UV-curable materials composition

Polymerizable surface active monomer
- Diurethane dimethacrylate (No436909 ALDRICH, UDMA)
- Isodecyl acrylate (No436956 ALDRICH, IDA)

SiO$_2$ nanoparticles, covered by organic shell + AuNP
- Dodecanethiol functionalized gold nanoparticles, 5nm (Nanoprobes, No3014, AuNP)
- SiO$_2$ nanoparticles, 7 nm (Aldrich No060K0110)

UV-Polymerizable nanocomposite

Requirement:
- high nanoparticles concentration; same time
- keeping of polymer's properties: transparency, homogenously, solubility, plasticity and processability.

View 2 x 2 um surface of nanocomposite. Formation of spheres around each nanoparticle well visible.

BisA/2Car (3/7) + ZnO nanoparticles (wt.%)
Properties of gold nanoparticles

- Stability;
- Gold nanoparticles are acceptors of electrons, also they can be catalyst of reaction;
- Plasmon resonance, which depends on size of nanoparticles and their shapes.

Synthesis of polymer-based nanocomposites with AuNP

Gold - SiO2 transparent nanocomposites

<table>
<thead>
<tr>
<th>Monomer</th>
<th>SiO2, wt%</th>
<th>Initiator</th>
<th>AuNPs, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>AmAc</td>
<td>14</td>
<td>0.2 wt% In2 or 0.5 wt% CQ</td>
<td>0.30</td>
</tr>
<tr>
<td>UDMA</td>
<td>10</td>
<td>0.2 wt% In2 or 0.5 wt% CQ</td>
<td>0.1 - 0.55</td>
</tr>
<tr>
<td>UDMA</td>
<td>26</td>
<td>0.2 wt% In2</td>
<td>0.1 - 0.55</td>
</tr>
<tr>
<td>UDMA/AmAc</td>
<td>70/30</td>
<td>0.2 wt% In2</td>
<td>0.1 - 0.3</td>
</tr>
</tbody>
</table>

Gold nanoparticles were deposited on SiO2 nanoparticle surface and these combinations were mixed in surface active monomers mixture.

**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-SiO2- 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 – dispersion at 55 °C during 24 hours.
Nanocomposites

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>14α-0.5</td>
<td>UDMA+IDA+10% SiO₂+In₂</td>
</tr>
<tr>
<td>14Au-0.5</td>
<td>UDMA+IDA+10% SiO₂+Au+In₂</td>
</tr>
<tr>
<td>30α-0.5</td>
<td>UDMA+IDA+10% SiO₂+Irg784</td>
</tr>
<tr>
<td>30Au-0.5</td>
<td>UDMA+IDA+10% SiO₂+Au+Irg784</td>
</tr>
</tbody>
</table>

Nanocomposites were prepared by mixing of SiO₂ nanoparticles in UV-curable monomers mixture with absorption in its surface of gold nanoparticles. Ultrasound stirring of nanocomposite as well as interaction between UDMA and SiO₂ nanoparticles surface will result of preparation of well dispersed homogenous transparent nanocomposite.
Polymerization initiators

**In 2 in toluene**

\[ \lambda = 325 \text{ nm} \]

**Irg784 in toluene**

\[ \lambda = 532 \text{ nm} \]
Gold nanoparticles stabilized in monomers and polymer

- TEM pictures of AuNPs in polymer matrix: UDMA/0.2 wt% AuNPs/10% SiO2 NPs (in the left);
- 0.2 wt% Au NP/UDMA with SiO2 (in the right).
- It is well visible that homogenous dispersion form only after deposition of AuNPs on Si]2 nanoparticle surface previously (left).

- Optical transmission spectra: for 10 wt% SiO2 - 0.3 wt% AuNPs-AmAc nanocomposite (1-monomer, 2-polymer).

Principle of the holographic recording of polymer-based nanocomposites and mechanism of the polymerization

- monomer
- nanoparticle

(hv)

Initiator $\rightarrow$ I

I$^\cdot$ + R1 (monomer) $\rightarrow$ I - R1$^\cdot$

I - R1$^\cdot$ + R2 (monomer) $\rightarrow$ I - R1 - R2$^\cdot$

I-R1 - R2$^\cdot$ + I-R1 - R2$^\cdot$ $\rightarrow$ 2I + R1 - R2 - R2 - R1

Distribution of components in nanocomposite a) before and b) during holographic recording.

Change of diffraction efficiency at AuNP addition.

- Curve 1 - without AuNP
- Curve 2 - with AuNP.
Surface grating with and without AuNP.

- With AuNP
- Without AuNP

Surface gating modulation dependence on presence of AuNP in composition
Four beam writing of 2D photonic crystal

- 2D grating on surface of nanocomposite
Conclusion

- Nanocomposite based on UV-curable monomers with gold nanoparticles stabilized by SiO2 nanoparticles is new transparent optical material with high AuNP concentration.
- By mean of light induced nanoparticles redistribution it is possible to writing hologram on this material and to produce photonic with plasmon effect on gold nanoparticles.