

Nanoplasmonic Multifunctionalization of Glycidyl Methacrylate Hydrogel Membranes for Adsorption-based Chemical Sensors with Enhanced Selectivity

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Abstract— Affinity-based devices utilizing plasmonic effects belong to the most sensitive chemical sensors. A membrane having a form which coincides with the distribution of surface electromagnetic waves coupled with collective oscillations of electron gas in the conductive part of the sensor represents an important building block for plasmonics. A way to boost selectivity of a plasmonic sensor is to functionalize such membrane and either to apply it on the sensor surface or even to use it as a stand-alone platform for sensing. In this work we considered a possibility to prepare multifunctional membranes for plasmonic sensing. In our experiments selectivity enhancement was achieved through the use of glycidyl methacrylate whose epoxy group is readily converted to a desired affinity group (e.g. amine, thiol, pyridine, dithiocarbamate) to preferentially capture a targeted species. Further plasmonic functionalization was obtained by forming a thin hydrogel film through copolymerization of glycidyl methacrylate with mono- and multi-functional methacrylates and then incorporating silver nanoparticles within these nanocomposites. These plasmonic nanoparticles were produced either photochemically or by chemical reduction. Different schemes for plasmonic sensor selectivity enhancement using multifunctionalized glycidyl methacrylate membranes are considered.

Index Terms—Nanotechnologies, Plasmonics, Membranes, Glycidyl Methacrylate, Nanoparticles.

I. INTRODUCTION

CHEMICAL and biological sensors are among the most important sensing devices generally [1, 2]. Mutual for them is that one or more analytes arrive to the sensor surface and are brought in contact with it. Thus the sensor parameters are changed, generating a proportional output. The sensor may be completely immersed in fluid, or analyte(s) may form an ultrathin film on its surface, down to monatomic/monomolecular thickness, but in both cases the part influencing the sensor behavior is typically the one immediately near the surface.

A problem with adsorption-based sensors is their

selectivity [2]. The parameter modified by the presence of analyte is "blind" regarding its exact species. In plasmonic sensors it recognizes only its refractive index/relative dielectric permittivity [3]. Thus it is necessary to improve the selectivity of the sensors.

The usual approach to boost sensor selectivity is to utilize some kind of binding agent on its surface that is specific towards a single analyte or a group of analytes [4]. Another obvious way is to utilize membranes to filter the fluid arriving to the sensor surface and to preconcentrate the target analyte [5].

The use of membranes has several advantages. They can be produced separately from the active part of the sensor itself and then simply mechanically placed onto its surface. Although in their basic form they are simple and allow for a relatively limited applicability, membranes can be functionalized through nanocompositing in a variety of ways, including introduction of functional groups that preconcentrate only the targeted species [6]. Another functionalization is the use of plasmonic nanoparticles (e.g. silver or gold), in which case the membrane itself serves as the active part of the sensor. Several of the quoted functionalities may be simultaneously imparted, for instance filtering/separation, pre-concentration and plasmonic activity.

Obviously, functionalization of membranes does not end with the mentioned functions. It can be in principle extended to a variety of other ways. For instance, it can include catalytic particles that facilitate desired reactions within the membrane. Thus a large freedom is ensured for the designers of sensors.

There is a number of methods to perform multifunctionalization of artificial membranes. The most noted approaches to this kind of nanocompositing are lamination (multilayering), inclusion of nanoparticle fillers, patterning, surface activation and surface sculpting [6, 7].

There are not many publications dedicated to the use of functionalized membranes in chemical sensing, in spite of their versatility. The body of literature regarding membranes is vast, and there are many sources dedicated to their use as separators (e.g. [8-12]). It is less so in the case of the use as pre-concentrators [14-16], and the plasmonic functionalization is relatively seldom mentioned [17-18].

One of the materials useful for membranes dedicated to the enhancement of affinity-based chemical sensors is

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glycidyl methacrylate (GMA). The epoxide group present in GMA is readily transformed into various functional groups that include amino, thiol, azole and pyrazole, pyridine and other groups [18]. All of these are useful for affinity enhancement of various analytes. Some prior applications include heavy metals adsorption [19] and enzyme immobilization [20].

