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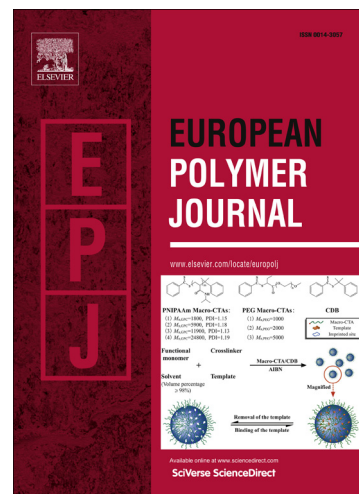
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FABRICATION AND CHARACTERIZATION OF GOLD/ACRYLIC POLYMER NANOCOMPOSITES

J. Burunkova[1], I. Denisiuk[1], N. Vorzobova[1],
L. Daroczi[2], Cs. Hegedus[3], S, Charnovych[2*], S. Kokenyesi[2]

[1]ITMO, St.Petersburg, Russia
[2]Institute of Physics, University of Debrecen, Hungary
csari86@gmail.com
[2]Faculty of Dentistry, University of Debrecen, Hungary

Abstract

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.

Keywords: *Gold nanoparticle, Acrylic polymer, Nanocomposite.*

1. Introduction.

It is known, that the composites unite useful properties of components to create more sophisticated materials, but the novel trends in materials science favour nanocomposites which can differ from those properties of analogous composites with larger particles. This trend offers a plethora of opportunities for the creation of materials with exceeding performance for a wide range of applications from optics and holography [1, 2] to medicine, dentistry [3-5]. Many more applications would become practically viable if one could find innovative ways to create a more extensive range of photosensitive, optically or mechanically improved structures as films, layers, etc. Particular distributions of the nanoparticles within the polymer matrix under the light treatment is a basis for efficient holographic recording [1, 2], the combination of nanoparticles increase the quality of dental acrylic materials [4].

Gold is one of the most preferred metal 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 nanoparticles. The reduction in light scattering, the change of colour, transparency upon usage of different nanoparticles can be of interest in combination with other properties which favourably improve characteristics of polymer materials, such as optical absorption or modification of refractive indices, mechanical properties. The problems of compatibility of AuNP with a given matrix, the aggregation effects appear frequently and stimulate intensive investigations of different fabrication methods.

There have been several attempts for the synthesis of polymer nanocomposites 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 [6]. For example, gold-poly(methyl methacrylate) nanocomposites were prepared [7] by an *in situ* method, by irradiating spin-coated films containing the polymer and the gold precursor dissolved in acetone. The reduction of gold ions results in the formation of Au that nucleates and grows within the polymer film. It is shown that, depending on the energy source, gold nanoparticles with different shapes can be formed.[7]. Also acrylic polymer–nanogold nanocomposites and their cast films were prepared from an acrylic copolymer and 3-mercaptopropyltrimethoxysilane (MPS) stabilized gold nanoparticles by a sol–gel reaction [8].

The incorporation of preformed nanoparticles into polymeric matrices is a direct physico-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. Direct mixing and melt processing of particles with polymers often

results gradients of the incorporated fillers in the matrix that leads to turbidity/translucency of composite materials because of the agglomeration of the nanoparticles. The incompatibility of the nanoparticles with the polymer matrix is one of the possible problems. In mixtures with monomers or 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. Compatibility can be achieved by proper treatment of the nanoparticle surface which is possible by coating with appropriate molecules.

The aim of our work was to develop a facile and manufacturable 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 filled up by nanoparticles.

2. Experimental details.

2.1. 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).

2.2. Preparation of Au-monomer system.

Two different systems were investigated in the framework of the same physical rout. The first was based on pure monomer mixture, to which the AuNP were added in the form of solution in toluene. The second contains the monomers with SiO_2 nanoparticles to which AuNPs were added in the form of solution in toluene.

Matrix material UDMA was mixed 3 hours in a magnetic mixer with initiator - camphorquinone (0.5 wt% concentration) and solution of AuNPs in toluene with concentartion 0.50 wt% was added to the monomer.

Compositions of Au-SiO_2- monomer composites are presented in Table 1. They were prepared in the next way. Silicon oxide nanoparticles were added to the above mentioned monomers and the homogeneous solution was prepared by UHF – dispergation at 55Cº during 24 hours. Solution of AuNP in toluene and initiator were added to this solution.

