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Some fundamental and applicative properties of [polymer/nano-SiC] hybrid nanocomposites

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Abstract. Hybrid nanocomposites which combine polymer as host matrix and nanocrystals as active elements are promising functional materials for electronics, optics or photonics. In these systems, the physical response is governed by the nanocrystal features (size, surface and defect states), the polymer properties and the polymer-nanocrystal interface. This work reviews some selective nanostructured architectures based on active elements such as silicon carbide (SiC) nanocrystals and polymer host matrices. Beyond an overview of some key properties of the nanocrystals, a main part will be devoted to the electro-optical (EO) properties of SiC based hybrid systems where SiC nanocrystals are embedded in polymer matrices of different chemical nature such as poly-(methylmethacrylate) (PMMA), poly-vinylcarbazole (PVK) or polycarbonate. Using this approach, the organic-inorganic interface effects are emphasised with regard to the dielectric or hole transporting behaviour of PMMA and PVK respectively. These effects are illustrated through different EO responses associated with hybrid composites based on PMMA or PVK.

1. Introduction

The physical properties of functional hybrid nanocomposites were intensively investigated during the last decade, and promising functionalities have been demonstrated in optics [1], electronics [2], photovoltaics [3] or optoelectronics [4]. Some of these hybrid architectures, based on inorganic semiconducting nanocrystals incorporated in organic matrices, are potentially suitable for technological applications such as solar cells, optical modulators or switches as well as photo-luminescent components in selective light windows. In this context, silicon carbide is a promising material due to its unique ability to adopt different crystalline polytypes which monitor the band gap, hence the electronic and optical properties [5-7]. Moreover, in hybrid materials based on inorganic

nanocrystals, the interface effects between the organic and inorganic components play a key role in the resulting physical properties. Thus, an effective control of the surface states of the nanocrystals remains a challenge in order to properly tune the physical responses of the composites and their efficiencies. In this context, surface modification of SiC nanoparticles with thin semiconducting polymer layers of a few nanometer thick is a relevant strategy. The resulting nanocomposites are expected to take benefit from the intrinsic properties of both components. Particluarly, SiC nanoparticles are characterized by versatile properties such dielectric behavior marked by interfacial polarizations [8-10], as well as vibrational and luminescence properties which point out the main role of interfaces [6, 7].

The main goal of this report is to shed light on some relevant properties of silicon carbide nanocrystals as isolated objects or associated with polymer matrices to realize functional materials for optics and optoelectronics. The main investigations developed on the as-prepared SiC nanocrystals aim the analysis of the vibrational [7, 5], dielectric [8, 9], and structural properties [10], as well as both linear and nonlinear optical behaviours [6]. For all these studies, predictive numerical methods were developed mainly using *ab-initio*, molecular dynamics and quantum chemistry calculations to interpret and point out the main parameters controlling the physical properties [6, 7]. However, as fine as the description of isolated nanocrystals can be, no valuable applications of these materials can be undertaken without their structuration within appropriate hosts, such as polymer matrices. Following this approach, large electro-optical activities were demonstrated in polymer-SiC composites through a large organic-inorganic surface area where interfacial polarizations are involved.

In this paper, a summary of the physical properties of nanoparticles and the EO activity of nanocomposites will be outlined.
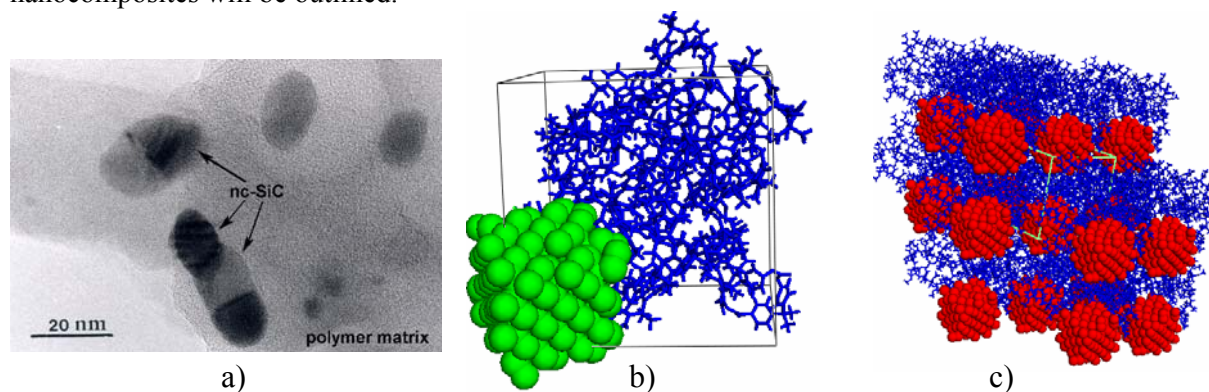

