

Research Article

Photogenerating Silver Nanoparticles and Polymer Nanocomposites by Direct Activation in the Near Infrared

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This work reports on an improvement of the photochemically assisted synthesis of silver nanoparticles by direct photoreduction of AgNO₃ with a laser source emitting in the near infrared range (NIR). For this, polymethine dyes were used as the photoactive agents. Both the effects of central chain structure and activation intensity were investigated. The reduction kinetics was followed up by UV-Vis spectroscopy, and the particles size was evaluated by transmission electron microscopy. The results showed that light intensity affects both the average size and size distribution of Ag nanoparticles generated through this process. The particles can also be generated *in situ* in a photopolymerizable formulation so that metal/polymer nanocomposites become available through a one-step photoassisted process on the basis of NIR activation. The process described herein is very fast (seconds to a few minutes), and it readily lends itself to automatization for mass production of micro-optical elements implemented directly onto integrated NIR sources.

1. Introduction

Recent developments in optics and photonics require novel, simple, and fast methods to fabricate metal nanoparticles (MNPs). In recent years, a whole bunch of synthetic methods for the preparation of MNPs have been developed: chemical, photochemical, and thermal. Amongst them, the photochemical synthesis of MNPs including direct photoreduction and photosensitization has attracted intense research interest, since it is a versatile and convenient process with distinguishing advantages such as space selectivity [1].

Embedding nanosized MNPs into polymer matrixes is also of great interest, because these materials combine properties from both inorganic and organic systems. Thus, MNPs homogeneously dispersed in polymer matrixes are already used as sensors [2–4], materials with solvent switchable electronic properties [5], optical limiters or filters [6, 7], optical data storage materials [8, 9], surface Plasmon-enhanced random lasing media [10], catalytic additives [11], or antimicrobial coatings [12, 13].

Metal-polymer nanocomposites are usually obtained via multistep methods. Dry silver NPs produced beforehand can be dispersed into a polymerizable formulation to obtain self-assembly functionalized structures. However, besides the specific hazards related to handling dry NPs, their size dispersity over a large scale is difficult to control, thus limiting the interest of this “*ex situ*” method [14, 15].

The “*in situ*” approach that involves the generation of MNPs directly in a polymerizable medium through reduction of a cationic precursors offers the advantages of better dispersion ability and facile chemical or photochemical reduction [16, 17].

Several examples of *in situ* synthetic routes to MNPs and polymer/metal nanocomposite were reported as yet and the formulations used contain a variety of monomers and a collection of photoinitiators/photosensitizers [18–22]. They highlighted the flexibility in terms of temperature, dispersion, and rapidity of the process used to trigger the (photo)chemically assisted reduction of metal precursors.

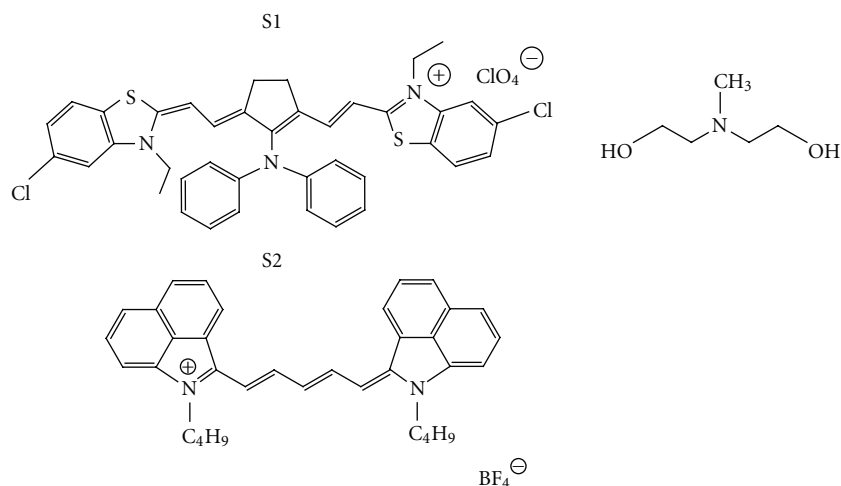


FIGURE 1: Structures of the sensitizers S1: (5,5'-dichloro-11-diphenylamino-3,3'-diethyl-10,12-ethylenethiatricarbocyanine perchlorate) and S2: (1-Butyl-2-[5-(1-butyl-1H-benzo[cd]indol-2-ylidene)-penta-1,3-dienyl]-benzo[cd]indolium tetrafluoroborate) and of the coinitiator (*N*-methyldiethanolamine).