2.3 Preparation of the polymer nanocomposite films.

Preparation of the polymer nanocomposite film consists in the UV- curing of Au-monomer solutions between glass and polyester film to prevent the inhibiting effect of oxygen. Light source for preparation of the AuNPs-SiO2- polymer nanocomposites with CQ (curing at 400 nm) was Traslux 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 characterised by TEM (JEM-2000FXII), AFM (Veeco di Caliber), and optical spectra were measured with Shimadzu 3600 UV/VIS spectrometer.

3. Results and discussion.

In spite of the desirable introduction of preformed AuNP to the host polymer matrix some special methods should be used to avoid agglomeration and ensure necessary parameters. The next three methods seems to be good for these purposes and were used in our work with AuNP-acrylat nanocomposites.

First, the organic shell, with higher affinity to the polymer matrix, can be produced by functionalization of the AuNP surface by tiols or amines. Capping of AuNPs by polymers is one way to realise this method, otherwise large light scattering and absence of plasmon resonance may occur. It means that the increase of compatibility between the matrics and NPs is necessary. Second, the selection of the proper polymer matrix should be made. 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 the next aminoacrylates: 2-(Dimethylamino)ethyl acrylate (AmAc) and Diurethane dimethacrylate mixture of isomers (UDMA). As it was mentioned above the presence of amino-groups in these monomers should promote their compatibility with AuNPs due to the electrostatic attraction [9]. Really the particles are not ideal spherical hard objects but covered with a soft organic ligand shell of which the charge distribution is in most of the cases not known. Heterogeneity in the surface coverage can exist as a result of changes dependent on external factors. In ligand-coated nanoparticles ligand molecules are attached to the nanoparticles surface, in most cases by a chemical functional group and this bond can be electrostatic [9].

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 toulene was used for homogenization. The extraction of toulene from the composite during the polymerization resulted an increased absorption and scattering, caused by agglomerized nanoparticles.

It was published [10] that AuNPs can be distributed uniformly in polymer composites with highly dispersive silicon oxide. It should be mentioned, that SiO_2 particles with large specific surface can act in this case as special dispergating agents. Silan derivatives also are used to promote the affinity of inorganic particles with monomers or polymers. The methods of capping Au nanoparticles by silicon from silanes for prevention of their agglomeration, as well as synthesis of Au nanocomposites using silanes are reviewed in [11].

According to our assumptions introduction of SiO_2 NPs should improve the compatibility of AuNPs with 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 peak was observed at 518 nm for the monomer solution and little shifted in the polymer (Fig. 1a,b) due to the differences in the refractive index of monomer and polymer.

Optical absorption spectra of AuNP- acrylate- SiO_2 nanocomposites are presented for two different acrilytes (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 is seen that the plasmon resonance absorption peak is more pronounced in the Au- UDMA - SiO_2 system 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 should be mentioned, that about 5 wt% of toulene, in which the AuNPs are dissoluted, should be preserved in the monomer composites to improve the AuNPs distribution. This amount of toulene 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 tryed 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 ensures decreased polymerization rate and creates a kind of shell which prevents agglomerization of AuNPs, playing the role of toulene in the previous rout.

So it is reasonable to use also AmAc monomer for composite fabrication, since it ensures more uniform distribution of components after UV curing. Therefore a mixture of the both monomers may be used in future for

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fabrication of high quality nanocomposites with preformed AuNPs. But here we try to show, what can be done with a single UDMA-based compositions containing preshaped spherical Au NPs.