Figure 1: (a) TEM image of a polymer matrix incorporating SiC nanocrystals, (b) simulated polymer fragment surrounding SiC cluster, (c) simulation of hybrid material associating polymer matrix and SiC clusters

2. Selected architectures based on SiC nanoparticles

An overview of the different composite architectures is briefly sketched in Fig. 1. Hybrid nanocomposites based on silicon carbide and polymer matrices were successfully synthesised and their electroptical properties were found comparable to those associated with conventional electro-optical monocrystals. Figures 1b and 1c present simulated geometries of these hybrid materials using quantum chemistry calculations and molecular dynamics.

Other architectures are based on the confinement of SiC nanocrystals by inorganic media. Figure 2 illustrates the incorporation of small SiC nanocrystals inside an alumina matrix by using the CVD

method. The photoluminescence (PL) spectrum shown in Fig.2b is calculated from the approach developed in Ref. [6] and is related to the photoluminescence response from confined nanocrystals under suitable light window excitation.
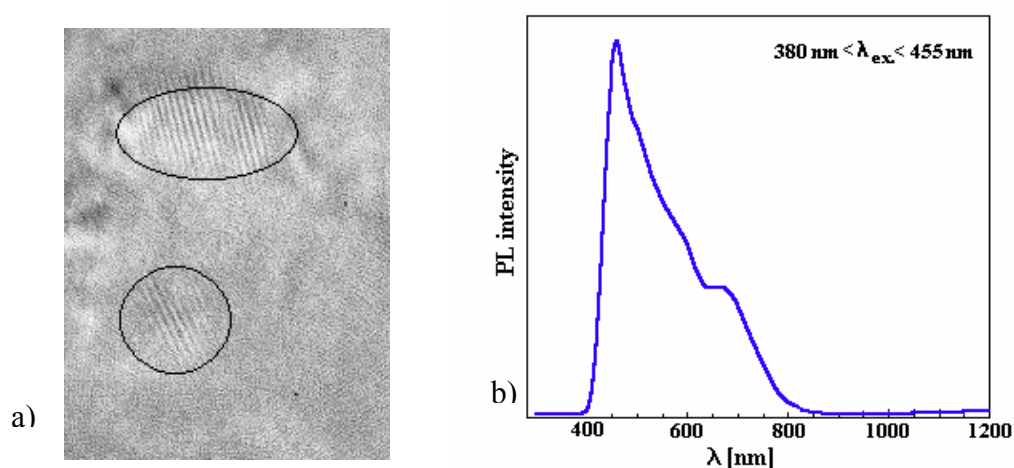

Figure 2: (a) TEM image of SiC nanocrystals confined in an alumina matrix and synthesised by CVD; (b) calculated photoluminescence spectra of SiC cluster from the approach developed in ref.[6].

Finally, figure 3 report the architecture of core-shell nanocomposites where a thin polyaniline film (2-5 nm) is grafted on the SiC nanoparticle surface. These original architectures are promising for their physical responses such as electroluminescent phenomena which occurs from the interfaces of the polymer with modulated electrical activity and the semi- conducting SiC nanoparticles [14]

The versatility of the SiC nanocrystals allows us to predict relevant associations with host matrices in order to develop hybrid functional materials. The proposed architectures take advantage of an easy processing for potentially low-cost alternative applications.

