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Fabrication and Characterization of Gold/Acrylic Polymer Nanocomposites

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We report the method of incorporation of preformed gold nanoparticles (AuNP) into the acrylic polymer (AP) matrices and optical, TEM characterization of AuNP/AP bulk and film composite. It was shown that incorporation of dodecanethiol-covered AuNP can be enhanced in the presence of SiO_2 nanoparticles, enabling at the same time a wider range of tailoring of composite properties for optical processing or medical applications.

Keywords: Nanocomposite, acrylic polymer, gold nanoparticles, structure, optical recording.

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Introduction

It is known, that the composites unite useful properties of components to create more sophisticated materials for photonics, medicine, etc. [1 - 3]. Gold is one of the most preferred metals which is used in glass and polymer nanocomposites due to its exceptional stability, biocompatibility and, not at last, because of plasmon resonance effects, which are easily observed in 500 – 800 nm spectral range in dependence of the size and shape of the Au nanoparticles (AuNP). The problems of compatibility of AuNP with a given matrix, the aggregation effects appear frequently and stimulate intensive investigations of different fabrication methods, that can be classified under two major categories: as physical and chemical methods. Physical methods include solvent processing; melt-processing, polymer melt intercalation whereas chemical methods are *in-situ* processes of NP creation, where the resulting shape and dimensions sometimes are not easy to foreseen.

The incorporation of preformed nanoparticles into polymeric matrices is a direct physical-chemical method. This route has the advantage that the best selected for certain needs, high quality nanoparticles with a given dimensions and form can be employed. But, in mixtures with polymers, the nanoparticles will generally aggregate into large clusters, which often deteriorate the properties of the nanoparticles and the nanocomposite. Methods have been developed to overcome these problems, for example by the capping, functionalisation of the surface of AuNP.

The aim of our work was to develop a facile and applicable direct physical method to produce gold-polymer nanocomposite with plasmonic effects. Results are reported, where the introduction of preformed gold nanoparticles and the polymerization of a photosensitive monomer(s) are simultaneously performed. These studies create also a basis for further technology development and new possibility of plasmonic nanoarray fabrication by optical recording or improvement of polymer dental materials filled up by nanoparticles.

I. Experimental

Initial materials.

The next materials and chemicals were used in this work: 2-(Dimethylamino) ethyl acrylate (330957 Aldrich, AmAc), Diurethane dimethacrylate, mixture of isomers (436909 Aldrich, UDMA), Dodecanethiol functionalized gold nanoparticles (Nanoprobes, №3014, AuNPs), Silica (S5505, nanoparticles size 0,014 μ, SiO_2), Camphorquinone (124893, Aldrich, CQ), 2,2-Dimethoxy-2-phenylacetophenone (19611-8 Aldrich, In2).

Preparation of Au-monomer system.

Matrix material UDMA was mixed 3 hours in a magnetic mixer with initiator - camphorquinone (0.5 wt% concentration) and 1 ml solution of AuNPs in toluene with concentration 0.50 wt % was added to the monomer. Compositions of Au-SiO_2- monomer composites are presented in Table 1. Silicon oxide nanoparticles were added to the above mentioned monomers and the homogeneous solution was prepared by UHF – dispergation at 55 °C during 24 hours.

Solution of AuNP in toluene and initiator were added to this solution.

Preparation of the polymer nanocomposite films.

Preparation of the polymer nanocomposite film consists in the UV- curing of Au-monomer solutions between polyester films to prevent the inhibiting effect of oxygen. Light source for preparation of the AuNPs-SiO_2-polymer nanocomposites with CQ (curing at 400 nm) was Translux E-C, B-6393 Wehrheim/Ts source. UV light source for preparation of the AuNPs-SiO2- polymer nanocomposites with In2 (curing at 365 nm) was mercury lamp OSRAM,HQV 125 W.

The resulting nanocomposites were characterized by TEM (JEM-2000FXII), AFM (Veeco di Caliber), and optical spectra were measured with Shimadzu 4016 UV/VIS spectrometer.

II. Results and discussion

The problem of increasing the compatibility of the polymer and inorganic NPs was solved as follows. First, nanoparticles with organic shells should be used to increase the affinity of the polymer matrix. Second, functional groups can be introduced to the polymer chain to improve the compatibility with inorganic NP. Third, the additional material can be used during the fabrication of host-guest system, which is compatible with the polymer matrix and inorganic particles as well.

In our work we have selected these aminoacrylates: 2-(Dimethylamino)ethyl acrylate (AmAc) and Diurethane dimethacrylate mixture of isomers (UDMA). The presence of amino-groups in these monomers should promote their compatibility with AuNPs due to the electrostatic attraction.

In our experiments the first and simple criteria of nanocomposite formation was the presence of plasmon resonance peak in the optical transmission spectrum, which supports the separation of gold nanoparticles of given dimensions and existence of proper resonance maximum. Plasmon resonance was observed in optical transmission spectra for the UDMA/AuNPs liquid composite, where toluene was used for homogenization. The extraction of toluene from the composite during the polymerization resulted in an increased absorption and scattering, caused by agglomerized nanoparticles.