The influence of the NPs on the monomer polymerization was investigated by studying Raman spectra, measured *in situ* in the 200-1800 cm^{-1} frequency range under homogeneous UV-light illumination (see Fig.2). The change of few spectral lines can be followed due to the presence of SiO$_2$ NPs, like the intensity of lines in 830-880 cm^{-1} range which can be related to the deformation vibrations of -NH and C-C valency vibrations in UDMA [13], as well as of the urethane group lines at 1720 cm^{-1} (amide I), 1450cm^{-1} (amide II) and 1250 cm^{-1} (amide III) [14]. These can testify the creation of hydrogen bonds between N-H groups and SiO$_2$. The strong line at 530cm^{-1} is visible in the Raman spectra of composites, which corresponds to the symmetrical vibrations of Si-O-Si tetrahedras in siloxanes [15]. Besides these, the lines at 970 cm^{-1} and 1150 cm^{-1} are present at the polymerization of pure UDMA, which correspond to the vibrations of epoxycycle and -C(CH$_3$)$_2$ groups [16]. These lines are absent in the IR spectra of composites. The 910-960 см$^{-1}$ line, which corresponds to the Si-OH deformation vibrations [17] shifts towards 1000 cm^{-1} in the composite. This fact can be explained as a partial dehydration of SiO$_2$ due to the interaction with UDMA. Besides this, the line appears at 1170 cm^{-1}, which is characteristic for SiO-CH$_3$ stretching vibrations [18]. All the above mentioned facts can testifie to the interaction between the N-H groups in UDMA and the SiO$_2$, as well as to the relation of the polymerization process to the surface of SiO$_2$ nanoparticles.

The change of the intensity of the selected line at 1640 cm^{-1} from the Raman spectra was used as a measure of polymerization (Fig. 3).The monomer conversion was measured by monitoring the intensity of the C=C peak in the acrylates (1640 cm^{-1}) and evaluated using the formula C(t) = A(t)/A$_0$, where A$_0$ and A(t) correspond to absorption of the film before and during the UV exposure. The conversion degree increases with addition of SiO$_2$ and Au nanoparticles.

From the changes in intensity of 1640 cm^{-1} line and of the C=C group valency vibrations at 1410 cm^{-1} lines [13] as well as from the data in Fig.3 it can be concluded that the introduction of gold nanoparticles increase the degree of monomer conversion under polymerization.

The nature of the SiO$_2$ effect may be explained on the basis of TEM cross-sections (Fig.4). 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 is seen in Fig 4, that Au nanoparticles are forming agregates up to hundred of nanometers in the nanocomposite without SiO$_2$ (Fig.4a). Introduction of SiO$_2$ nanoparticles prevents aggregation of AuNPs. Gold

nanoparticles are distributed in the polymer nanocomposite with SiO_2, being separated at SiO_2 nanoparticles (Fig. 4b) and the initial dimensions, the shape of AuNPs, are preserved (Fig 4c).

The investigated UDMA/0,2 wt% AuNPs/10 wt% SiO_2 composition was used as a reference light-sensitive media for holographic recording of diffraction gratings (Fig.5) and compared with some other compositions, film thicknesses *d* (see the Table 2). The layers were formed on a glass substrate in the gap between the glass and a polyester film, their thickness was 60 micrometers. Holographic recording was conducted in an interference field with a period 2 micrometers, created by the interaction of two plane coherent laser beams with wavelengths of 325 nm (the monomer was sensitized by In2, 2-Dimethoxy-2-phenylacetophenone) with exposure 8 minutes. The diffraction efficiency was determined at a wavelength of 633 nm as a ratio of the first-order diffraction intensity to the incident radiation intensity. After that exposure by an uniform UV-radiation was made to delete completely the residual monomer, and thus the pattern have been fixed.

The diffraction efficiency and surface topology of the gratings were also investigated. 3D surface topology and cross section of the grating with the period 2 μm is shown in Fig. 5 for UDMA/ 0.2 wt% AuNPs/ 10% SiO_2 NPs. The relief height of the grating for the same recording conditions changes from 20 to 93 nm depending on the material used (Table 2).

Even such small – 0.15% Au NPs concentration was sufficient to provide the increase in diffraction efficiency from 47% (for UDMA-10% SiO_2) to 67% (for UDMA-10% SiO_2/0.15%AuNPs) and 50% (for UDMA-AmAc-8%SiO_2-0.15% AuNPs).

Thus, the Au NPs influence the molecular structure, polymerization process and, consequently, the shrinkage of the nanocomposite in the illuminated region. This may be due to the redistribution of the monomers having different refractive index between the grating planes as well as due to the periodical segregation of the NPs. Therefore, AuNPs are not completely inert additive to the polymer matrix. The proposed mechanism of the refractive index contrast amplification (as compared to a monomer mixture without NPs) includes the interception of free radicals by the AuNPs. This slows down the free-radical photopolymerization promoting the increase in lateral periodic redistribution of the curable components during holographic exposure.