In the following paragraphs, we focus on some fundamental properties of SiC nanoparticles and on the the development of hybrid SiC/polymer nanocmposites presenting an efficient electro-optical response.
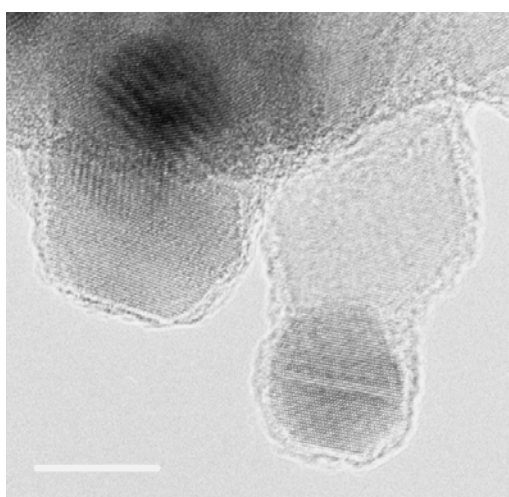

Figure 3: TEM image of core-shell hybrid nanocomposites where a thin layer of polyaniline is surrounding SiC nanocrystals.

3. SiC nanoparticles

3.1. Synthesis, morphology, structure and surface states

The SiC nanocrystals synthesis was performed by laser pyrolysis of a gaseous mixture (SiH_4, C_2H_2) as in Ref. [12], following the original process developed by M.Cauchetier in CEA-Saclay-France in 1988. Depending on the initial flux of the gaseous reactants, the obtained nanoparticles present an excess of silicon or carbon which migrates at the nanoparticles boundaries. The powders are constituted by SiC grains coated by thin oxide, oxicarbide layer (0.5 nm thick) or by turbostratic carbon. Thus, inhomogeneous surfaces from stoechiometry and structures aspects are in general involved in the as-formed nanopowders [5]. Annealing the nanopowders for one hour under argon atmosphere improves the crystalline order of the nanoparticle cores and the stochiometry of their surfaces. The particle diameters distributed in the range 3-30 nm for samples annealed at 1200°C increase in the micron range when annealing at 1700°C. Furthermore, the SiC grain structure, initially predominantely composed by the hexagonal α-SiC (6H) polytype, becomes mainly composed by the cubic β-SiC (3C) polytype for annealing above 1400°C. All morphological, structural and compositionnal data were investigated as a function of annealing and are reported elsewhere [5,13].

It is worth noting that whatever the initial synthesis conditions, an annealing temperature of about 1400°C is a critical temperature to improve the quality of the nanoparticles structures and surfaces with only small increase of the particle mean diameter. We will refer below to the nanopowder batches SiC212, SiC218 and SiC237, which present atomic C/Si ratios of 1.04 (carbon-rich), 0.85 (silicon rich) and ~1 (nearly stochiometric) respectively.
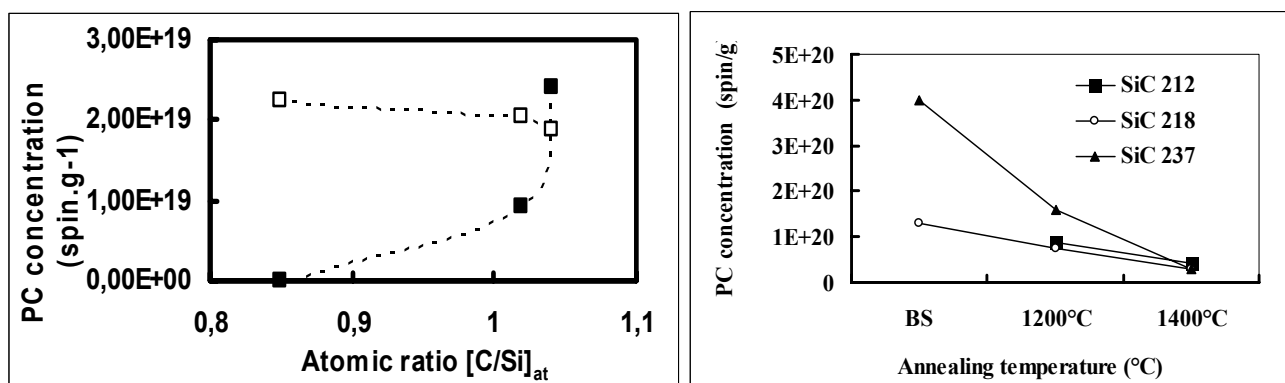
Figure 4: Left: concentration of paramagnetic centres versus the atomic C/Si ratio monitored by the rate of gaseous reactants (silane and acetylene) used during the particle synthesis. Black squares denote the concentration of carbon dangling bonds and white squares the paramagnetic centres associated with the nanoparticle cores.   Right: evolution of the absolute concentration of paramagnetic centres versus annealing temperature for the different SiC batches synthesised using different C/Si ratios.

