host systems which is dependent mainly on the decomposition temperature (T_d) of the organic chromophores.[16]

Chromophore-Linked Sol–Gel Materials

The above issues can be resolved by linking NLO-active molecules to the inorganic matrix. The latter allows better control of the concentration of the added chromophore and chemical and processing parameters. The desired chromophore that has optimized molecular structure (for example, DR1) is linked to the alkoxysilane by a Si–R′ covalent bond, $R'Si(OR)_3$, and then

Table 1

NLO-Active Chromophore	Hybrid System	Matrix	Linear Optical Properties	Nonlinear Optical Properties	Ref.
 **DR1** ($\beta = 125 \times 10^{-30}$ esu $\mu = 8.7$ D)[2b]	Guest-Host	SiO_2	λ_{max} (thin film) = 497 nm λ_{max} (solution) = 450 nm	d_{33} = 75 pm/V at 1064 nm fundamental wavelength.	13d
	Guest-Host	PMMA-SiO_2		$\chi^{(2)}$ = 4 pm/V	14a
	Side-Chain Tethered	SiO_2 (DR1 + -isocyanato-propyl-$Si(OEt)_3$ + $Si(OEt)_4$)	λ_{max} (thin film) = 460 nm at 160 °C	d_{33} = 55 pm/V at 1064 nm fundamental wavelength.	21
	Main Chain Embedded	SiO_2; $R_1 = CH_3$; R_2 = H; R' = CO-NH$(CH_2)_3Si(OEt)_3$	λ_{max} (thin film) = 460-470 nm	d_{33} = 20-80 pm/V at 1.34 μm fundamental wavelength.	29
	Main Chain Embedded	SiO_2; R_1 & R_2 = H or R_1 = H, R_2 = OCONH$(CH_2)_3Si(OEt)_3$; R' = CONH$(CH_2)_3Si(OEt)_3$	λ_{max} (thin film) = 460 nm	d_{33} = 16-29 pm/V at 1064 nm fundamental wavelength.	30
	Main Chain Embedded	SiO_2; R_1 & R_2 = H; R' = CONH$(CH_2)_3Si(OEt)_3$	λ_{max} (thin film) = 440 nm	r_{33} = 3.7-12.4 pm/V at 1.3 μm fundamental wavelength.	31
	Main Chain Embedded	SiO_2; R_1, R_2 & R' = H	λ_{max} (thin film) = 480 nm	$\chi^{(2)}$ = 14-23 esu at 1064 nm fundamental wavelength.	35

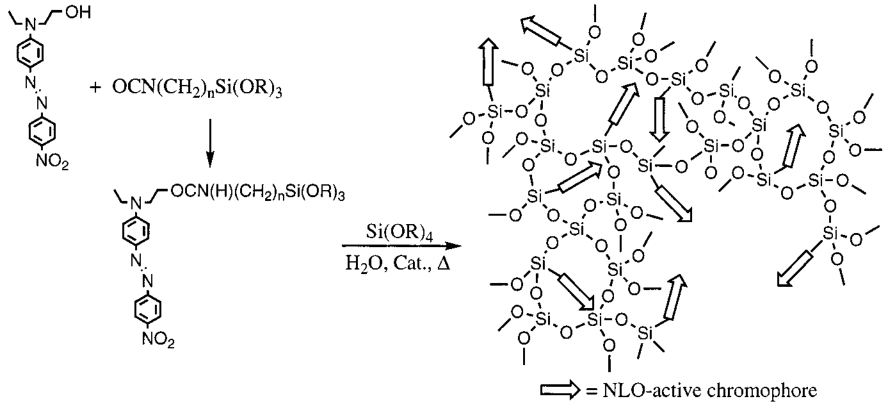
processed by hydrolysis and condensation. The number of covalent bonds of the organic chromophore with the inorganic matrix classify such hybrid materials into side-chain (one covalent bond) and main-chain (two or more bonds) hybrid materials.[17] Siloxane-based precursors such as $Si(OR)_4$ and $R'_xSi(OR)_{4-x}$ offer several advantages including relatively low cost and an ease of control of their reactivity and have been extensively utilized for the synthesis of Class II type optically active inorganic–organic hybrid materials. The chemical attachment of the chromophore prevents it from aggregating and an adequate number density of it can be loaded in the network. Incorporation of organic chromophores into the networks imparts better elasticity to the otherwise stiff SiO_2 backbone, preventing the formation of cracks during the fabrication of thin films. The degree of cross-linking in these networks could be enhanced by adding different amounts of tetraalkoxysilanes during sol–gel processing. It strengthens the physical robustness of the resulting nanocomposites and leads to an improvement of their T_g.