It means that the combination of different nanoparticles can further increase 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, 12]. It is worth to mention, that the plasmon resonance is preserved after the recording the structures, that supports the absence of agglomeration of AuNPs

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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 AuNPs is foreseened. These investigations are also under extention to the changes of the mechanical parameters as well, which are important for other applications.

Conclusions

Gold/polymer nanocomposites have been successfully prepared by a direct physical rout 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 do 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.

Acknowledgement

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Table captions:

Table 1. Au-SiO$_2$ - monomer compositions

Table 2. Relief height and diffraction efficiency of the created holographic gratings.

Figure captions:

Figure 1. Optical transmission spectra:

(a) - for 10wt%SiO_2-0,3wt%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.

Figure 2. Raman spectra of the investigated composites before (a) and after (b) the UV-induced polymerization: UDMA-black, single line; UDMA-10SiO_2- green, dotted line; UDMA-10SiO_2-0.1%Au – red, dash line.

Figure 3. The normalised degree of polymerisation calculated from the change of 1640 cm^{-1} line: 1- UDMA; 2 - UDMA /10%SIO; 3 - UDMA /10%SIO/0,1%Au.

Figure 4. TEM pictures of AuNPs in different matrix: (a) 0,1 wt% AuNP/UDMA without SiO_2, (в) 0,2 wt%Au NP/UDMA with SiO_2, (c) Au nanoparticles in toluene.

Figure 5. a) Diffraction grating created by holograqphic recording at 325 nm on UDMA/ 0,2 wt% AuNPs/ 10% SiO_2 NPs. b) Surface profile measured by AFM.
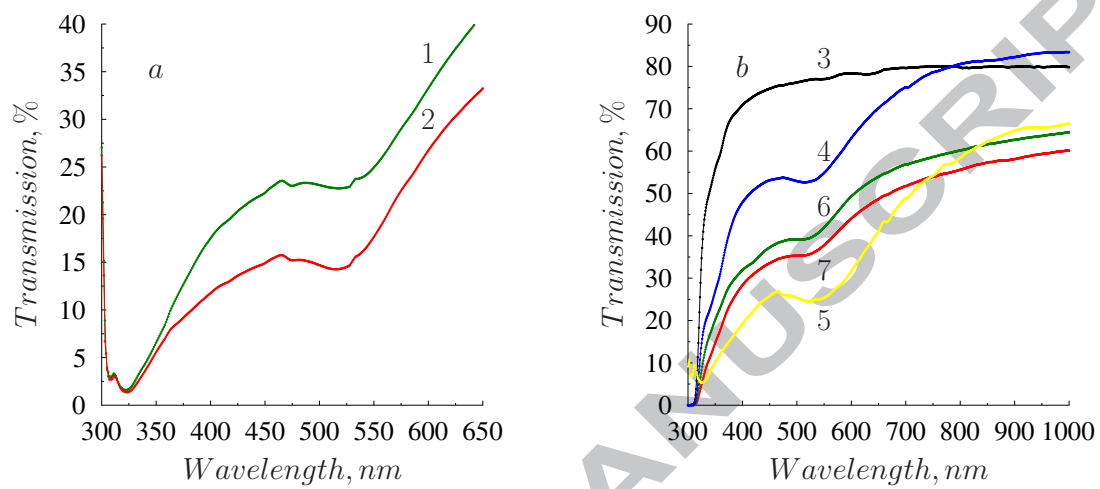
Table 1

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

Table 2

Composition	UDMA-10%SiO$_2$	UDMA-10%SiO$_2$-0.2%Au	UDMA-AmAc-8%SiO$_2$-0.15%Au
Relief height , Δh	20 nm	38nm	93nm
Diffraction efficiency, D	47% (d=45 µm) 67% (d=200 µm)	67% (d=60 µm)	50% (d=40 µm)