It was published that AuNPs can be distributed uniformly in polymer composites with highly dispersive silicon oxide and silane derivatives. [4]. SiO_2 particles with large specific surface can act in this case as special dispergating agents. According to these data and our assumptions, introduction of SiO_2 NPs should improve the compatibility of AuNPs with the selected organic matrix. Therefore monomer compositions with SiO_2 nanparticles were prepared (Table 1). Monomer compositions and thick films, which were obtained after UV-curing, were uniform, had pink color and low light scattering level. Plasmon resonance pike was observed at 518 nm for the monomer solution and in the polymer (Fig. 1, a, b). Optical absorption spectra of AuNP-

Table 1

Au-SiO_2- monomer compositions

monomer	SiO_2, wt%	initiator	AuNPs, wt%
AmAc	14	0,2 wt% In2 or 0.5 wt % CQ	0.30
UDMA	10	0.2 wt% In2 or 0.5 wt % CQ	0.1 - 0,55
UDMA	26	0.2 wt % In2	0.1 - 0.55
UDMA/ AmAc= 70/30	10	0.2 wt% In2	0.1 - 0.3

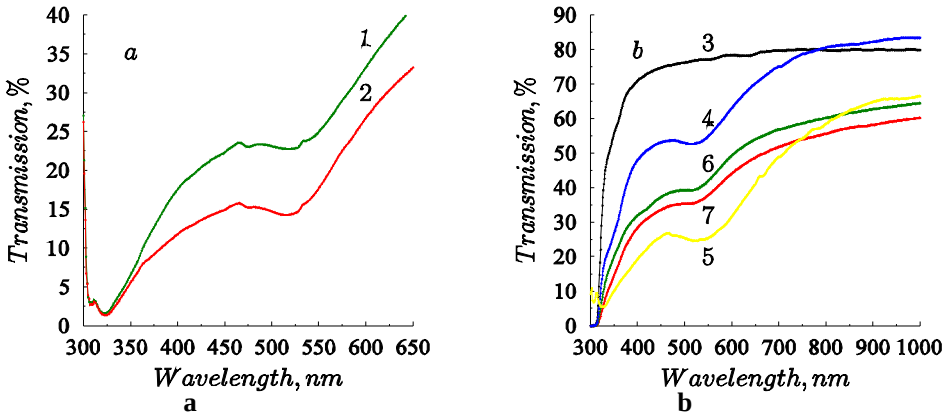
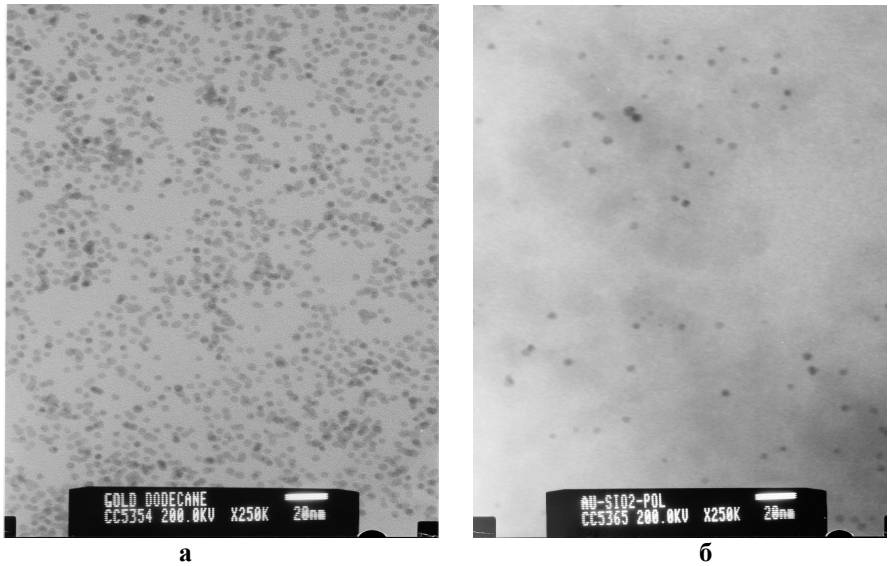


Fig. 1. Optical transmission spectra : (**a**) - for 10 wt % SiO_2 - 0,3 wt%AuNPs-AmAc nanocomposite (1-monomer, 2-polymer); (**b**) - for SiO_2-0,2 wt%AuNPs-UDMA nanocomposites: (3) - 10 wt%SiO_2/UDMA polymer; (4) 26wt%SiO_2/ 0.2 wt% AuNPs/ UDMA, monomer; (5) - 26wt%SiO_2/ 0.2wt% AuNPs/ UDMA, polymer; (6) - 10wt%SiO_2/ 0.2wt% AuNPs/ UDMA, monomer; (7) -10wt%SiO_2/ 0.2wt% AuNP/ UDMA, polymer



