

A Novel Photoconductive PVK/SiO₂ Interpenetrated Network Prepared by the Sol–Gel Process

Gonzalo Ramos,^{†,‡} Tomás Belenguer,^{†,§} Eusebio Bernabeu,[§] Francisco del Monte,^{*,‡} and David Levy^{†,‡}

Instituto Nacional de Tecnología Aeroespacial-INTA, Laboratorio de Instrumentación Espacial-LINES, Torrejón de Ardoz, 28850, Madrid, Spain, Instituto de Ciencia de Materiales de Madrid-ICMM, Consejo Superior de Investigaciones Científicas-CSIC, Cantoblanco, 28049, Madrid, Spain, and Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Ciudad Universitaria, 28040, Madrid, Spain

Received: August 14, 2002

In this work, we describe the preparation of a novel photoconductive sol–gel material based on an organic/inorganic interpenetrating network (IPN). The composition of the sol–gel photoconductive material mimics the well-known polymeric one based on poly(*N*-vinylcarbazole) (PVK) as the charge-transporting matrix and 2,4,7-trinitro-9-fluorenone (TNF) as the sensitizer. The resulting photoconductive material (PVK/SiO₂ IPN) shows a photosensitivity of 10^{−11} cm/(Ω W) in range to that reported for some analogue polymeric compounds and the highest ever reported for hybrid sol–gel materials.

Photoconductivity in organic materials consists of two processes (photogeneration of charge carriers and their subsequent transport) and is usually wavelength and electric-field dependent.¹ The organic photoconductive materials have drawn a great deal of attention during the last three decades, given their involvement in interesting fields as xerography (both classical and holographic)^{2–4} and photorefractivity.^{5–10} Besides thermoplastic behavior in holographic xerography applications or optical nonlinearity in photorefractivity, photoconductivity is a required property that will determine the optimum work of the material.

Photoconductivity has been observed in a number of polymers doped with either organic or inorganic entities which act as charge-transfer complexes.^{1,2,6,11,12} Among them, poly(vinylcarbazole)/2,4,7-trinitro-9-fluorenone (PVK/TNF) composites have been widely explored because of the extraordinary properties of PVK as charge-transporting matrix (hole transporting) and of TNF as sensitizer.^{4,6,10,13–17} The photoconductivity in PVK/TNF composites results from the formation of a charge-transfer complex between the TNF and the carbazole units of the PVK.^{18,19}

The sol–gel approach appears as a very promising route for the preparation of photoconductive materials. The mild synthesis conditions offered by the sol–gel route (the process begins at the solution stage and takes place at room temperature) allow the incorporation of the optically active organic molecules within the porosity of the resulting matrix. Thus, functional sol–gel materials can be prepared by mimicking the polymeric ones, but in the supporting material (silica versus polymer) which will provide an improvement of the stability besides optimum optical quality.^{20,21} During the last years, photoconductive sol–gel materials have been mainly obtained through the incorpora-

tion of disperse carbazole units within the porosity of the silica matrix, whether or not covalently bonded to the silica network, e.g., carbazole functionalized silane sol–gel precursor,^{1,20} or ethylcarbazole,²² respectively.

This work describes the preparation and characterization of a novel sol–gel material with photoconductive properties. The novelty of this approach consists of the formation of a PVK/SiO₂ interpenetrated network (IPN) rather than in the discrete incorporation of carbazole units dispersed within the silica matrix. The sol–gel photoconductive materials were prepared through the acid hydrolysis (pH = 1, 11.0 mmol) of the sol–gel precursor, glycidoxypolytrimethoxysilane (GPTMS, 5.5 mmol), under vigorous stirring. On the clear and homogeneous sol, 0.65 mmol of *N*-vinylcarbazole (NVC, from Aldrich), 5 × 10^{−3} mmol of 1,1-dimethoxy-1-phenylacetophenone (IRG-651, from CYBA), 4 × 10^{−2} mmol of 2,4,7-trinitro-9-fluorenone (TNF, from Ultra Scientific) and 0.9 mL of pyridine (from Aldrich) were added drop by drop under vigorous stirring. The sol was heated at 75 °C for 10 min prior to the addition of 25 μL of 2-(dibutylamino)-ethanol (from Aldrich). The resulting brownish sol was filtered (0.2 μm) prior to the dip coating of an indium tin oxide glass substrate (ITO). Films with thickness of 8 μm (Deck Tak III profilometer) were obtained. Samples were thermal treated at 50 °C overnight. The PVK network was obtained through the photopolymerization (UV illumination along 2 h with a ULTRA-VITALUX lamp) of the NVC caged within the porous silica matrix. NVC polymerization was monitored by the appearance of the peaks at 328 and 342 nm at the UV–Vis spectrum (Figure 1).^{23,24} The photoconductive measurements were carried out using a simple DC photocurrent technique.⁵ Counter electrodes were fabricated on the film surface just by Ag painting (0.02 Ω/cm²). Polyimide tape (Kapton), with thickness of 80 μm, was used to avoid the Ag paint impregnation of the sol–gel matrix. The irradiance of the excitation source (Ar⁺ laser) used to measure the photoconductivity ranged from 3 to 9 mW/cm².