Fig 1

Figure 2

Figure 3

Figure 4

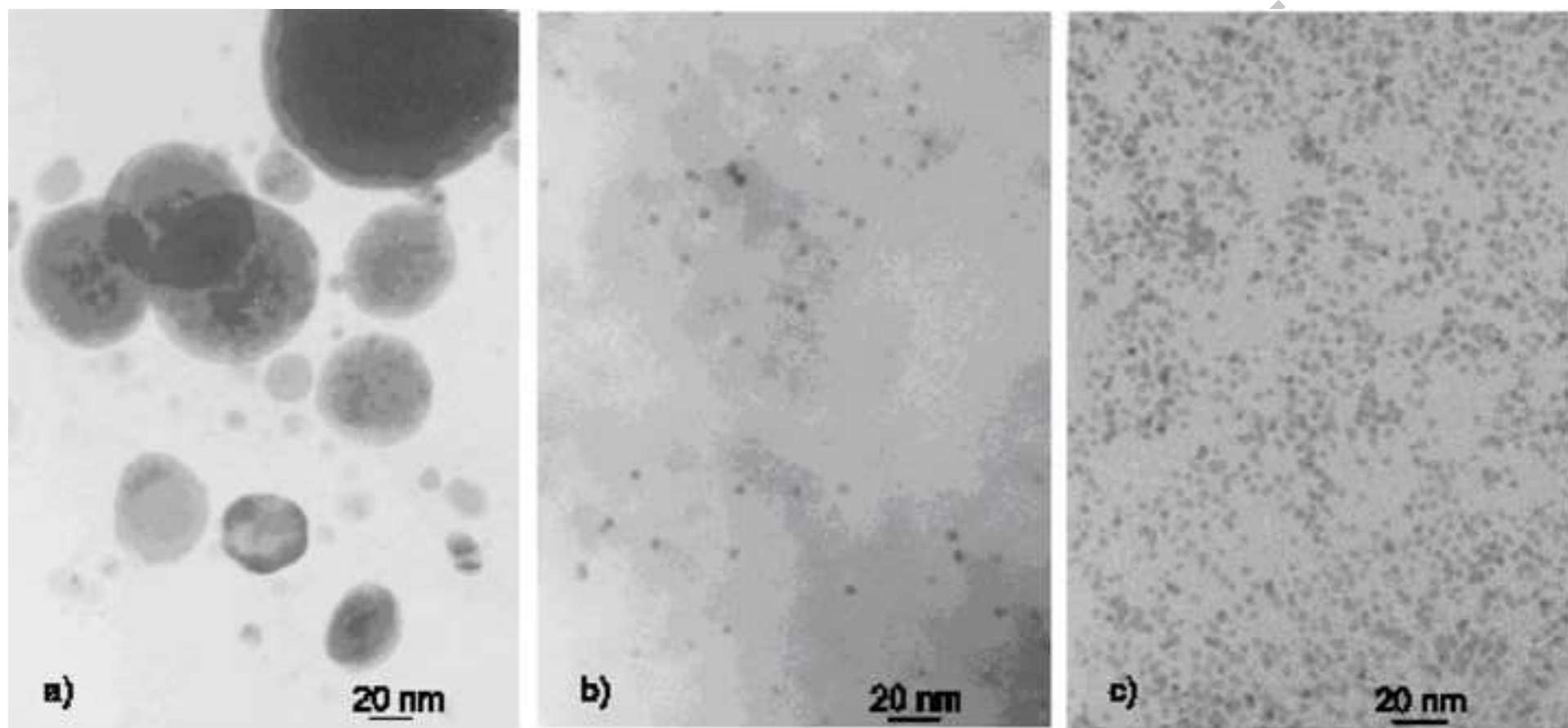a) 20 nm b) 20 nm c) 20 nm

Figure 5

a)

x: 10 µm

b)

