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In-situ fabrication of polyacrylate–silver nanocomposite through photoinduced tandem reactions involving eosin dye

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ABSTRACT

A silver–acrylate nanocomposite was prepared using a novel one-pot strategy involving eosin dye as visible sensitizer and an amine derivative as radicals' source. The mechanism highlighted by steady state photolysis and time-resolved absorption spectroscopy lies on the initial formation of a strong ion-pair complex between eosin and Ag^+. Upon visible irradiation, the excited triplet state of the metal complex efficiently abstracts a hydrogen atom from the amine and produces an α-aminoalkyl radical. In acrylate monomer matrix, such a strong reactive species initiates a free radical photopolymerization and also provides the reduction of the silver cation. Through this 'in-situ' fabrication method, the kinetics formation of the nanocomposite and its detailed structural analysis are characterized by UV–visible, real-time FTIR absorption spectroscopy and by transmission electron microscopy.

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1. Introduction

Progresses in size- and shape-selective synthetic routes to produce metal nanoparticles have become the subject of extensive investigations over past decade. Their size-dependent physical properties [1,2] clearly constitute one of the most attractive aspects which has promoted the emergence of a very large set of applications in optics [3–6], microelectronics [7,8], high density data storage [9,10], catalysis [11,12] and energy conversion [13,14]. Nanocomposite materials, which combine the properties of polymers and silver nanoparticles, are considered to be promising systems for advanced functional applications [15]. For instance, coaxial nanocables [16] with a nanometric silver core and covered by a polymer shell exhibit superior performance as nanocircuits [8] or nanosenors [7]. Such nanowires can be synthesized by either solution-phase methods using capping reactants [17,18] or by templating methods using inorganic porous material [19], polymer membranes [20,21], or block copolymer [22]. Another type of nanocomposites consists in a dispersion of metal particles into a polymeric matrix such as poly(vinyl alcohol) [23,24], poly(methyl methacrylate) [25] or poly(vinyl pyrrole) for instance [26,27]. Typically, in-situ and ex-situ methods [28–30] are the two main synthetic routes that lead to silver–polymer nanocomposites. The ex-situ method consists in dispersing dry silver nanoparticles produced beforehand by an appropriated chemical process into a polymer medium to generate highly ordered periodic arrays of nanoparticles [31]. In the in-situ method, metal nanoparticles are generated directly in the matrix through chemical reduction of a cationic precursor previously dissolved in the bulk [24]. Photochemical reduction by irradiating a dye sensitizer in the presence of silver ions also provides a convenient way to produce embedded nanoparticles in polymer [21,32–35]. Moreover, a concomitant functionalization of the nanoparticles with dyes can occur, which is a valuable feature for applications in photochemical solar cells [14,36]. In all cases, the high performance of nanomaterials depends on the controlled distribution of uniformly shaped and sized particles. Therefore, the development of synthetic strategies to control particles' growth and/or agglomeration during nanocomposite fabrication appears quite obviously as a key challenge.

The present work reports a strategy involving the photoinduced formation of homogeneous silver nanoparticles in a polyacrylate polymer stemming from a cross linking photopolymerization of pentaerythritol triacrylate monomer (Scheme 1a). In this one-step approach, a combined system employing eosin dye as visible photosensitizer (Scheme 1b) and *N*-methyl diethanolamine as

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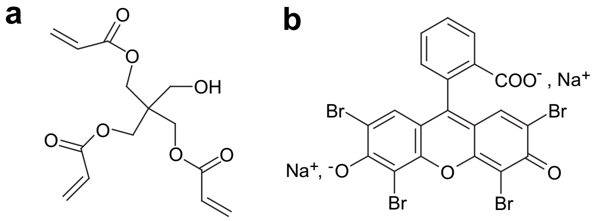

Scheme 1. Structures of pentaerythritol triacrylate (PETA) and of eosin Y disodium salt.

co-initiator is used to photogenerate Ag nanoparticles and to photoinitiate a free radical polymerization at the same time. After a mechanistic insight provided by steady state and laser flash photolysis experiments, the analysis of the elementary steps leading to the metal nanocomposite will be correlated to the structural properties of the materials.

2. Experimental section

2.1. Reagents

Silver nitrate ($AgNO_3$) with a purity >99% was purchased from Fluka. Eosin Y disodium salt, *N*-methyl diethanolamine (MDEA), tetra-*n*-butylammonium hexafluoroborate were purchased from Aldrich. Mixture of pentaerythritol tri- and tetra-acrylate (PETA) monomers stabilized with monomethyl ether hydroquinone (MEHQ – 400 ppm) was purchased from Sartomer. All solvents were Aldrich and Fluka Spectrograde.

2.2. Instrumentation

The absorption measurements were carried out with a Perkin Elmer Lambda 2 spectrometer. A FluoroMax 4 Luminescence Spectrometer was used for the fluorescence and time-gated phosphorescence. Low temperature measurements were performed in a glassy matrix of isopropanol using a 5-mm diameter quartz tube inside a Dewar filled with liquid nitrogen. The emission spectra were spectrally corrected in all cases.