In this paper we consider the applicability of GMA-based membranes for affinity-based sensors. We prepared these membranes as hydrogels by photopolymerization of GMA, 2-hydroxyethyl methacrylate (HEMA) and a trifunctional crosslinking agent, trimethylolpropane trimethacrylate (TMPTMA), in a common solvent *N*-methyl-2-pyrrolidone (NMP). HEMA is often used as a co-monomer in hydrogel formulations and its inclusion was expected to promote hydrogel swelling and increase molecular mobility within hydrogel that may facilitate gel functionalization and generation of silver nanoparticles. Silver nanoparticles were formed within these hydrogels by chemical or photochemical means. Chemical means were based on epoxide ring opening by diethylene triamine (DETA) followed by reduction of silver nitrate (AgNO_3) in the presence of amine groups. Photochemical approach was based on simultaneous reduction of AgNO_3 to metallic silver, polymerization and crosslinking of the methacrylate network during UV irradiation. We give some characterization results and outline some possible future directions.

II. EXPERIMENTAL

A. Materials

GMA (reagent grade), TMPTMA, NMP (99 % purity), (3-aminopropyl) trimethoxy-silane (97% purity), DETA (reagent grade) and AgNO_3 were obtained from Sigma-Aldrich. HEMA (96% purity) was obtained from Samchun Chemicals. The photoinitiator (PI) bis(2,4,6-trimethylbenzoyl)-phenyl-phosphineoxide (Irgacure 819) was obtained from Ciba SC as a gift. All chemicals were used as received without further purification. Biaxially-stretched polypropylene (PP) membranes with 115 μm thickness, 85% bulk porosity and 0.8 μm bubble point pore size were obtained from 3M as a gift.

B. Hydrogel preparation

We prepared free-standing hydrogel samples using the following procedure. Monomers (GMA, HEMA and TMPTMA), NMP and PI were mixed in a vial, then dispersed on a small watch glass, put in the enclosure blanketed with nitrogen gas, and exposed to UV irradiation through a glass window on top of the enclosure for 10 minutes. The exposure dose, mainly in the UVA region, was 4.5 J/cm^2 , as measured by YK-35UV light meter. UV exposure initiated polymerization and crosslinking of GMA to create a gel-like structure. After UV curing, polymerized samples weighing around 1g were transferred into 50 mL of distilled water to extract NMP and monomer residuals overnight and form a hydrogel.

Free-standing hydrogel samples were functionalized with DETA by heating them in a solution containing 5g DETA

and 100g distilled water for 8 hours at 80° C under reflux. Functionalized samples were immersed in a 2 wt. % aqueous solution of AgNO_3 in order to generate silver nanoparticles by a chemical reduction method.

We prepared hydrogel membranes with photochemically-generated silver nanoparticles using the following procedure. Monomers (GMA, HEMA and TMPTMA), NMP, PI and AgNO_3 , were mixed in a vial, then spread as droplets between two microscope slides separated by a 100 μm adhesive tape, and exposed to UV irradiation for 10 minutes. The upper microscope slide was removed and the sample was immersed in distilled water for 1 hour to extract NMP and residuals, then covered again with the microscope slide and stored before further analysis.

We prepared a thin hydrogel membrane with photochemically-generated silver nanoparticles using the following procedure. A Si-wafer polished on one side and having a 0.5 μm oxide layer on both sides was cut into 2 x 2 cm squares and dipped for 2 minutes in a 2wt. % solution of (3-aminopropyl) trimethoxysilane in a 95/5 mixture of ethanol and water.

After brief rinsing in pure ethanol, squares were cured 15 minutes at 100°C to complete surface silanization. Monomers (GMA, HEMA and TMPTMA), NMP, PI and AgNO_3 , were mixed in a vial and drop coated on the polished side of the functionalized Si-square, put in the enclosure blanketed with nitrogen gas, and exposed to UV irradiation through a glass window on top of the enclosure for 10 minutes. After UV curing thin hydrogel membranes were immersed in distilled water for 1 hour to extract NMP and residuals, then stored before further analysis.

C. Hydrogel characterization

Conversion of monomers (GMA and TMPTMA) was determined by classical gravimetry. Hydrogel samples made from monomer solutions covering a broad range of compositions were filtered through a polypropylene microfiltration membrane followed by drying for 3 h in an oven at 50°C. The degree of conversion, DC, was calculated from

$$DC = \frac{m_2}{\sum_i m_i^0} \quad (1)$$

where m_2 is the mass of dried polymer and m_i^0 are initial masses of monomers.