In our recent studies, we have reported a novel approach for the preparation of metal-polymer nanocomposites in which MNPs were obtained by direct UV or visible photoreduction [20–22]. This powerful *in situ* approach, involving irradiation of an appropriated formulation, induces a homogeneous distribution of MNPs in a crosslinked polymer network.

However, some recent developments in the field of applied micro-optics or nanofabrication turn round to producing highly integrated devices, and whenever the corresponding fabrication processes include photochemical steps, small-scale and low-cost light sources with low power consumption are preferred.

In another respect, scientists involved in fundamental plasmonics are demanding systems capable of generating MNPs *in situ* through photochemical processes that could be triggered by NIR light sources. And lastly, the possibility of generating MNPs—with bactericidal or antimicrobial activity—directly in a living medium or as a thin film polymer top coating does not fail to stimulate interest in the field of microbiology. However, the spectral window in which the photogeneration can be carried out is often restricted to the far red or NIR, because the absorption of the sample itself obstructs the other regions of the spectrum.

In this context, the present paper deals with the photochemically assisted fabrication of silver nanoparticles *in situ* in a polymerizable medium using a near infrared (NIR) source. Thus, the challenge consisted of tailoring a currently used process so that it could be activated with laser diodes (and even VCSELs) emitting in the 750 to 900 nm range instead of sources emitting in the visible or near UV.

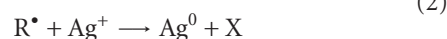
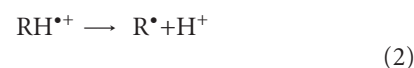
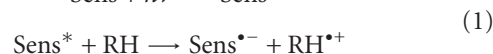
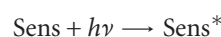
So far, this report is the first to deal with the synthesis of silver nanoparticles and polymer-metal nanocomposites through an NIR-assisted photoprocess. Even though some examples of NIR resins were reported during the past decade [23–25], pushing the sensitivity limits of the process,

generating silver nanoparticles *in situ* up to ca 900 nm, turns out to be an important breakthrough.

2. Experimental

The formulations used in this work contained a sensitizer absorbing in the NIR (5,5'-dichloro-11-diphenylamino-3,3'-diethyl-10,12-ethylenethiatricarbocyanine perchlorate, (S1) and 1-Butyl-2-[5-(1-butyl-1H-benzo[cd]indol-2-ylidene)-penta-1,3-dienyl]-benzo[cd]indolium tetrafluoroborate, (S2) from Sigma-Aldrich) associated with a coinitiator, *N*-methyldiethanolamine (MDEA) from Sigma-Aldrich and a triacrylic monomer (pentaerythritoltriacyrylate from Sartomer). The chemical structures of the sensitizer and cosensitizer are shown on Figure 1. The precursor of silver nanoparticles was silver nitrate (ACS Reagent 99% from Aldrich). It was added to the formulation under stirring and maintained one hour before use.

The mechanism used to produce silver nanoparticles and initiate polymerization is the following: upon NIR irradiation, the dye sensitizer which absorbs in the 750–900 nm range (see Figure 2) is photoexcited and reacts with the coinitiator (1). Amine-derived radical species ($\text{RH}^{\bullet+}$) is capable of inducing reducing of silver cations (2) and free-radical polymerization of the monomer (M) (3)