Class II: Side-Chain-Tethered Inorganic–Organic Hybrid Materials

In this category of hybrid materials NLO-active chromophores are designed to have one reactive end group which participates in the sol–gel process. A typical reaction sequence for the synthesis of such a hybrid is shown below in Scheme 3. The covalent bond of the optically active chromophore to silica through a Si–C bond is inert toward hydrolysis under the sol–gel processing conditions. The hydrolytic condensation, in general, needs to be catalyzed with use of an acid or base or under neutral conditions using fluoride anions at elevated temperatures. Under acidic conditions the hydrolysis of alkoxide groups is promoted, and base catalysts enhance the degree of condensation.[18] It has recently been demonstrated that divalent transition metal (Co(II), Ni(II), Cu(II), and Zn(II)) bis(acetylacetonate) complexes can also be used as condensation catalysts with gelation times of tetraalkoxysilanes similar to those obtained with conventional base catalysts.[18b] They offer potential in introducing organic/organometallic species sensitive to inorganic bases commonly used in traditional sol–gel methodology; however, their widespread use may require a detailed investigation of their overall suitability.

The resulting networks are similar in their mode of attachment of the organic entity to the side-chain-tethered linear polymers and are insoluble in common organic solvents. Therefore, a precursor generated during hydrolysis and partial condensation (sol) is routinely

Scheme 3. Chromophore-Linked Side-Chain-Tethered Hybrids



used to cast thin films which are thermally cured to enhance networking on the substrate.[19] The sols which are only oligomers in solution allow freedom to NLO molecules to align when electrically poled. Upon thermal curing the stiff matrix behaves as a lock for the NLO-active chromophores, preventing relaxation to a random orientation.

A nonlinear optical chromophore is covalently attached to a polymerizable silane to yield a precursor which can be copolymerized with a tetraalkoxysilane under sol–gel hydrolysis/condensation processing conditions to yield a hybrid material. A number of inorganic–organic hybrid materials have been prepared using several chromophore-grafted silane precursors with moderate success in achieving high and stable nonlinear optical efficiencies.[18,20] Some of the recent efforts in this area using NLO-active molecules with large hyperpolarizabilities are summarized here. DR1 was covalently linked to 3-isocyanatopropyltriethoxysilane and the resulting precursor was copolymerized with tetraethoxysilane. The reaction conditions were manipulated to affect hydrolysis under acidic conditions followed by base-promoted condensation. Thin films of the resulting sol were spin-coated on to glass and upon further curing and corona-discharged poling yielded a resonance-enhanced second-order nonlinear optical efficiency (d_{33}) of 55 pm V^{-1} (Table 1) with appreciable room-temperature temporal stability of the second-harmonic response.[21] No significant decrease in the value of the poling-induced second-harmonic generation (SHG) response was observed at room temperature over a period of 1 week.

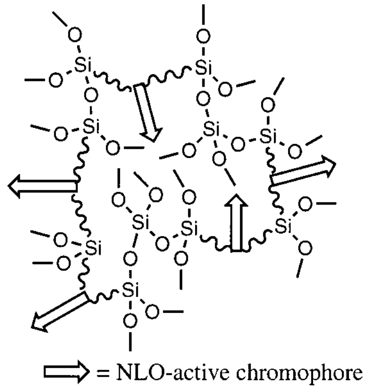
Choi et al. prepared sol–gel precursors by linking 4′-[(2-hydroxyethyl)methylamino]-4-nitrostilbene (λ_{max} = 438 nm) and 4′-[(6-hydroxyhexyl)methylamino]-4-nitroazobenzene (λ_{max} = 498 nm) to 3-isocyanatopropyltriethoxysilane which were processed using acid-promoted hydrolysis followed by condensation.[22] The poled thin films of the resulting hybrid materials showed a red shift in their λ_{max} by 20 nm and exhibited SHG efficiency (d_{33}) of 20–44 pm/V at the fundamental wavelength of 1064 nm. A 20–24% decay of the second-harmonic signal was observed over a period of 1 month at ambient temperature.[22]