Laser flash photolysis at nanosecond time scale was carried out with an Edinburgh Analytical Instruments LP900 equipped with a 450-W pulsed Xe arc lamp, a Czerny-Turner monochromator and a fast photomultiplier. The samples were irradiated with the second harmonic ($\lambda = 532$ nm, ~10 ns, 4 mJ per pulse) of a Nd/YAG Powerlite 9010 from Continuum. The sample was purged with argon for 15 min prior to photophysical studies.

The acrylate formulation, typically eosin (0.1 wt%), MDEA (3 wt%) and $AgNO_3$ (1 wt%) in PETA, was sandwiched between two glass plates with a calibrated thickness spacer setting the optical path length to 30 μm. Photochemical reactions were carried out at 532 nm with a cw 532 nm Verdi laser from Coherent. The progress of the reaction was monitored via UV–vis absorption spectra.

The photopolymerization was followed up in situ by real-time Fourier transformed infrared spectroscopy with an AVATAR 360 FTIR spectrometer from Nicolet. The laminated formulation (25 μm thick), deposited on a BaF_2 pellet, was irradiated at 532 nm with a green laser diode module from Crystalaser. The conversion rates were deduced from the disappearance of the vinyl C=C stretching vibration band at 1630 cm^{-1}.

Transmission electron microscopy (TEM) was used to characterize the size and shape of Ag nanoparticles. The nanocomposites were cut by means of a microtome (LKB model 8800) and placed onto the observation grid to get their TEM images. Transmission electron microscopy measurement is carried out at 200 kV using a Philips CM20 instrument with Lab6 cathode.

The ^{13}C NMR spectra were recorded in CD_3CN on a 400 MHz Brucker NMR spectrometer using cyclohexane as the internal standard.

3. Results and discussion

3.1. Formation of a strong ion-pair complex with Ag^+

The lowest energy absorption band of EO^{2-} is localized in the 450–575 nm region with a maximum at 530 nm in acetonitrile (Fig. 1). This band corresponds to the S_0–S_1 electronic transition with a π–π^* character localized on the xanthene moiety [37]. The geometry optimization by AM1 method reveals that 2-benzoate and xanthene sub-units are twisted with an angle of 77°, which indicates a weak electronic conjugation between the two aromatic moieties. The fluorescence spectrum of EO^{2-} is mirror image of its absorption band with a slight Stokes shift (535 cm^{-1}) suggesting a weak geometrical relaxation in the singlet state. The 0–0 transition energy measured from the intercept of normalized absorption and fluorescence spectra corresponds to 2.31 eV in acetonitrile. The phosphorescence spectrum of EO^{2-} is located in the 600–700 nm range with a maximum emission at 652 nm which leads to a triplet energy of about 1.90 eV (inset of Fig. 1).

As depicted in Fig. 2, the addition of silver nitrate to a solution of EO^{2-} in acetonitrile leads to a slight red shift of the last absorption band of the chromophore ($\Delta\lambda_{max} = +4$ nm). The presence of two isosbestic points located at 498 nm and 530 nm clearly indicates the occurrence of equilibrium reaction. Moreover, the addition of tetra-*n*-butylammonium hexafluoroborate (3×10^{-2} M) excludes any variation of the ionic strength during the reaction. Therefore we can ascribe these effects to a coordination reaction of Ag^+ by EO^{2-} which leads to the formation of ion-pair complex $[EO–Ag]^-$. According to the stronger acidic character of the hydroxylic group with respect to that of the carboxylic one [38,39], such a cation exchange reaction should mainly involve the chelation of silver cation by the 'phenolate' oxygen. This is also in line with the Pearson's hard–soft acid–base (HSAB) principle [40–43] which presumes a better stabilizing interaction of Ag^+ (Soft Lewis acid) with the phenolate group than with the carboxylate function. However the participation of the carboxylate function to the coordination reaction cannot be excluded. In order to determine the reaction constants, the absorption changes as a function of the

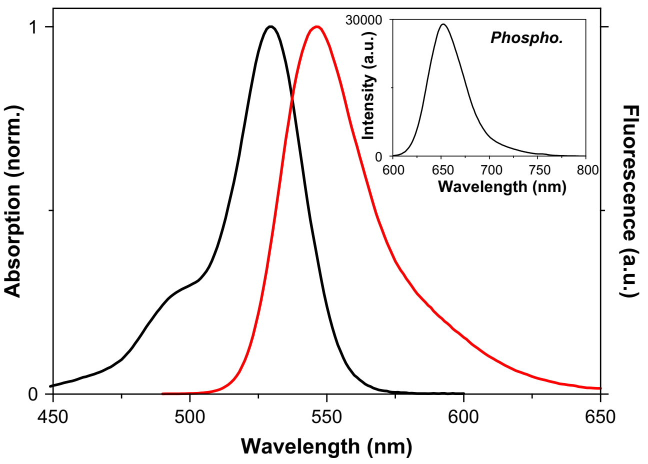

Fig. 1. Normalized absorption and fluorescence spectra of EO^{2-} in acetonitrile. Inset: time-gated phosphorescence spectrum of EO^{2-} in glassy matrix of isopropanol (delay: 50 μs).

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