### 3.2. Active electronic centres in SiC nanoparticles

Electron paramagnetic resonance (EPR) technique is used to monitor the nanoparticles surface reactivity through the electronic active centres involved on the nanoparticle surfaces or in their cores. The three SiC batches referred as SiC212, SiC218 and SiC237 show different paramagnetic features: dangling bonds on the nanoparticle surfaces for the batch SiC212 and SiC237 which are absent in the SiC218 sample more marked by a silicon excess at its surface. Furthermore, internal paramagnetic centres consisting in carbon vacancies exist in all the samples whatever the initial synthesis conditions.

Figure 4 summarises the absolute concentration of paramagnetic centres in the investigated samples. It is possible from the deconvolution of the EPR spectra to distinguish between the paramagnetic centres due to dangling bonds from the carbon in excess and those related to charged vacancies in the nanoparticles cores [10, 13]. Annealing the samples reduces drastically the overall concentration of paramagnetic centres. Whatever the sample stochiometry, annealing at 1400°C reduces the concentration of paramagnetic centres to the same value, and improves also the nanoparticle surface states and the crystalline order of their cores.

Furthermore, EPR experiments were also used to probe the reactivity of the nanoparticles surfaces against air or oxygen atmosphere. Thus, for silicon-rich SiC nanoparticles placed under air or under partial oxygen pressure, the shapes of the EPR spectra differ markedly from the EPR spectrum recorded for particles under vacuum. This observation is consistent with an interaction of the paramagnetic centres located at the surface with oxygen. This interaction induces relaxation effects which result in the broadening of the EPR lines. In contrast, carbon-rich SiC nanoparticles are more inert and didn't react with the ambient atmosphere. These results are of primary importance with regard to the physical properties of hybrid nanocomposites based on SiC nanoparticles in a surrounding medium (polymer, dielectric matrix, etc.) and evidence the reactivity of the particle surface as a fundamental parameter for these systems, as it will be shown below.

3.3. Role of interfaces on the vibrational properties of SiC nanoparticles
When X-ray diffraction experiments are performed on the SiC nanopowders, the diffraction lines are consistent with quite well crystallised nanoparticles, although size effects (~10-20 nm) result in a relative line broadening. The involved polytypes are mainly cubic 3C-SiC or hexagonal 6H-SiC. Their relative fraction in a given SiC batch change with the annealing temperature. Hexagonal polytypes are mainly involved for low annealing temperatures up to 1400°C, while a more cubic structure is stabilised by annealing above 1500°C [7,13]. However, vibrational properties probed by Raman spectrometry are dominated by the nanoparticle surface signatures. Indeed, even if the crystalline structure exists in the nanoparticle cores, as supported by X-ray investigations, the Raman spectra are consistent with a density of states in the low wave-number range as illustrated in Fig.5.
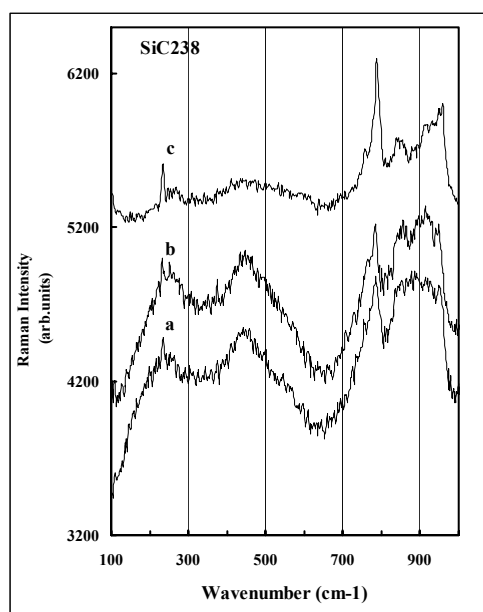

Figure 5: Vibrational density of states (VDOS) from the surface of SiC nanoparticles. The active Raman modes are resolved only when the annealing temperature is above 1400°C. For lower annealing temperatures, broad features from VDOS dominate the Raman spectra.