We determined volumetric degree of swelling, Q_v , after boiling dried hydrogel samples for 30 min in distilled water and weighing the swollen samples from the following equation

$$Q_v = \frac{1}{\Phi_2} = \frac{1}{1 - \frac{m_1 / \rho_1}{m_1 / \rho_1 + m_2 / \rho_2}} \quad (2)$$

where ϕ_2 is the polymer volume fraction in hydrogel, while m_i and ρ_i represent the mass and the density of water and polymer, respectively. The density of polymer was

considered equal to the average value of GMA and HEMA monomers.

FTIR-ATR analysis was conducted with Thermo Scientific Nicolet 6700 instrument equipped with Smart ATR Diamond accessory.

UV-Vis spectroscopy was performed in a transmission mode using Thermo Scientific Evolution 60 instrument in the range from 380 to 500 nm.

III. RESULTS AND DISCUSSION

A. Response Surface Methodology (RSM)

Before investigating the formation of silver nanoparticles in glycidyl methacrylate hydrogel membranes, we conducted an experiment to select monomer compositions resulting in hydrogels with a sufficient degree of conversion and swelling. The sufficient degree of swelling is necessary to increase the molecular mobility within the gel in order to facilitate gel functionalization and formation of silver nanoparticles. GMA is a relatively hydrophobic monomer, so the inclusion of hydroxyl groups with the co-monomer HEMA was expected to increase gel hydrophilicity and the degree of swelling. A Central Composite Design was set up based on a full RSM design with 3 factors and 6 center points to investigate the effects of monomer concentrations on the degree of conversion and volumetric degree of swelling. The star points in the design (α) were set up at ± 1.68 in order to ensure design rotatability. Monomer concentration expressed in mol/L includes GMA and HEMA. Concentration of the crosslinking agent (TMPTMA) was expressed in mol % based on the monomer concentration. PI concentration was 1% based on the total weight of the monomers and the crosslinking agent.

TABLE I
EXPERIMENTAL SETUP FOR CENTRAL COMPOSITE DESIGN

	$-\alpha$	0	α
Monomer conc. (mol/L)	1	1.5	2
HEMA fraction	0	0.5	1
TMPTMA conc. (mol %)	5	10	15

The results of the designed experiment showed at 0.1 level of significance that the degree of conversion increased with the concentration of monomers and the concentration of the crosslinking agent (TMPTMA), while the degree of swelling increased with the monomer concentration and the HEMA fraction. No second order variables or interactions were statistically significant. The contour plots in Fig. 1 show the effects of monomer concentrations on the degree of conversion and the volumetric degree of swelling. Based on the results of designed experiment we selected a hydrogel formulation having 1.5 mol/L of monomers, HEMA fraction of 0.5, and 15 mol % TMPTMA for further experiments. This formulation exhibited a degree of conversion above 90% and the volumetric degree of swelling above 10%,

which should facilitate gel functionalization and formation of silver nanoparticles. In addition, this formulation contained 0.75 mol/L GMA having the epoxide groups that can be used for chemical functionalization.