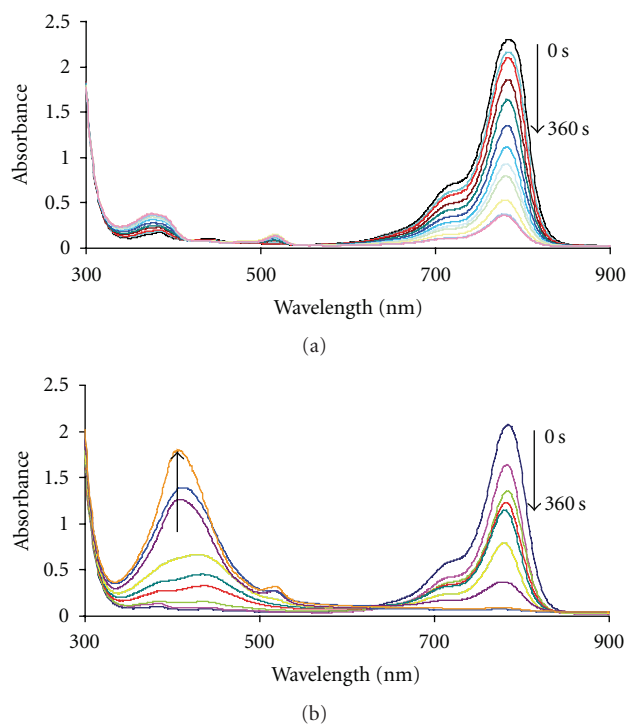


FIGURE 2: Time evolution of absorption spectra of the samples with S1 upon irradiation at 800 nm: (a) without silver cations and (b) with silver cations. Incident light power was 300 mW/cm^2 in laminated conditions, and irradiation times were chosen between 0 and 360 sec.

This process is known to be very sensitive to oxygen quenching [26]. For this reason, the samples were sandwiched between two glass slides. Typically, the thickness of the sample was about $20 \mu\text{m}$.

In order to simplify some kinetic studies, a femtosecond mode locked Ti/Sapphire laser with pulse duration around 100 fs and 80 MHz repetition rate was used as a tunable light source. The available wavelengths (690 to 1020 nm) allowed a convenient screening of the wavelength dependence of the resin sensitivity and power of to 2 W/cm^2 at 800 nm could be achieved. The progress of the reaction was monitored via UV-visible absorption spectra using a Perkin-Elmer Lambda 2 spectrophotometer.

Transmission electron microscopy (TEM) was used to characterize the size and shape of Ag nanoparticles. The samples were irradiated directly onto the copper grid. TEM measurements were carried out using a Philips CM20 instrument with LaB_6 cathode.

3. Results and Discussion

3.1. Fabrication of Silver Nanoparticles Embedded in a Polymer Matrix. A formulation of ethoxylated pentaerythritol tetraacrylate monomer from Sartomer containing the NIR sensitizer (0.1 wt%), MDEA (8% wt), and AgNO_3 (1 wt%) was photopolymerized upon irradiation at 800 nm.

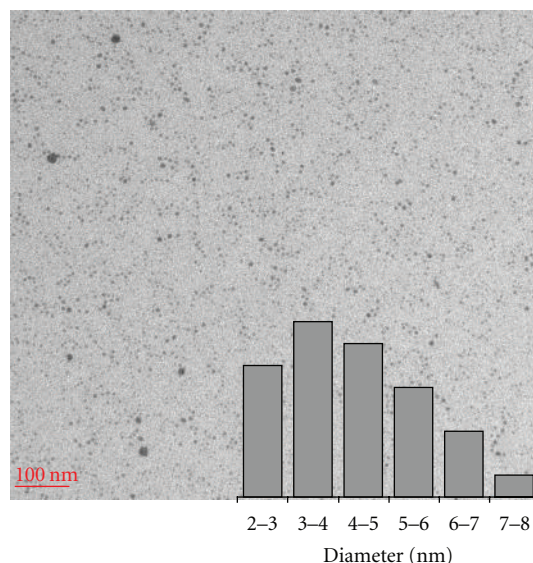


FIGURE 3: TEM image and the corresponding particle size distribution of silver nanoparticles in the polymer matrix obtained using S1 and intensity power equal at 300 mW/cm^2 .

A followup of the stationary photolysis of the sensitizer/electron donor system was carried out with a view to confirming the initiation process of photopolymerization in the specific formulation used in this work. Figure 2(a) shows the time evolution of the absorption spectrum of a formulation irradiated with a light power of 300 mW/cm^2 at 800 nm with exposures ranging from 0 to 360 sec.

The bleaching of the sensitizer goes along with the development of a very weak absorption in the blue. This behavior is consistent with what is reported in the literature [27, 28]. Upon NIR irradiation, the strong band corresponding to the absorption of the dye (700–900 nm) gradually faded. The major interest of this sensitizer is bleach upon irradiation (photobleaching), a feature which is of utmost importance for micro-optics fabrication, since the final material has to become transparent at the operating wavelength (typically ca 800 nm).

When silver cations were present in the formulation (Figure 2(b)), the bleaching rate of the sensitizer was about twice as fast, and the well-known characteristic absorption band related to the plasmon of silver nanoparticles appeared in the blue region. This broad band with a quasispherical shape has its maximum at 414 nm and a full-width-at-half-maximum of ca 130 nm.