Sung et al. covalently attached DR1 to toluylene-2,4-diisocyanate which upon reaction with γ-(aminopropyl)triethoxysilane yielded the chromophore-bound silane precursor. The latter was copolymerized with tetraethoxysilane and the resulting sol was used to spin-coat thin films (λ_{max} = 472 nm) which were thermally cured and upon poling gave a d_{33} value of 46 pm/V at the fundamental wavelength of 1.06 μm.[23] They also observed high thermal stability of the poled thin films.

An attempt to enhance the temporal stability of the SHG response by cross-linking the organic moieties in the hybrid material was carried out by Choi et al. They first covalently linked DR1 to 3-isocyanatopropyltriethoxysilane and the resulting precursor was (i) processed alone using sol–gel methodology and (ii) mixed with a 50 mol % solution of (3-glycidoxypropyl)trimethoxysilane. Spin-coated thin films of these were thermally cured and corona-poled to give d_{33} values of 54 and 42.7 pm/V for (i) and (ii), respectively. Temporal stability of the SHG signal was significantly enhanced upon cross-linking with (3-glycidoxypropyl)trimethoxysilane.[24] In the thin films which were not cross-linked with (3-glycidoxypropyl)trimethoxysilane, the SHG signal intensity was reduced to 10% of its initial value at 100 °C upon the removal of the poling electrical current. However, upon increasing of the cross-links with (3-glycidoxypropyl)trimethoxysilane, the signal maintained its intensity at 85–90% of the initial value at 100 °C. In the former, due to the lack of intensive cross-linking, the dye has enough free space to relax to a random orientation. Introduction of organic derivatives such as 4-(2-hydroxyethoxy)chalcone that can be photo-cross-linked once attached to inorganic matrixes has also been demonstrated to improve second-order nonlinear optical efficiencies of the organic–inorganic hybrid materials.[25] New methodologies have also been employed by mixing prepolymers of melamines and an alkoxysilane-functionalized dye in a bid to enhance compatibility between the organic and inorganic phases and thus reduce phase separation.[26] An improvement of the glass transition temperature was observed when equal amounts of melamine precursor and the functionalized dye were mixed. Thin films of these hybrids after poling and thermal curing exhibited second-order nonlinear optical efficiencies (d_{33}) of 10–54 pm/V with good temporal stability of the nonlinear optical coefficient at 100 °C.

Han et al. have investigated the nonlinear optical properties of silsesquioxanes prepared from sol–gel processing of α,ω-bis(trimethoxysilyl)-1,4-dipropoxybenzene containing side chains of NLO-active molecules *N*-(4)-nitrophenol-(L)-prolinol.[27] These hybrids exhibit high thermal stabilities, moderate second-order nonlin-

Scheme 4. Chromophore-Linked Class II Hybrids



ear optical efficiencies (2−3.2 × 10^{-8} esu), and longer temporal stabilities of the SHG signal. The latter properties were attributed to the fixation of dipolar components in size-matched pores of silsesquioxanes after alignment.

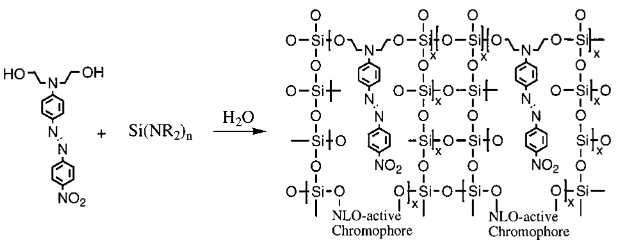
Class II: Main-Chain-Embedded Inorganic−Organic Hybrid Materials

One of the major issues with side-chain-tethered sol−gel second-order nonlinear optical materials is the low temporal stability of the SHG signal. The nonlinear optical properties of the sol−gel-based hybrid materials can be further optimized by reducing the degrees of freedom of the NLO-active molecules and by increasing the rigidity of the inorganic matrix. This can be achieved by (i) increasing the number of covalent links between the matrix and the organic chromophore, e.g., by grafting it at both ends (Scheme 4), and (ii) enhancing the glass transition temperature which can be attained by increasing the ratio of added tetraalkoxysilanes for sol−gel processing.