Photosensitivity is defined as the photoconductivity (σ_{ph}, photocurrent density per unit of applied electric field), normal-

* Corresponding author. Fax: +34 91 3720623. E-mail: delmonte@icmm.csic.es.

[†] Instituto Nacional de Tecnología Aeroespacial-INTA, Laboratorio de Instrumentación Espacial-LINES.

[‡] Instituto de Ciencia de Materiales de Madrid-ICMM, Consejo Superior de Investigaciones Científicas-CSIC.

[§] Universidad Complutense de Madrid, Ciudad Universitaria.

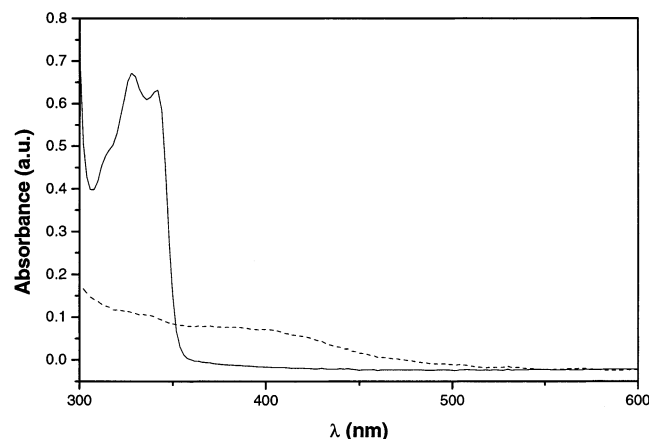


Figure 1. Absorption spectra of the NVC/TNF sol-gel material before (dash line) and after UV illumination (solid line). UV illumination gives rise to the formation of the PVK/SiO₂ IPN.

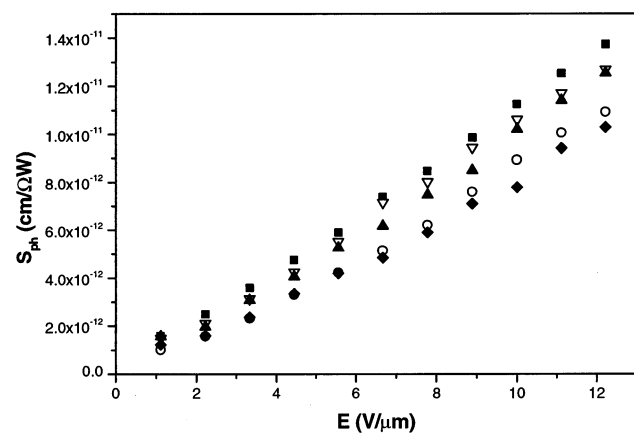


Figure 2. Photosensitivity response of the PVK/SiO₂ IPN photoconductive material at 514 nm (◆), 501 nm (○), 496 nm (▲), 488 nm (▽), and 476 nm (■).

TABLE 1: Photosensitivity Values Reported for the PVK/SiO₂ IPN Photoconductive Material and for Some Analogue Polymeric Compounds^a

S_{ph}^a cm/(Ω W)	type of material	reference
1.4×10^{-11}	PVK/TNF/SiO ₂ IPN	this work
10^{-12}	PVK/CdS-nanocrystal polymer composite	5
10^{-11}	full-functionalized polymer composite	9
10^{-14}	PVK/ECZ/TNF/chromophore polymer composite	14
10^{-14}	carbazole discrete units within a sol-gel matrix	20
10^{-10}	PVK/TNF/chromophore polymer composite	25
10^{-10}	PVK/ECZ/C ₆₀ /chromophore polymer composite	28

^a The S_{ph} value has been calculated through the application of eq 1 in those cases where it was not provided.

ized by the illumination irradiance (I), according to eq 1:^{5,20}

$$S_{ph} = \frac{J_{ph}}{EI} = \frac{\sigma_{ph}}{I} \quad (1)$$

The PVK/SiO₂ IPN shows a photosensitivity of 1.4×10^{-11} cm/(Ω W) for an applied external electric field of around 12 V/μm (Figure 2) which, up to our knowledge, is the highest ever reported in a hybrid sol-gel material (Table 1). It is remarkable that the S_{ph} value measured for the PVK/SiO₂ IPN is in range to those recently reported for analogue polymers based on PVK/TNF (see Table 1).