TEM image (Figure 3) confirmed the fabrication of individual nanoparticles in the polymer matrix.

These nanoparticles are spherical with a diameter ranging from 2 to 7 nm as clearly visible on Figure 3. In spite of no addition of a capping agent to stabilize the nanoparticles, the TEM images show a good dispersion of the nanoparticles which are imprisoned and stabilized by the polymer network.

3.2. Effect of the Reaction Conditions on Silver Nanoparticles Embedded in the Polymer Matrix. The effect of irradiance

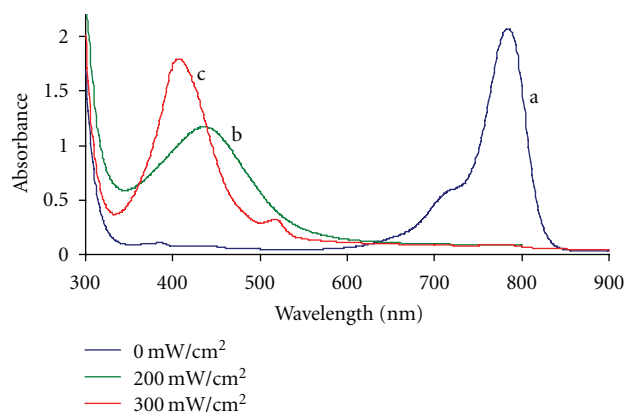


FIGURE 4: Time evolution of absorption spectra of the samples upon irradiation at 800 nm and using S1 (a) without silver cations, (b) with silver cations, incident light power 200 mW/cm², and (c) with silver cations, incident light power 300 mW/cm². Time irradiation 360 s.

light power on nanoparticles growth was studied. Figure 4 shows the effect of power irradiation on the Ag⁺ reduction by UV-Vis spectroscopy, in which the experiments were performed under the conditions of 0, 200 and 300 mW/cm² in presence of S1.

No band appears in the region of 400–450 nm on the UV-Vis absorption spectrum of nonirradiated sample (0 mW/cm²). At both 200 mW/cm² and 300 mW/cm², the brown yellow films were obtained accompanied with the appearance of absorption band at 440 nm and 414 nm, respectively. Higher irradiance allows smaller and monodisperses particles in size to be generated. Irradiations at 200 and 300 mW/cm² produce nanoparticles of 14 ± 1 nm and 4.5 ± 0.9 nm, as shown on Figures 5 and 3, respectively.

The sensitizer used to the reaction system could also affect the reduction rate of Ag⁺. UV-Vis spectroscopy (Figure 6) showed the effect of two different sensitizers used on the Ag⁺ reduction while keeping the AgNO₃ content unchanged. For the same reaction time and light power, 360 s and 300 mW/cm², the absorption peak intensity in the case of S2 it is very weak and broad compared with S1 (Figure 6).

3.3. Effect of the Dye Sensitizer Structure on the Photoreduction Reaction. Quite interestingly, both the kinetics of the MNPs generation and the size distribution of the particles can be related to structural effects of the dye sensitizer. Indeed, it is a well-established fact that any structural change likely to introduce some rigidization in the polymethine central chain of the sensitizer has the effect of decreasing singlet to singlet internal conversion due to mixing of the electronic and vibrational levels [29]. Consequently, the quantum yield of intersystem crossing to triplet increases in proportion that makes the reaction with electron donor (MDEA) and the photoreduction of silver precursors more efficient [30, 31]. Along the same lines, the heavy atom effect is also known to induce a significant increase of the triplet quantum yield.

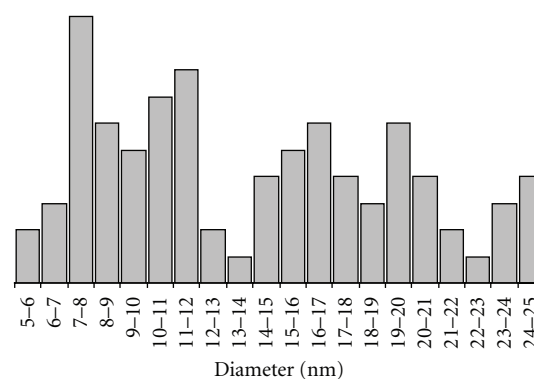
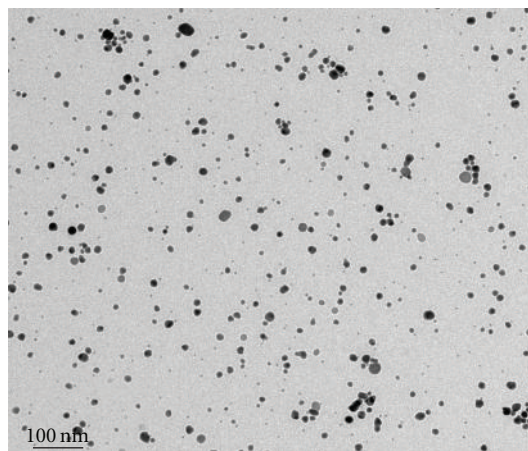