Several such systems have been prepared using this methodology.[28] For example, NLO-active dye Red 17 (4-(amino-*N*,*N*-diethanol)-2-methyl-4′-nitroazobenzene) has the desired functionalities for its incorporation into the sol−gel matrix as a main-chain-incorporated hybrid material. Two sol−gel precursors of this dye were prepared by reacting it with (i) 3-isocyanatopropyltriethoxysilane (ICTES−Red 17) and (ii) methyldiethoxysilane (MDES−Red 17). These were then mixed with tetramethoxysilane and processed by hydrolysis under an acidic medium followed by condensation.[29] A sol of the latter mixture was used to spin-coat thin films and then cured and poled at 100 °C for 2 h and then at 150 °C for 30 min. The resulting thin films showed d_{33} values of 70−80 pm/V for the thin films prepared from ICTES−Red 17 and 20−24 pm/V for those prepared from TMOS−Red 17. The former showed higher temporal stability of the SHG signal which decreased to 40 pm/V after 5 days, while in the films with TMOS−Red17 as the chromophore, it decayed to 5 pm/V during the same time.

Sung et al. prepared[30] multifunctional chromophores 2,2′-{4-[(4-nitrophenyl)azo]phenyl}imino-bisethanol(DR19), 2′-bis[(2-hydroxyethyl)oxy]-4-diethylamino-4′-nitroazobenzene, 2′-{4-[2-(2-hydroxyethyl)oxy-(4-nitrophenyl)azo]-phenyl}imino-bisethanol, and 2,2′-bis[anhydrictrimellitoxy]-4-diethylamino-4′-nitroazobenzene. These were then coupled with 3-isocyanatopropyltriethoxysilane to produce NLO-chromophore-alkoxysilane precursors which were mixed with tetraethoxysilane and hydrolyzed in an acidic medium to yield main-chain chromophore-embedded polymers. The thin films of these hybrid materials upon corona poling exhibited d_{33} values of 16−29 pm/V.