а **б**

Fig. 2. TEM pictures of AuNPs in different matrix: Material – **a**) UDMA/ 0,2 wt% AuNPs/ 10% SiO_2 NPs; (**b**) 0,2 wt% Au NP/UDMA with SiO_2

acrylate- SiO_2 nanocomposites are presented for two different acrylates (UDMA and AmAc) in Fig. 1. The intensity, shape of plasmon resonance peak should be compared in acrylates with SiO_2 to support the selection of the best composition. It was established, that the increase of SiO_2 NPs concenration causes the increase of the intensity of plasmon resonance absorpton for monomer and polymer as well. It is seen that the plasmon resonance absorption peak is more pronounced in the Au- UDMA - SiO_2 system.

It should be mentioned, that about 5 wt % of toluene, in which the AuNPs are dissoluted, should be preserved in the monomer composites to improve the AuNPs distribution. This amount of toluene do not prevents the UV polymerization, which results in transparent pink colored composite. After the UV curing the solvent is removed by drying at room temperature. We tried to avoid this approach by introducing an another nitrogen-containing monomer - AmAc. It was established, that the mixture of UDMA and AmAc polimerized well and formed hard films. AmAc is compatible with the given AuNPs and possesses low polymerization rate at UV curing. During the UV polymerization AmAc posseses low polymerization rate and creates a kind of shell which prevents agglomerization of AuNPs, playing the role of toluene in the previous route.

So it is reasonable to use also AmAc monomer, since it ensures more uniform distribution of components after UV curing during the nanocomposite fabrication. Therefore a mixture of the both monomers may be used in future for fabrication of high quality nanocomposites with preformed AuNPs. But here we try to show, what can be done with a simpler compositions containing preshaped spherical Au NPs.

The nature of the effect may be explained on the basis of TEM cross-sections (Fig. 2). Separated AuNPs are visible in the starting solution and in the polymerized matrix, but the AuNPs seems to be connected, concentrated around the SiO_2 NPs.

It was established, that Au nanoparticles are forming aggregates up to hundred of nanometers in the nanocomposite without SiO_2. Introduction of SiO_2 nanoparticles prevents aggregation of AuNPs. It is well seen that AuNPs are distributed in the polymer nanocomposite with SiO_2 nanoparticles, being separated at SiO_2 nanoparticles (Fig. 2,b) and the initial dimensions, the shape of AuNPs are preserved (Fig. 2,a).

The investigated UDMA/0,2 wt % AuNPs/10 wt % SiO_2 composition was used as light-sensitive media for holographic recording of diffraction gratings (Fig. 3). The layers were formed on a glass substrate in the gap between the glass and a polyester film, their thickness was 60 micrometers. After that exposure by uniform UV-radiation was made to delete completely the residual monomer, and thus the pattern have been fixed. The efficiency of such holographic grating was 67 % in transmission mode of readout for nanocomposition with SiO_2 and Au nanoparticles in comparison with 41 % without AuNPs. It means that the combination of different nanoparticles further increases the efficiency of phase modulation due to the redistribution of nanoparticles in the non-uniform interference field during the polymerization, like it was published for NPs–filled acrylates [2].

It is worth mentioning, that the plasmon resonance is

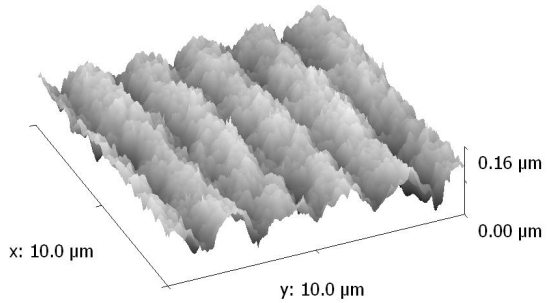


Fig. 3. AFM picture of the surface diffraction grating created by holograqphic recording at 325 nm.

preserved after the recording the structures, that supports the absence of agglomeration of Au NPs during the stimulated transport, lateral redistribution of SiO_2/Au NPs in the layer before the final polymerization. So the basis for further investigations of plasmonic arrays and non-linear optical effects in the presence of plasmon fields excited in Au NPs is foreseened. These investigations are also under extension to the changes of mechanical parameters as well, which are important for other applications.

Summary

Gold/polymer nanocomposites have been successfully prepared by a direct physical route of incorporation of the given Au NPs into the monomer matrix of two composition with subsequent photopolymerization. The experiments indicate that the agglomeration of AuNPs can be avoided by addition of SiO_2 nanoparticles to the composition. The polymerization process did not change the separation of gold nanoparticles, so high quality solid polymer films and nanocomposites can be produced or holographic gratings with increased efficiency can be recorded in such a complex media due to the spatial redistribution of nanoparticles.

Acknowledgements

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