FIGURE 5: TEM image and the corresponding particle size distribution of silver nanoparticles in the polymer matrix obtained using S1 and intensity power equal at 200 mW/cm².

This effect is related to the presence of heavy atoms in the substituents carried by a given structure [32].

Thus, it is clearly visible from Figures 2 and 3 that the photoreduction kinetics is faster with S1 (the rigid polymethine structure and the structure carrying two chlorine atoms). Likewise, the absorption due to plasmon resonance of silver particles is weaker and much broader with S2 (the flexible polymethine structure) that denotes a large size distribution. These observations are consistent with a slower nucleation process that is propitious to size dispersion.

This analysis was corroborated by using other polymethine sensitizers, either with highly flexible central chain (2-[7-(1,3-Dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)hepta-1,3,5-trienyl]-1,3,3-trimethyl-3H-indolium iodide), or with heavy atoms and a hydrocarbon bridge rigidifying the central chain (2-[2-[2-Chloro-3-[2-[1,3-dihydro-3,3-dimethyl-1-(4-sulfobutyl)-2H-indol-2-ylidene]-ethylidene]-1-cyclohexen-1-yl]-ethenyl]-3,3-dimethyl-1-(4 sulfobutyl)-3H-indolium hydroxide, inner salt, sodium salt). The first one does not work at all, while the second one induces both photoreduction with a sharp size distribution of silver nanoparticles and crosslinking photopolymerization of the dispersion medium.

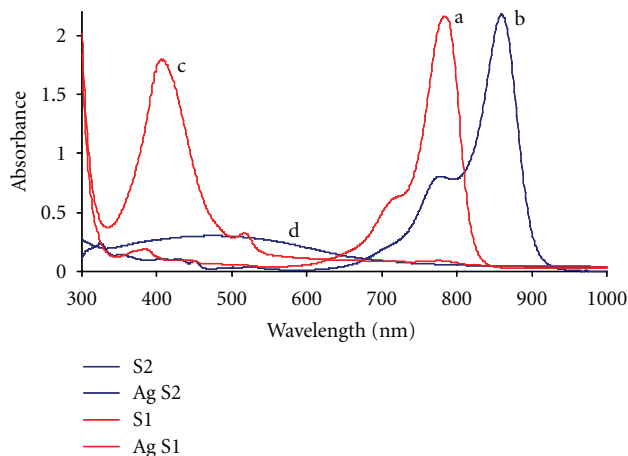


FIGURE 6: Time evolution of absorption spectra of the samples (a) with S1, exposure 0 s, (b) with S2, exposure 0 s, (c) with S1, exposure 360 s with an incident light power 300 mW/cm^2 upon irradiation at 800 nm and (d) with S2 exposure 360 s with an incident light power 300 mW/cm^2 upon irradiation at 850 nm.

4. Conclusions

This work demonstrates the possibility of extending the concept of photochemically assisted synthesis of metal nanoparticles by direct reduction of metal ions or complex to the NIR range, a spectral region of crucial interest for *in situ* implementation of integrated optical functions but where the weak electronic energy carried by photons makes photochemical activation often critical.

A photopolymerizable formulation was tailored to allow initiation by the transient species used to reduce silver cations. It was found that a 300 mW/cm^2 light intensity forms metal nanoparticles homogeneously dispersed in corresponding polymer material, generating thus a metal/polymer nanocomposite that is fabricated upon NIR light activation. Specific effects of the structure of the polymethine sensitizers that strongly suggest the involvement of their triplet state were noticed.

This achievement should open up new vistas in several research fields, where the *in situ* photochemical synthesis of MNPs triggered by NIR might allow technical bottlenecks to be overcome.

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