Scheme 5

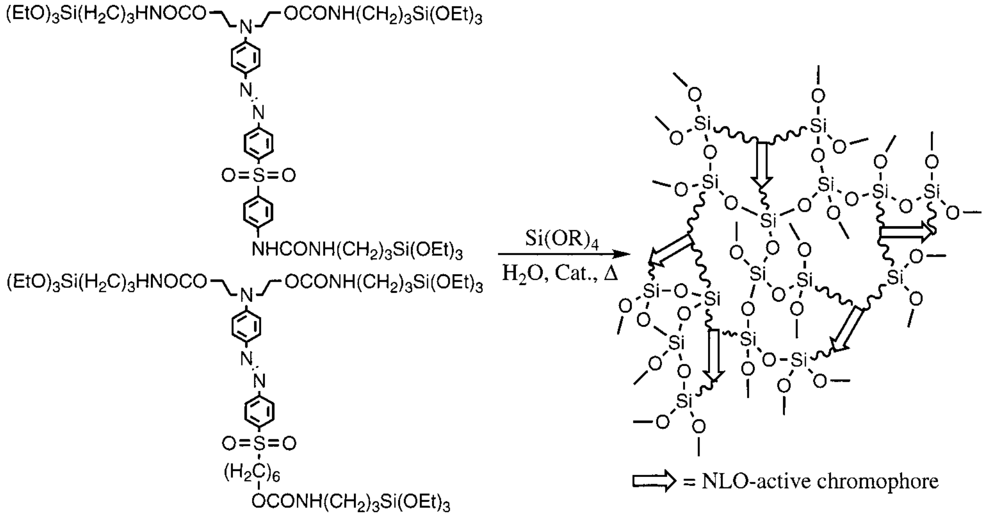


Kim et al. reported[31] the synthesis of hybrid materials containing NLO-active chromophores in the main chain from 4-[*N*,*N*-bis(2-(triethoxysilanoxyethylamino))-4′-nitrostilbene, 4-[*N*,*N*-bis(2-(triethoxysilanoxyethylamino))-4′-hexyl-sulfonylstilbene, and tetraethoxysilane. The thin film of such a hybrid from 4-[*N*,*N*-bis(2-(triethoxysilanoxyethylamino))-4′-nitrostilbene upon curing and corona poling gave a d_{31} value of 72 pm/V. The latter film also exhibited high temporal stability with the r_{33} signal decaying to only 80% of its original value at 150 °C.

Because of the insolubility of the hybrid materials containing covalently linked chromophores, their sols that are generally oligomers with very low viscosity are employed in the fabrication of thin films. The latter are thermally cured to form a network on the substrates which lowers their optical quality. The structural control of the hybrid materials is dependent on a number of factors including the type of catalyst, pH of the reaction mixture for controlling the degree of condensation, nature of the solvent and organic species, and temperature. The hydrolysis and condensation reactions rates can also be diminished by the presence of methanol and ethanol that are produced as byproducts. Such issues continue to provoke a widespread interest and offer an insight into the chemical parameters that need to be controlled to achieve optimal properties.[32] It may be advantageous to fabricate processable organic−inorganic hybrid materials using new silane reagents that can be synthesized by hydrolysis and condensation without any additional catalysts.

The Si−NR$_2$ bond in aminosilanes ($Si(NR_2)_4$; R = CH_3, CH_2CH_3) is much more basic than the Si−OR bond of tetraalkoxysilanes commonly used in the sol−gel processing of materials. Its hydrolysis with chromophores containing terminal OH groups and H_2O is much more facile. Condensation of the resulting Si−OH bonds is known[33] to be catalyzed by bases such as amines, and NR_2H (a potential catalyst) is formed as a byproduct in the above hydrolysis of the Si−NR$_2$ bond in aminosilanes. An alternative methodology for preparing hybrid materials has been developed using aminosilanes as network-forming reagents and NLO-active chromophores (Scheme 5).[34] The approach is similar in principle to the traditional way of processing sol−gel materials but requires no added catalysts for hydrolysis and condensation steps.

Scheme 6. Class II Hybrids with Three Points of Linkage of the Chromophore



Two types of chromophores, (i) bifunctional such as Disperse Red 19, 1-methyl-4,4′-[*N*,*N*-bis(2-hydroxyethyl)-amino]styryl}pyridinium and 1-bis(3-hydroxypropyl)-amino-4-nitrobenzene, and (ii) monofunctional such as Diperse Red 1 were employed in this study.[35] The former leads to main-chain-embedded hybrid materials and the latter are atypical for making side-chain-tethered networks. The chromophores were first reacted with a tetraaminosilane in different ratios, and then a required amount of water was added to hydrolyze the remaining Si−NR$_2$ bonds. The mixtures were then heated to condense Si−OH moieties resulting in NLO-active hybrid materials. A variety of hybrids were prepared by varying the molar ratios of chromophore, aminosilane, and water. The networks prepared from monofunctional chromophores were found to be insoluble in common organic solvents; however, those corresponding to main-chain-embedded chromophores were soluble in high boiling solvents such as *N*-methylpyrrolidinone and dimethyl sulfoxide. The solubility of the latter materials was found to be inversely proportional to the degree of cross-linking which was controlled by the amount of aminosilane added to the mixture. Thus, when the amount of cross-linker and water added during synthesis is controlled and subtle variations in the processing conditions are carried out, important physical characteristics of these hybrid materials including glass transition temperature and thermal stability could be easily tailored.

The above network materials exhibited high glass transition temperatures (150−297 °C) and thermal stabilities (240−372 °C) that allowed poling of their thin films above T_g. The latter helps to achieve a good degree of alignment of the NLO-active chromophores and these hybrids depicted high efficiencies in second-harmonic generation ($\chi^2 = 2-37 \times 10^{-8}$ esu). Their SHG signal intenstities showed excellent temporal stabilities at room temperature and 80 °C. These supramolecular structures containing NLO-active chromophores embedded in an inorganic matrix that can be isolated as powders offer substantial advantages in constructing thin-film-based acentric materials with large and stable bulk $\chi^{(2)}$ and offer promise in building new materials with optical clarity.

