Journal of Photochemistry and Photobiology A: Chemistry 359 (2018) 111–120

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Peculiarities of interaction of gold nanoparticles with photoinitiators in polymer nanocomposites for holographic recording

J. Burunkova[a], M.-J. Ohoueu[b], I. Csarnovics[c,*], M. Veres[d], A. Bonyár[e], S. Kokenyesi[c]

[a] ITMO University, Saint-Petersburg, Russia
[b] New Mexico Highlands University, NM, USA
[c] Institute of Physics, University of Debrecen, Debrecen, Hungary
[d] Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary
[e] Department of Electronics Technology, Budapest University of Technology and Economics, Budapest, Hungary

ARTICLE INFO

Article history:
Received 24 January 2018
Received in revised form 8 March 2018
Accepted 3 April 2018
Available online 4 April 2018

Keywords:
Photopolymerization
Polymer nanocomposites
Photoinitiator bis (.eta.5-2,4-cylcopentadien-1-yl)-bis (2,6-difluoro-3-(1H-pyrrol-1-yl)-phenyl) titanium
Photoinitiator 2,2-Dimethoxy-2-phenylacetophenone
Gold nanoparticles
Decomposition of photoinitiator
Optical recording process
Holographic recording

ABSTRACT

The influence of gold nanoparticles (AuNPs) on the decomposition of two widely used types of photoinitiators (Bis (.eta.5-2,4-cylcopentadien-1-yl)-bis (2,6-difluoro-3-(1H-pyrrol-1-yl)-phenyl) titanium/Irg784/and 2,2-Dimethoxy-2-phenylacetophenone/In2/) was investigated in this work, both, in simple toluene solutions or solutions with AuNPs, as well as in SiO_2 nanoparticles and AuNPs containing monomer acrylate nanocomposites during photopolymerization. These processes are important for efficient, one-step creation of photonic structures by holographic recording based on polymer nanocomposites containing AuNPs with plasmonic properties.

Analysing such processes, activated by irradiation with wavelengths of 532 nm and 325 nm, their efficiency and parameters of grating recording, as well as examining the related multistep photopolymerization processes by IR and UV–vis spectroscopy the influence of AuNPs on the decomposition of the photoinitiators was shown and explained by the mechanism of complex formation. Thereby, it is concluded that by combining the type of initiator, polymer matrix components, and illumination conditions the decomposition of initiators can be manipulated, that in turn affect the resulting optical modulation characteristics and the efficiency of the photonic elements recording in a one-step process.

1. Introduction

1 Photo-curable nanocomposite materials are mixtures of monomers and organic or inorganic compounds, and they serve as the basis for the development of smart materials for electronics, photonics, etc. [1,2]. A wide number of polymer nanocomposites with different inorganic and organic nanoparticles was investigated and developed for hologram recording by Y.Tomita with co-authors [3–8]. The redistribution of neutral components plays an essential role in the recording processes, as described in [9] as well. Blending gold nanoparticles (AuNPs) with photocurable materials gives new abilities at the stage of photosensitive element fabrication or new functionalities in devices based on these materials and elements. These effects can be extended to other applications of AuNPs in composites, where the electronic, optical and plasmonic effects determine new functionalities in photonics, optoelectronics, catalysis, and bioengineering [10–15]. Yang Tian and Tetsu Tatsuma reported the visible light induced plasmon resonance in AuNPs which resulted in charge separation and redox reactions [16,17]. This makes AuNPs potentially useful as photocatalysts, elements of photovoltaic fuel cells, and for optical patterning as well. Fox et al. studied properties of *trans*-stilbene- and *o*-nitrobenzyl-ether-functionalized AuNPs [18], while Kamat and Thomas investigated intramolecular energy and electron-transfer reactions in fullerene- and pyrene-functionalized AuNPs [19]. These experiments demonstrated that AuNPs could be used as electron acceptors or modifiers of light-stimulated processes in different matrixes, and these modifications may depend on the type of functionalization of AuNPs as well. Nakashima and Nonoguchi first reported the use of a semiconductor nanocrystal as donor-acceptor electron transfer initiator in the presence of an onium salt for radical photopolymerization of an ionic liquid-based acrylic monomer [20]. The radical photopolymerization of an acrylic monomer with 5-mercapto-2,2′-bithiophene functionalized AuNPs using [4-[(acetyloxy)phenyl] phenyl] iodonium hexafluoroantimonate as

* Corresponding author.
E-mail address: csarnovics.istvan@science.unideb.hu (I. Csarnovics).

https://doi.org/10.1016/j.jphotochem.2018.04.006
1010-6030/

a co-initiator and respectively without the use of conventional photoinitiators has been described in [21,22]. For this reason and possible peculiar applications, photo-curable polymer composites containing AuNPs are worthy of serious attention in research and development. For example, nowadays photonic crystal (PhC) structures (including ones with localized surface plasmon resonance effect) are among the main objects of scientific research and application of nanotechnology in photonics, sensors [23,24]. There are various well-known multistep methods to produce PhC using different materials. Mostly they are formed as 1D and 2D structures, while only a few of them allow the fabrication of 3D ones. One of the possible ways to produce them is the multibeam interference holographic recording method using polymer nanocomposites on the basis of different monomers and inorganic nanoparticles [25–28]. Here the processes of photostimulated polymerization of monomers and associated diffusion of nanoparticles and monomers are responsible for the creation of photonic structures by holographic recording in the selected nanocomposite. These polymer nanocomposites allow the direct, single-step creation of PhC with localized surface plasmon resonance effect too. In last few years our group produced polymer nanocomposites with AuNPs for holographic recording of photonic crystal structures [27–29]. A nanocomposite containing Er and Yr nanoparticles besides AuNPs was developed and it was shown [25] that as a result of the metallic nanoparticles addition the luminescence was enhanced 8-times.