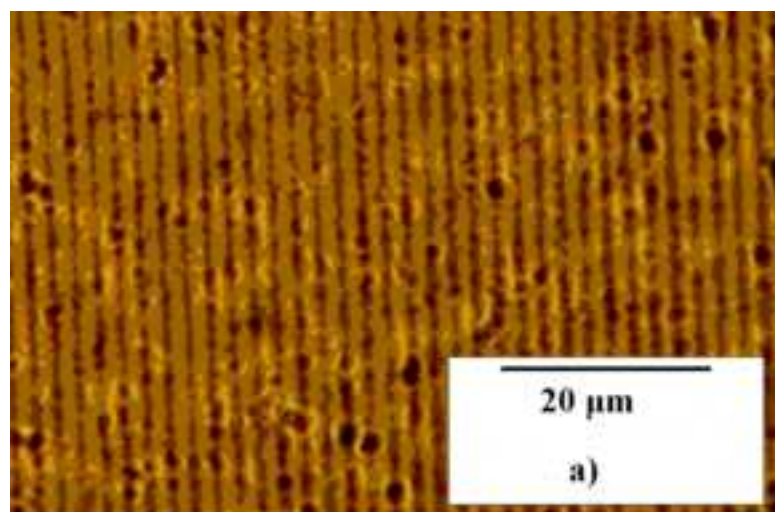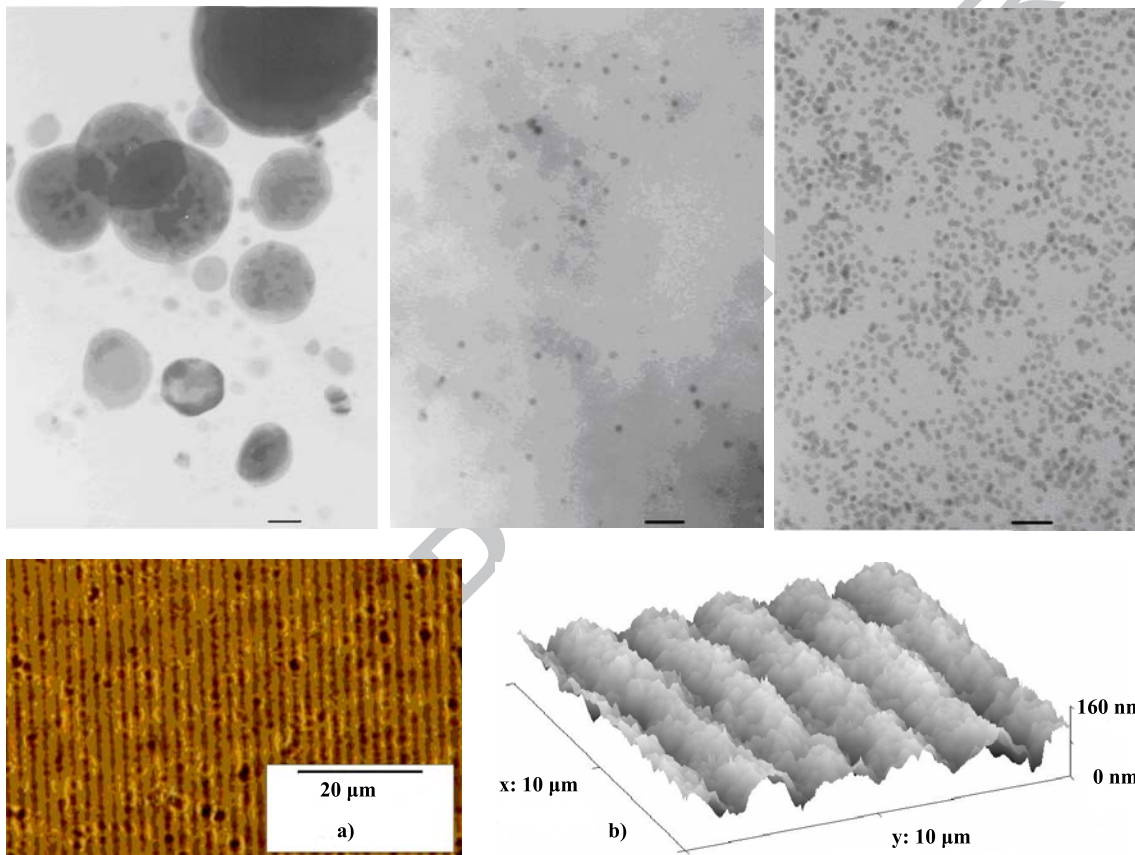y: 10 µm