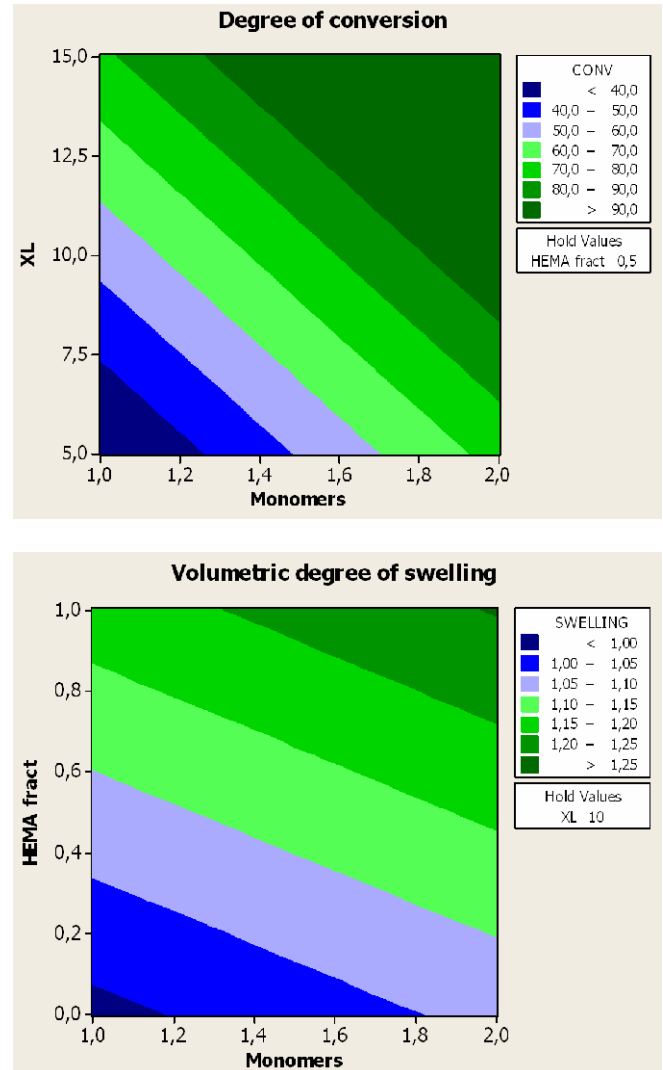


Fig. 1. Contour plots of the degree of conversion (above) and volumetric degree of swelling (below). The x-axis is the concentration of monomers [mol/L], while the y-axes are the TMPTMA concentration (mol %) and HEMA fraction, respectively.

B. Crosslinked GMA hydrogels with chemically-generated silver nanoparticles

Free-standing hydrogel samples were prepared under nitrogen blanketing using the procedure described earlier. The starting formulation contained 1.5 mol/L of monomers (GMA and HEMA), HEMA fraction of 0.5, 15 mol % TMPTMA, and 1% PI in NMP. Free-standing samples were functionalized with DETA and immersed in a 2 wt.% aqueous solution of AgNO_3 . After approximately 10 min immersed samples started to turn yellow indicating the formation of silver nanoparticles. UV-Vis spectra in Fig. 2 show an increase in the absorbance of functionalized hydrogel samples as a function of time with a maximum around 400-410 nm which corresponds to a mean particle size of 15-20 nm. Silver cations diffuse slowly into the

functionalized hydrogel where they are reduced in the presence of amine groups leading to the formation of silver nanoparticles.

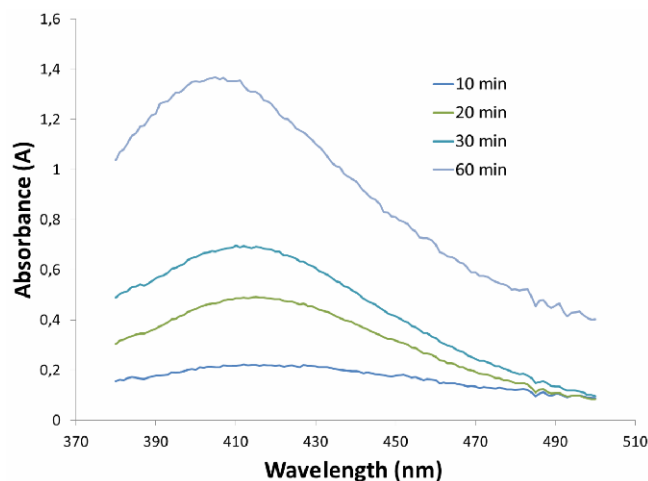


Fig. 2. UV-Vis spectra of functionalized hydrogel samples with chemically-generated silver nanoparticles. The reaction times ranged from 10 to 60 minutes.

C. Crosslinked GMA hydrogel membranes with photochemically-generated silver nanoparticles

We investigated preparation of crosslinked GMA hydrogel membranes with silver nanoparticles generated by photochemical means. The starting formulation contained 1.5 mol/L of monomers (GMA and HEMA), HEMA fraction of 0.5, 15 mol % TMPTMA, and various concentrations of PI and AgNO_3 in NMP. The membranes were prepared by UV irradiation of the starting formulation between microscope slides and following the procedure described earlier. During the UV exposure PI undergoes α -cleavage generating 2,4,6-trimethylbenzoyl and phenylphosphonyl radicals which simultaneously induces the formation of silver nanoparticles through reduction of AgNO_3 and initiates the radical polymerization and crosslinking [21]. Fig. 3 shows UV-Vis spectra of membranes prepared using formulations containing 1 to 3% AgNO_3 and 1 to 3% PI. In all cases a distinct absorption peak around 410-420 nm confirmed the presence of silver nanoparticles within hydrogel membranes. Observed differences in absorption intensity were mostly associated with different thickness of individual membranes which ranged from 15 to 60 μm .