It was observed in these works that AuNPs affect on the recording process depending on the monomer compositions, type of the photoinitiator and irradiation parameters. They influence the rate and magnitude of conversion in the photopolymerization processes and so the surface magnitude of resulting PhC structures, wherein the localized surface plasmon resonance of AuNPs remains unchanged after recording such structures and may be active in sensing applications of such PhCs. However, the influence of AuNPs on the processes occurring during polymerization of nanocomposites, especially the mechanism of such effects, has not been identified yet. Since polymerization is a multistep process and each stage can be affected by the AuNPs, the detailed analysis and understanding of the possible effects are quite important. To the best of our knowledge, there are no works discussing the influence of AuNPs on the decomposition of photoinitiators during the photopolymerization process.

In this paper, we investigate in details the influence of AuNPs on the process of photopolymerization in polymer nanocomposites, highlighting their influence on photoinitiators, their decomposition and so on the resulting efficiency of optical recording, as it was observed earlier in our paper [25–28]. The results of our study may be useful for further development and applications of light-sensitive polymer nanocomposites, combining their parameters for direct, one-step fabrication of different photonic elements.

2. Experimental methods

2.1. Materials for the preparation of the polymer nanocomposites

The following monomers, nanoparticles, and photoinitiators were used for the investigation:

- Diurethane dimethacrylate (No. 436909, Aldrich, UDMA)
- Isodecyl acrylate (No. 408956 Aldrich, IDA),
- Dodecanethiol functionalized AuNPs (No. 3014, Nanoprobes, Au-$SCH_2(CH_2)_{10}CH_3$. Size concerning TEM measurement – 5 nm),
- SiO_2 nanoparticles (Aldrich S5130–Silica NPs powder, size concerning TEM measurement – 7 nm)
- 2,2-Dimethoxy-2-phenylacetophenone, No. 19611-8 Aldrich (In2). Chemical formula $C_{16}H_{16}O_3$, see the chemical structure in Fig. 4.
- Bis(.eta.5-2,4-cylcopentadien-1-yl)-bis(2,6-difluoro-3-(1H-pyrrol-1-yl)-phenyl) titanium (Irg784). Chemical formula $C_30H_22F_4N_2Ti$, see the chemical structure in Fig. 4.

The resulting nanoparticles and nanocomposites were characterized by TEM (Transmission Electron Microscope) JEOL-2000FXII (see Fig. 1b).

2.2. Preparation of the solutions

A certain amount of initiator corresponding to the desired weight percent in the nanocomposite (see data in Table 1) was dissolved in toluene. For the preparation of the AuNPs containing a mixture, a calculated amount of AuNPs solution, having a concentration of 0.0032 g/ml in toluene was added to the initiator solution. In the case of the Irg784 solution, the weighted compound was initially dissolved in dichloromethane prior to the addition of toluene. To investigate the influence of the AuNPs, a solution with a different amount of compounds was created (see Table 1). To change the ratio of photoinitiator/AuNPs the amount of used photoinitiator was different, while the amount of AuNPs was the same. The exact composition of the solutions is presented in Table 1. Solutions are labeled by S, nanocomposites – by P, and the type of initiators, the presence of AuNPs are shown additionally.

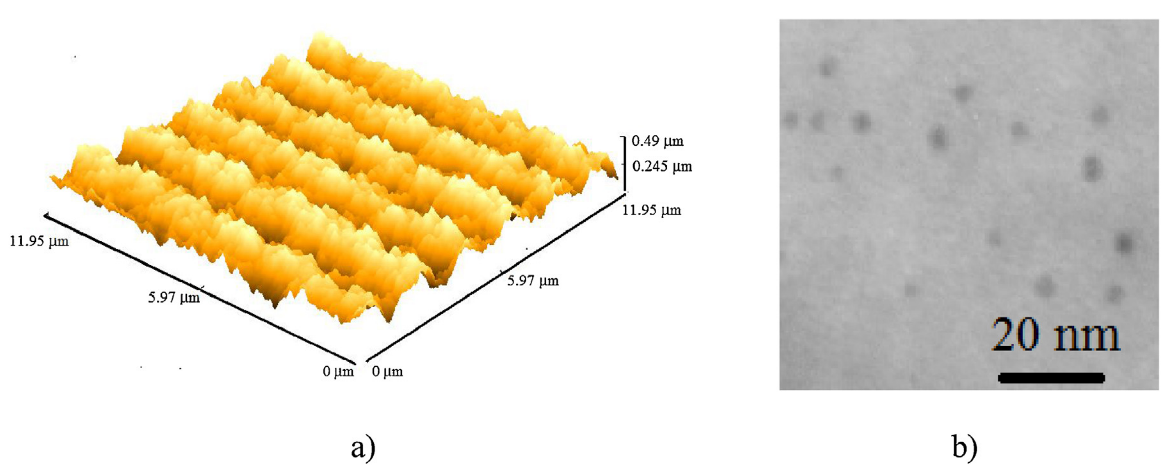

Fig. 1. a) AFM picture of a free surface of polymer grating sample after the recording,b) TEM picture of AuNPs in UDMA/IDA nanocomposite.