160 nm

0 nm

20 µm
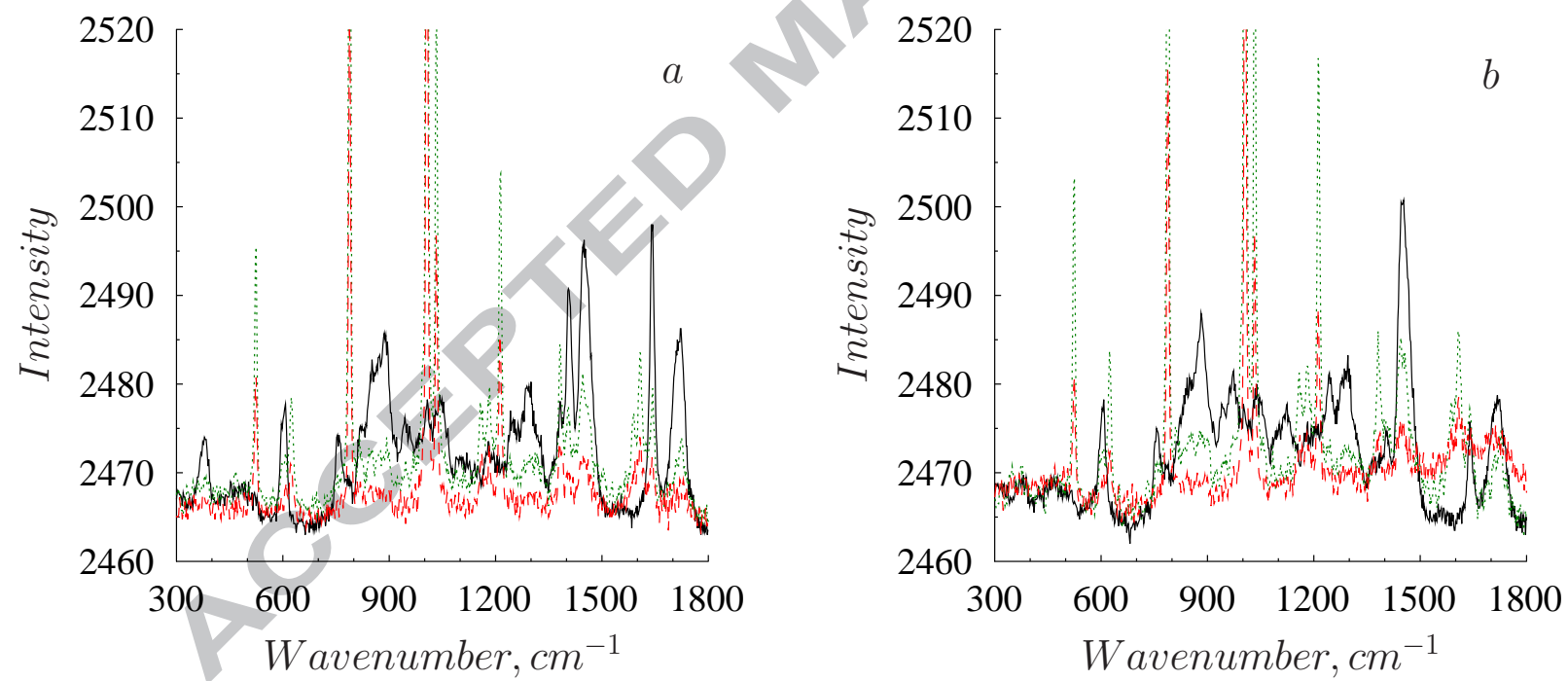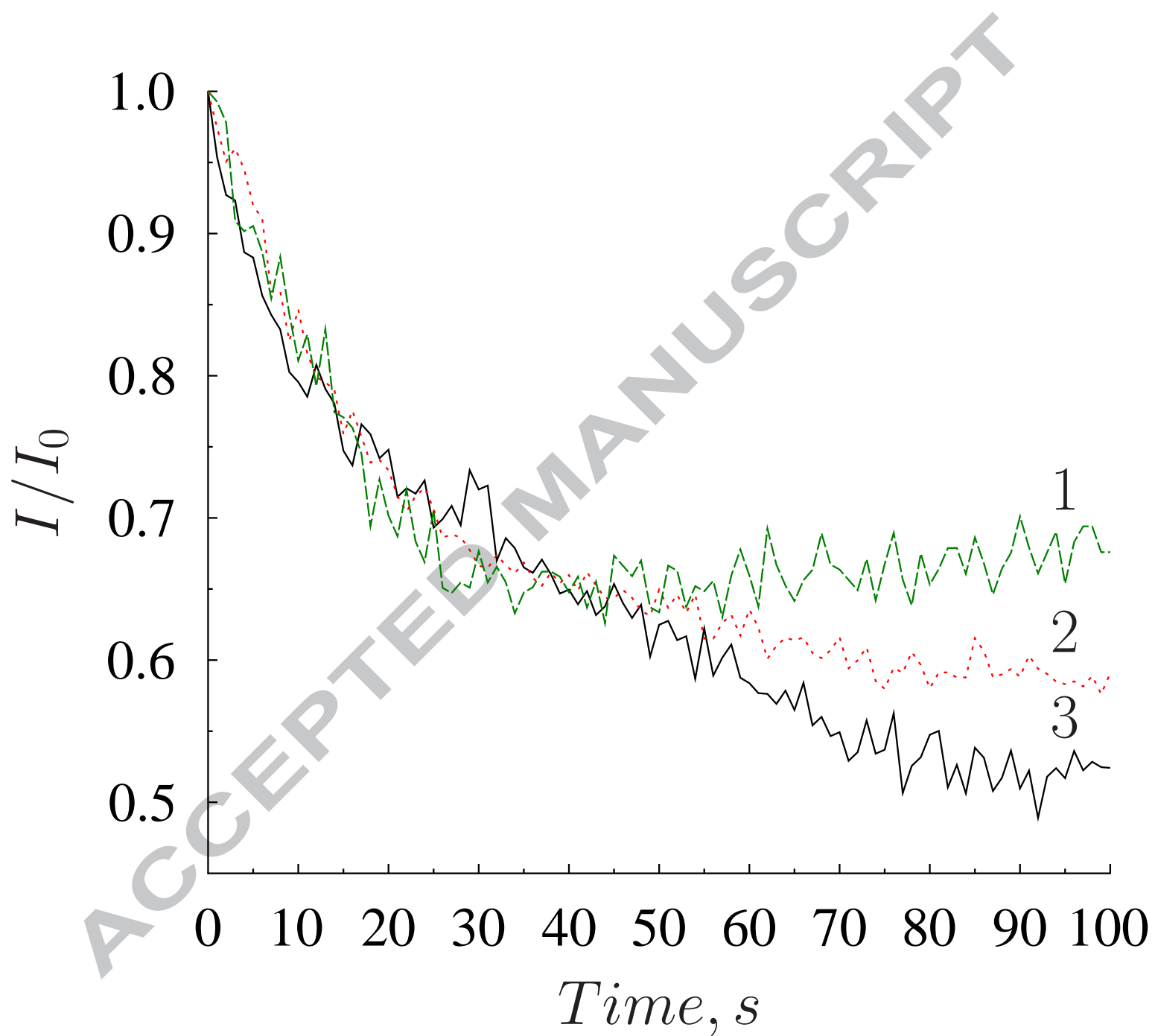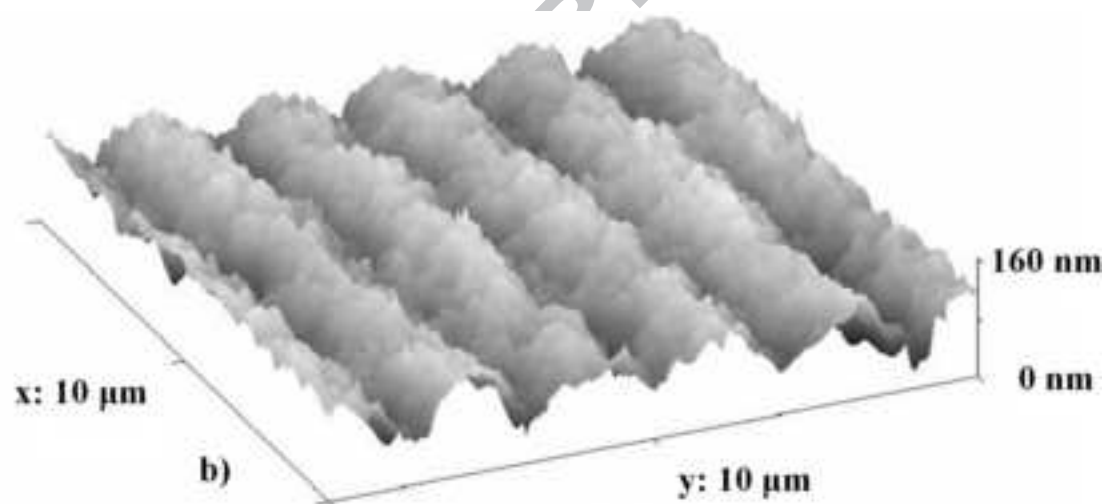
Graphical abstract

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Highlights

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