Fig. 4 shows a FTIR-ATR spectrum of a thin hydrogel membrane with photochemically-generated silver nanoparticles prepared by drop coating on the functionalized Si-square. The starting formulation contained 1.5 mol/L of monomers (GMA and HEMA), HEMA fraction of 0.5, 15 mol % TMPTMA, 1% PI and 2% AgNO_3 in NMP. A strong carbonyl peak originating from monomers and the crosslinking agent is visible at 1721 cm^{-1} , while the peak associated with the epoxide group present in GMA can be seen at 906 cm^{-1} . Thickness of the hydrogel membrane measured by profilometry was 7 μm .

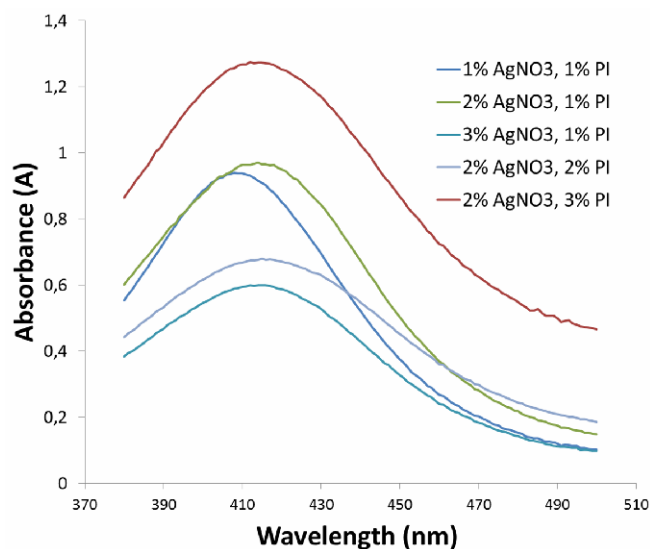


Fig. 3. UV-Vis spectra of crosslinked GMA hydrogel membranes with photochemically-generated silver nanoparticles. The initial concentrations of AgNO_3 and PI ranged from 1 to 3%.

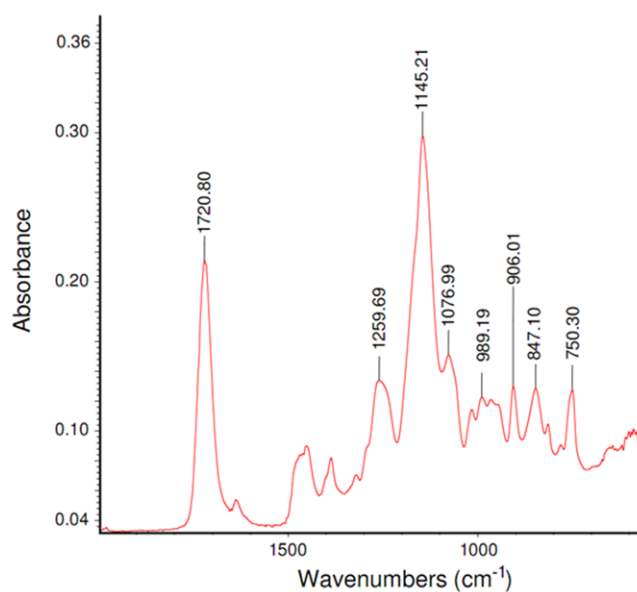


Fig. 4. FTIR-ATR spectrum of a thin hydrogel membrane with photochemically-generated silver nanoparticles. The membrane was deposited onto the polished side of a Si-square functionalized with (3-aminopropyl) trimethoxysilane.

IV. CONCLUSION

We performed multifunctionalization of membranes intended for the use in adsorption-based plasmonic sensors. We used glycidyl methacrylate whose epoxy group is readily converted to amine, thiol, pyridine, dithiocarbamate, etc. groups that can be further used for preconcentration of targeted species. Additional functionalization of our membranes was imparted by incorporating silver nanoparticles within a thin hydrogel film fabricated through copolymerization of glycidyl methacrylate with mono- and multi-functional methacrylates. Besides being applicable in plasmonic sensing, the obtained multifunctionalized membranes have a wider applicability in other types of affinity-based chemical and biological sensors, as well as in different systems like catalytic microreactors and

photoenhanced reaction systems.

In our future research we intend to functionalize GMA toward preconcentration of certain particular analytes, including some environmental pollutants.

ACKNOWLEDGMENT

This work has been partially funded by Serbian Ministry of Education, Science and Technological Development within the framework of the projects TR 32008 and III 43009.

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