Meanwhile, for large wavenumber scale, the Raman spectra (fig.6) are marked by the occurrence of large and broad features due to luminescence phenomena. They are induced at the particle surface, where a deviation from the stochiometry and amorphous arrangements occur. In order to enhance the luminescence from the surfaces, we realised an oxidation of the nanoparticles at temperatures up to 900°C under oxygen atmosphere. The broad features are as high as the oxidation temperature increases and point out the effects of the surface origin of the observed luminescence phenomena.
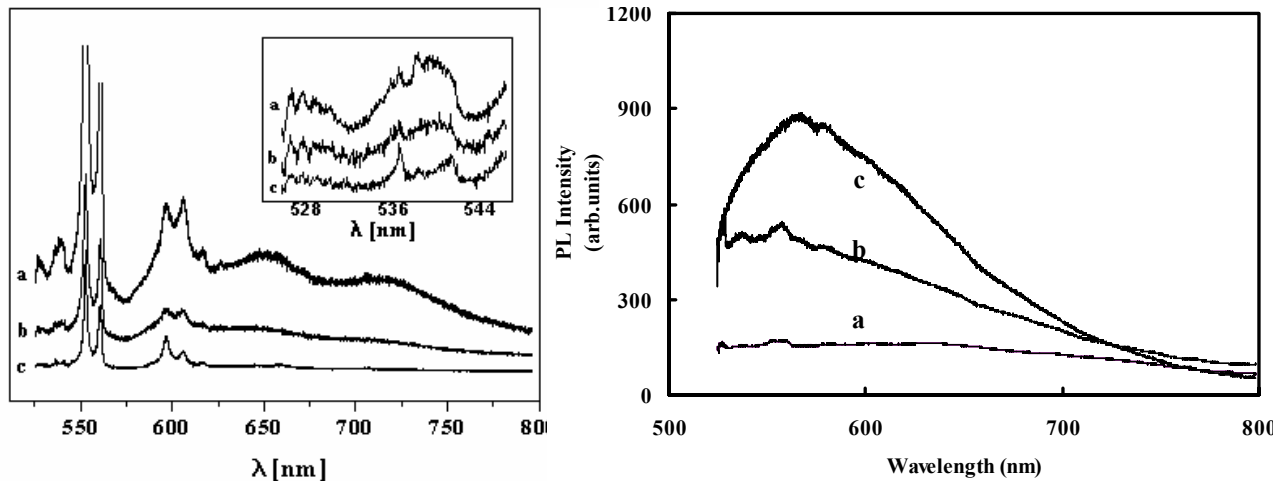
Figure 6: Raman spectra of SiC nanoparticles on a large wavenumber scale. Broad photoluminescence features from the surfaces are shown (Left: a: as-formed, b: annealed at 1200°C and c: annealed at 1400°C) and enhanced by a suitable oxidation treatment (Right) at different temperatures : a- as formed, b- 440°C, c- 870°C.
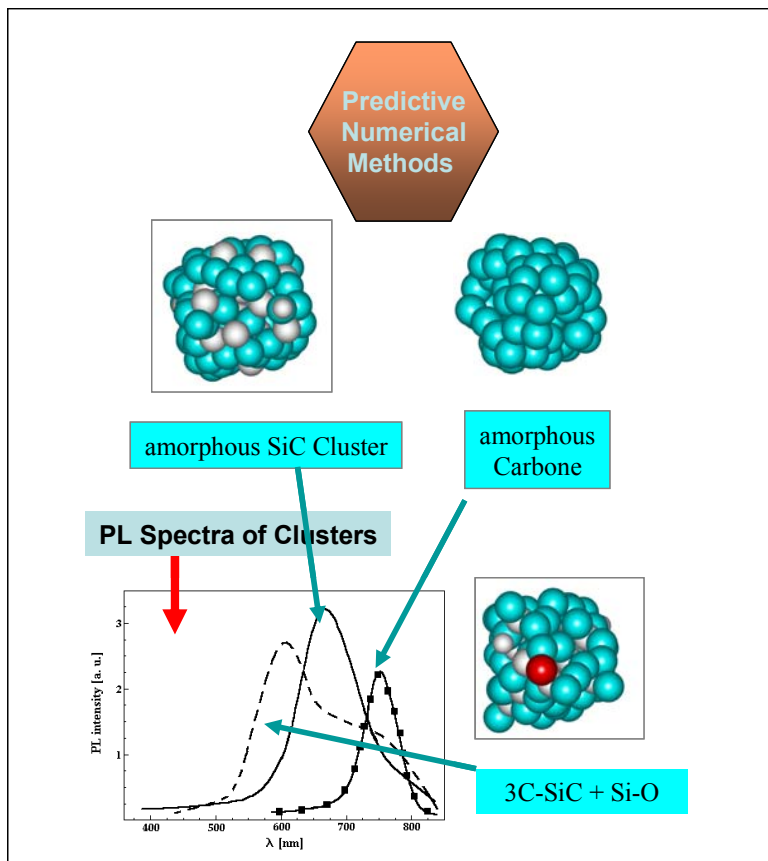
Figure 7: Simulated photoluminescence spectra of an amorphous SiC cluster, a carbone cluster and SiC cluster with O - bonds at the surfaces. The clusters are built using quantum chemistry codes and a model was developed for the computation of the PL spectra [6].