Figure 2 also shows how the use of shorter wavelengths (e.g., 476 nm) results in an improvement of the photoresponse of the

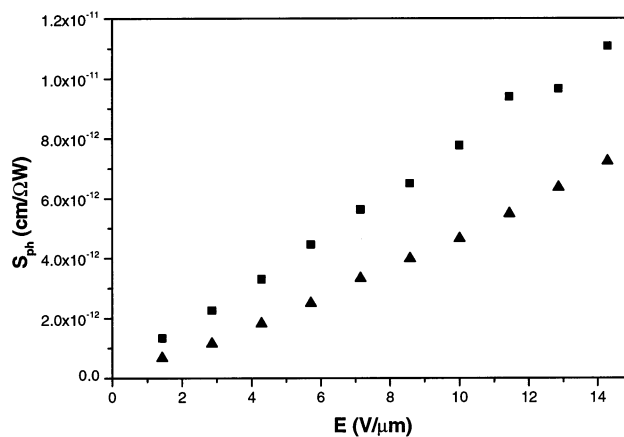


Figure 3. Photosensitivity response of the NVC/TNF sol-gel material (▲), and the PVK/SiO₂ IPN photoconductive material (■), at 514 nm.

PVK/SiO₂ IPN photoconductive material (up to 30%). This behavior has been reported as a consequence of the better photon absorption of the PVK/TNF charge-transfer complex at 476 than at 514 nm.²⁵ The low level of dark current found in the PVK/SiO₂ IPN photoconductive material (J_{dark} in the order of 10^{-13} A/cm² for no applied field and 10^{-11} A/cm² for a moderate applied field of around 10 V/μm) is also remarkable, since it is highly desirable for a photoconductor to exhibit no conductive activity under dark conditions.^{5,26} In addition, it is noteworthy the photoresponse observed at non external electric field ($J_{ph} \sim 10^{-13}$ A/cm², for an irradiance of 3 mW/cm²). This behavior must be explained in terms of the generation of a gradient of photoexcited charge-carriers across the sample as a consequence of the main light absorbance at the incoming surface of the film.²⁶

The improvement in the S_{ph} found for the PVK/SiO₂ IPN photoconductive material as compared to the nonpolymerized sample (NVC/TNF sol-gel material prior irradiation) was found to be ~50% (Figure 3). Such an improvement must be related to the favored transport of the charge-carriers in the continuous medium formed by the PVK chain. Larger differences in S_{ph} between nonpolymerized and polymerized samples should therefore be expected for lower NVC concentrations. The improvement of the S_{ph} in the polymerized sample reflects the IPN character of the PVK/SiO₂ material. Besides, the silanol groups of the porous surface can be considered as impurities which it is well-known that act as trapping centers for the holes.⁸ In our case, the existence of the glycidoxypopyl groups provides a local environment which isolates the PVK network from the silica backbone and results in the enhancement on the charge carriers mobility. Furthermore, the PVK/SiO₂ IPN photoconductive material shows higher stability in the photocurrent signal than the NVC/TNF sol-gel material.

In summary, the PVK/SiO₂ IPN photoconductive material reported in this work has exhibited an excellent low level of dark current besides a photosensitivity in the range to that reported for PVK/TNF polymeric samples,²⁵ and better than photoconductive sol-gel materials based on the incorporation of disperse carbazole units.^{20,22} Furthermore, the goodness of the photoconductivity data measured on the PVK/SiO₂ IPN photoconductive material is promising for the future application of sol-gel materials in photorefractivity, since it provides an improvement of the response time.^{20,22}

Acknowledgment. The authors are grateful to the CICYT for the research grant MAT 2001-5073-E. Gonzalo Ramos is also grateful to INTA for a Rafael Calvo Rodés fellowship.