Class II: Main-Chain Highly Cross-linked Inorganic−Organic Hybrid Materials

It is inferred from the discussion above that the incorporation of the NLO-active chromophore in the main chain of the inorganic matrix is advantageous in tuning the nonlinear optical efficiencies of these hybrid materials. It may be possible to further enhance the temporal stability of the SHG signal intensity by increasing the number of covalent links between the chromophore and the matrix. To evaluate this approach, chromophores that have three polymerizable Si(OR)$_3$ end units attached to them have been synthesized.[31,36] The silane precursors and the resulting networks obtained upon sol−gel processing are shown in Scheme 6. Kim et al. prepared a trifunctional chromophore, 4-[*N*,*N*-bis(2-hydroxyethyl)amino]-4′-(6-hydroxyhexyl)-sulfonylstilbene, that was linked with 3-isocyanatopropyltriethoxysilane to yield the desired silane precursor 4-[*N*,*N*-bis(2-(triethoxysilanoxy-ethylamino))-4′-(6-triethoxysilanoxyhexyl)sulfonylstilbene. The latter was either hydrolyzed alone or mixed with tetraethoxysilane and then processed by sol−gel methodology. The thin films of the sols were fabricated on ITO-coated glass and subjected to corona poling and thermal curing. The electro-optic cofficients (r_{33} at 1.3 μm) of these thin films were found to be low (2.7−4.3 pm/V), which was attributed to inefficient poling of the chromophore dipoles due to high cross-linking in the networks. Since the chromophore is linked to the matrix at both ends, its free motion becomes severely restricted.

Using a similar approach, Sung et al. prepared a cross-linkable chromophore with high thermal stability, 4-[(4″-aminophenyl)sulfonyl]-4′-[*N*,*N*-bis(2-hydroxyethyl)-amino]azobenzene.[36] The latter was reacted with 3-isocyanatopropyltriethoxysilane to yield the corresponding chromophore-alkoxysilane precursor which was mixed with tetraethoxysilane. The thin films of the resulting sol were fabricated on ITO-coated glass. A similar problem as mentioned above of inefficient poling of the “fixed” chromophore in the highly cross-linked networks is still an issue. To resolve this, thin films were corona-poled at 200 °C with an applied voltage of 5.5 kV to yield a d_{33} value of 32 pm/V. They also studied the temporal stability of the SHG signal at different temperatures.

At 100 °C the signal remained stable but started to decay above 130 °C. At 160 and 200 °C the SHG signal was reduced to 75 and 50%, respectively, of the original intensity. The latter may be attributed to chromophore decomposition and relaxation of the chromophore to a random orientation.

Conclusions

Sol−gel methodology offers great promise in the fabrication of new materials for second-order nonlinear optics that will eventually meet the basic requirements in building photonic devices. The optimization of chemical and physical processing parameters is of paramount importance, and a significant effort in this direction has been devoted in the past few years. New network-forming precursors show potential, and a detailed investigation of their chemistry and that of related reagents will provide more insight into evaluating them as materials of choice for sol−gel processing. Interaction of the NLO-active chromophores with the inorganic matrixes seems also to have a significant influence on the quality of thin films and their nonlinear optical efficiencies. By embedding them in the main chain by covalent bonds, one can fabricate thin films of better optical quality that exhibit large and sustainable second-harmonic generation. It may also be advantageous to develop new synthetic methodologies that will efficiently mix chromophore-bound organic polymers with inorganic matrixes and yield materials with high T_g and thermal stabilities. Variations in the physical processing of sols have also played a great role in tailoring the structural properties by increasing the cross-links in the matrix. The latter can lead to a significant improvement in the temporal stability of the nonlinear optical signal in the final material. With the increasing attention paid to discerning all the steps involved in sol−gel processing of materials for second-order nonlinear optics, we may be getting closer to building a synthetic photonic device.

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