In parallel to these experimental investigations, numerical methods were carried out on SiC clusters [6]. Taking into account the crystal order of the clusters and their surface features, different broad contributions are reported in the corresponding photoluminescence spectra by these numerical approach based on quantum chemistry calculations (Figure 7). Particularly, 3C-SiC clusters with Si-O bonds give rise to characteristic PL signatures which account qualitatively for the experiments.

To sum up this part devoted to silicon carbide nanoparticles, the following points can be emphasised:
- The synthesis method is relevant to obtain SiC nanoparticles with calibrated sizes and a narrow size distribution.
- Suitable annealing improves the crystalline order in the nanoparticle cores and leads to homogeneous surfaces.
- Original physical responses are found in these systems including dielectric, electronic and optical properties.
- The physical properties of SiC nanoparticles are mainly influenced by the surface states.

However, taking benefit from the intrinsic properties of the nanoparticles requires their structuration in host matrices. In the following part, we describe a key functionality of hybrid nanocomposites based on SiC nanoparticles and polymer matrices. The considered architectures consist in guest-host systems which exhibit original electro-optical properties and offer a competitive alternative to electro-optic inorganic monocrystals or organic-organic materials. It will be shown below that all the processes can be controlled from the isolated nano-objects to final functional components.

4. Guest-Host hybrid nanocomposites nc-SiC/polymer for electrooptics
4.1. Preambles
Original architecture based on the association of SiC nanoparticles as active chromophores and polymer as host matrix is realised. Such nanocomposite presents a significant electro-optical response, which takes benefit from the intrinsic properties of the nanoparticles and the organic-inorganic interfaces. The ambition is to realise components such as a Mach-Zehnder interferometer which could be used as optical switches or electro-optical modulator based on the Pockels effect.

These electro-optical hybrid materials present many advantages compared to already operating materials as monocrystals (LiNbO3) or organic-organic guest-host systems due to the time stability of all polymer systems. The main advantages are an easy and potentially low-cost synthesis, their flexibility which allows their integration in original optoelectronic devices, as well as the high EO reponses and time stability of the active layer.