References and Notes

- (1) Zhang, Y.; Burzynski, R.; Ghosal, S.; Casstevens, M. K. *Adv. Mater.* **1996**, *8*, 111.
- (2) Penwell, R. C.; Ganguly, B. N.; Smith, T. W. *J. Polym. Sci. Macromol. Rev.* **1978**, *13*, 63.
- (3) (a) Urbach, J. C.; Meier, R. W. *Appl. Opt.* **1966**, *5*, 666. (b) Hariharan, P. *Optical Holography. Principles, Techniques and Applications*; Cambridge University Press: Cambridge, 1984.
- (4) Carreño, F.; Martínez-Antón, J. C.; Bernabeu, E. *Thin Solid Films* **1995**, *263*, 206.
- (5) (a) Winiarz, J. G.; Zhang, L.; Lal, M.; Friend, C. S.; Prasad, P. N. *Chem. Phys.* **1999**, *245*, 417. (b) Winiarz, J. G.; Zhang, L.; Lal, M.; Friend, C. S.; Prasad, P. N. *J. Am. Chem. Soc.* **1999**, *121*, 5287.
- (6) Moerner, W. E.; Silence, S. M. *Chem. Rev.* **1994**, *94*, 127.
- (7) Bolink, H. J.; Krasnikov, V. V.; Malliaras, G. G.; Hadziioannou, G. *J. Phys. Chem.* **1996**, *100*, 16356.
- (8) Malliaras, G. G.; Krasnikov, V. V.; Bolink, H. J.; Hadziioannou, G. *Appl. Phys. Lett.* **1995**, *67*, 455.
- (9) Gubler, U.; He, M.; Wright, D.; Roh, Y.; Twieg, R.; Moerner, W. E. *Adv. Mater.* **2002**, *14*, 313.
- (10) West, K. S.; West, D. P.; Rahn, M. D.; Shakos, J. D.; Wade, F. A.; Khand, K.; King, T. A. *J. Appl. Phys.* **1998**, *84*, 5893.
- (11) Jung, J.; Glowacki, I.; Ulanski, J. *J. Chem. Phys.* **1999**, *110*, 7000.
- (12) Okamoto, K.; Nomura, T.; Park, S.; Ogino, K.; Sato, H. *Chem. Mater.* **1999**, *11*, 3279.
- (13) Winiarz, J. G.; Zhang, L.; Park, J.; Prasad, P. N. *J. Phys. Chem. B* **2002**, *106*, 967.
- (14) Däubler, T. K.; Bittner, R.; Meerholz, K.; Cimrová, V.; Neher, D. *Phys. Rev. B* **2000**, *61*, 13515.
- (15) Cottin, P.; Lessard, R. A.; Knystautas, É. J.; Roorda, S. *Nucl. Instrum. Methods Phys. Res. B* **1999**, *151*, 97.
- (16) Bittner, R.; Meerholz, K.; Stepanov, S. *Appl. Phys. Lett.* **1999**, *74*, 3723.
- (17) Safoula, G.; Bernede, J. C.; Touihri, S.; Alimi, K. *Eur. Polym. J.* **1998**, *34*, 1871.
- (18) West, K. S.; Rahn, D. P.; Shakos, J. D.; Wade, F. A.; Khand, K.; King, T. A. *J. Appl. Phys.* **1998**, *84*, 5893.
- (19) Mercher, E.; Bräuchle, C.; Hörhold, H. H.; Hummelen, J. C.; Meerholz, K. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1749.
- (20) Darracq, B.; Chaput, F.; Lahlil, K.; Boilot, J. P.; Levy, Y.; Alain, V.; Ventelon, L.; Blanchard-Desce, M. *Opt. Mater.* **1998**, *9*, 265.
- (21) Wang, Y.; Wang, X.; Li, J.; Mo, Z.; Zhao, X.; Jing, X.; Wang, F. *Adv. Mater.* **2001**, *13*, 1582.
- (22) Cheben, P.; del Monte, F.; Worsfold, D. J.; Carlsson, D. J.; Grover, C. P.; Mackenzie, J. D. *Nature* **2000**, *408*, 64.
- (23) Wang, S.; Yang, S.; Yang, C.; Li, Z.; Wang, J.; Ge, W. *J. Phys. Chem. B* **2000**, *104*, 11853.
- (24) Chen, Y.; Cai, R. F.; Xiao, L. X.; Huang, Z. E.; Pan, D. *J. Mater. Sci.* **1998**, *33*, 4633.
- (25) Sandalphon, Kippelen, B.; Peyghambarian, N.; Lyon, S. R.; Padias, A. B.; Hall, H. K., Jr. *Opt. Lett.* **1994**, *19*, 68.
- (26) Saleh, B. E. A.; Teich, M. C. *Fundamental of Photonics*; Goodman, J. W., Ed.; John Wiley & Sons: New York, 1991; Chapter 18.
- (27) Herlocker, J. A.; Fuentes-Hernández, C.; Ferrio, K. B.; Hendrickx, E.; Blanche, P. A.; Peyghambarian, N.; Kippelen, B.; Zhang, Y.; Wang, J. F.; Marder, S. R. *Appl. Phys. Lett.* **2000**, *77*, 2292.
- (28) Hendrickx, E.; Zhang, Y.; Ferrio, K. B.; Herlocker, J. A.; Anderson, J.; Armstrong, N. R.; Mash, E. A.; Persoons, A. P.; Peyghambarian, N.; Kippelen, B. *J. Mater. Chem.* **1999**, *9*, 2251.