Regarding the electro-optical properties, the main physical parameter is the macroscopic polarization of the material under the application of a static electric field E which modifies the dielectric permittivity of the layer and its ability to propagate light. Thus, under applied electric field E and using a probing light associated with the optical field E^{ω}, the macroscopic polarization in the electro-optic medium is given by:

$$\vec{P} = \vec{P}^0 + \varepsilon_0 \left\{ \chi^{(1)}(-\omega;\omega) + \chi^{(2)}(-\omega;0,\omega)\vec{E} + \chi^{(3)}(-\omega;0,0,\omega)\vec{E}^2 + \cdots \right\} \vec{E}^{\omega} \qquad (1)$$

With P^0 the intrinsic polarization, $\chi^{(i)}$ the optical susceptibility of ith rank. Thus, electro-optical modulation is induced by the second order (Pockels) and the third order (Kerr) optical susceptibilities. This expression requires that the observation of a Pockels effect is possible only in non-centrosymmetric media. This condition is usually fulfilled by electrical alignment, known as poling procedures, of the microscopic dipole moments in the active layer.

4.2. Realisation of hybrid materials

Selected batches of SiC nanoparticles are used as dopant (1-3 wt.%) of polymer matrices of PMMA, Polycarbonate or Polyvinyl Carbazole. The choice of the polymer matrix is guided by its thermo-mechanical properties and optical transparency. In the hybrid film processing, achieving a homogeneous dispersion of the SiC particles within the polymer matrix remains the main step to be controlled. From these homogeneous precursor solutions, thin film of suitable optical quality is deposited by spin-coating. The final electro-optical cell is depicted in figure 8.
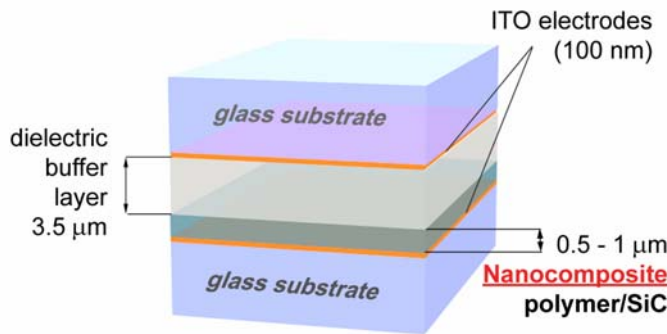
Figure 8: Active hybrid nanocomposites associating polymer matrix and SiC nanoparticles. The film is sandwiched between two ITO electrodes and a dielectric buffer layer.

The ITO electrodes allow the application of a static voltage required for the poling procedure, and the buffer layer is used to avoid short-circuit during both the poling step and the electro-optical measurement. As a general rule, the poling is performed with the sample being heated close to the glass temperature of the polymer. Thus, for PMMA matrix, the relevant parameters for electrical poling are a temperature about 135°C and a static electric field about 15 V/µm.

4.3. Results and discussion

The experimental set-up used to probe the electro-optical properties of the nanocomposites is based on an adapted Sénarmont where the electro-optical birefringence is induced by a modulated voltage $V(t) = V_\Omega \sin \Omega t$. When the sample, initially under *V(t)*, is crossed by a polarized light beam of intensity I_0, the transmitted light is modulated according to the relation:

$$I(V_\Omega) = I_0 \sin^2\left(\frac{\Gamma(V_\Omega)}{2}\right) \qquad (2)$$

With a dephasing term:

$$\Gamma(V_\Omega) = \frac{2\pi L \Delta n(V_\Omega)}{\lambda} \qquad (3)$$

The electro-optical birefringence is given by:

$$\Delta n(V_\Omega) = \Delta n^0 + \frac{1}{2} n_0^3 \cdot r_e \cdot \frac{V_\Omega}{d_f + d_b} + \lambda B_e \left(\frac{V_\Omega}{d_f + d_b}\right)^2 \qquad (4)$$

In this expression, Δn° represents the natural birefringence of the sample, n_0 is the ordinary refractive index of the material, r_e the EO Pockels coefficient and B_e the EO Kerr parameter. d_f and d_b represent respectively the film and the dielectric buffer layer thicknesses.

The transmitted light intensity is modulated at the first and second harmonic of the applied electrical voltage according to:

$$I(t) = I_{DC} + I_{\Omega} \sin \Omega t + I_{2\Omega} \sin 2\Omega t \tag{5}$$

The measurements of the modulated transmitted light intensities I_{Ω} and $I_{2\Omega}$ allow us to evaluate the electro-optical coefficients, which are summarized below as a function of the used polymer matrix (figure 9).
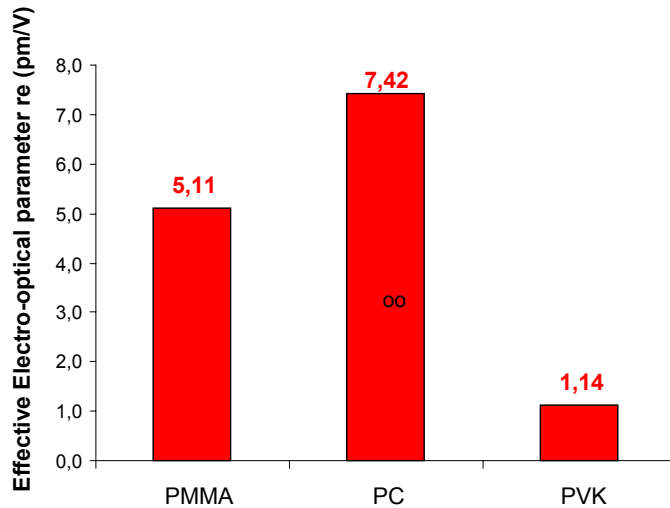
Figure 9: Effective EO parameter versus the polymer nature. PMMA and PC give rise to enhanced EO parameters in the order of 5.11 pm/V for PMMA and 7.42 for PC. A lower value about 1.14 pm/V is obtained for the PVK based nanocomposite.

The difference in the EO activity of the different samples is mainly attributed to the presence of polar groups in PMMA and PC, which result in an enhancement of the interfacial polarizabilities. The corresponding EO coeffcents, in the order of 5-7 pm/V, are comparable with those associated with traditional EO monocrystals already operating in optoelectronic systems. Unlike PMMA and PC, the PVK matrix, which present a photoconductive behaviour, lowers the efficiency of the polarization effects, resulting in a poorer EO parameter.

Furthermore, the EO performance obtained for PMMA and PC present a relative stability versus time, as illustrated on a PMMA/SiC composite which presents significant EO parameters after 600 hours (figure 10). This criterion is of a primary importance for practical applications of these nanocomposites in integrated optoelectronics.
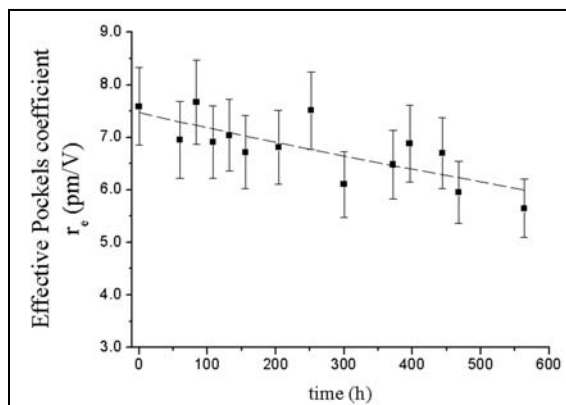
Figure 10: Evolution of the EO effective parameter in a PMMA based nanocomposite versus time.

Finally, it is worth noting that the EO activity is effective with regard to the eventual contribution to the light modulation from piezo-optical effect. Frequency-dependent measurements up to 100 kHz have evidenced a relatively stable light modulation, but definite conclusion requires tests at higher frequencies (up to 10 GHz). This requierement remains one of the main conditions for the development of competitive optoelectronic devices.

5. Conclusion

SiC nanocrystals are promising nano-objects with regards to their versatile electronic and optical properties. A large modulation of their physical properties can be realized through the choice of the experimental parameters used during their synthesis, as well as by using suitable annealing treatments. In particular, a significant EO response was evidenced in SiC/polymer nancomposites, which illustrates the relevance of the association of inorganic nanocrystals and organic hosts to design functional materials. Apart from the EO activity and considering the role played by the organic/inorganic interfaces in the physical response of such systems, this work illustrates the strong potential of hybrid systems in optics, optoelectronics and photonics.

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