

Multifunctionalized Self-supported (Nano) Membranes as Integrated Platform for Plasmonic Metamaterials

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Abstract— We considered the possibility to fabricate multifunctional nanocomposite membranes as a platform for plasmonic metamaterials, simultaneously incorporating pores, built-in functional groups and active nanoparticles. To this purpose we combined lamination and inclusion of nanofillers into the membrane host. For the basic material we chose macroporous crosslinked copolymers based on glycidyl methacrylate (GMA). The epoxy group present in GMA molecule is readily transformed into various functional groups that further serve as affinity enhancers, ensuring the usability of the membranes as pre-concentrators of selected agents in plasmonic sensors. To form GMA-based membranes we used a recently proposed method combining the traditional immersion precipitation with photopolymerization and crosslinking of functional monomers. Further functionalization is obtained by in-situ formation of noble metal nanoparticles directly within the GMA host. In this way membranes with simultaneous plasmonic, adsorbent and catalytic functionality are obtained. We considered the use of the our structures for plasmonic chemical sensors where separator, pre-concentrator and binding agent are integrated with the plasmonic crystal, as well as for plasmonic enhancement of photocatalytic reactions in microreactors. Our approach gives a highly tailorable element compatible with microelectromechanical systems (MEMS) technologies and readily transferable across platforms.

1. INTRODUCTION

Plasmonics is a burgeoning field of electromagnetics that ensures electromagnetic fields confinement and manipulation at nanoscale through the use of metal-dielectric nanostructures [1]. Some of its applications are enhanced light trapping in photodetectors or solar cells, photo-assisted catalysis and ultra-sensitive chemical and/or biological sensors.

In plasmonics an electromagnetic field with a wavevector exceeding that in free space is bound to an interface between materials with positive and with negative relative dielectric permittivity and is evanescent in both directions perpendicular to that interface. The planar distribution of the field maximum coincides with the form of ultrathin membranes. Such overlap makes membranes a platform of interest for plasmonics. Through a proper control of membrane properties one is in principle able to tailor the response of the whole plasmonic system. Among notable examples are freestanding (self-supported) nanomembranes, structures with a thickness below 100 nm and extremely large aspect ratios, often in excess of 1,000,000 [2, 3]. They are electromagnetically symmetrical, proven to support propagation of long-range surface plasmons polaritons [4] and can be used to enhance the design freedom in all of the quoted application fields.

In their basic form membranes are simple and thus allow for a relatively limited applicability, but their fields of use and tailorability can be vastly expanded through nanocompositing [5]. This is not unlike to the case of living organisms, the most complex and sophisticated natural form, where membranes are the most widespread building block, and where the difference between the living and inanimate is achieved through functionalization of very simple lipid bilayer structures [6].

There are a number of methods to perform multifunctionalization of artificial membranes. The most noted nanocompositing approaches are lamination (multilayering), inclusion of nanoparticle fillers, patterning, surface activation and surface sculpting [5, 7].

Membranes are a new building block in plasmonics. Thus publications dealing with this issue are relatively rare, but their number is rapidly increasing. Although multifunctionalization is the key to a successful application of membranes in plasmonics, currently only a small fraction of publications is dedicated to this field [8].

One of the materials convenient for membranes in plasmonics is glycidyl methacrylate (GMA). The epoxide group present in GMA molecules is readily transformed into various functional groups including amino, thiol, azole and pyrazole, pyridine and other groups [9] that further serve as affinity enhancers. Some examples of such functionalizations include heavy metals adsorption [10] and enzyme immobilization [11].

In this paper, we consider the applicability of GMA-based membranes as a platform for plasmonic metamaterials. After outlining our concept of multifunctionalization for plasmonics, we present some experimental results dedicated to simultaneous formation of pores within GMA-based membranes, functionalization of their epoxy groups and introduction of metal nanoparticles. We give some characterization results and outline some possible future directions.

2. CONCEPT

Figure 1 shows the basic concept of our approach. A membrane made of dielectric material (in our case copolymerized GMA) is in contact with the plasmonic part (material with free electron gas, typically noble metal) — Fig. 1(a). Membrane is functionalized to ensure enhanced active area for adsorption (through inclusion of pores), has target-specific binding agents (functional groups that bind to targeted analyte) and possibly nanoparticles of plasmonic material or catalyst. The membrane overlaps with the region of evanescent surface plasmon polariton (SPP) field. Thus conventional dielectric is replaced by a multifunctionalized one.

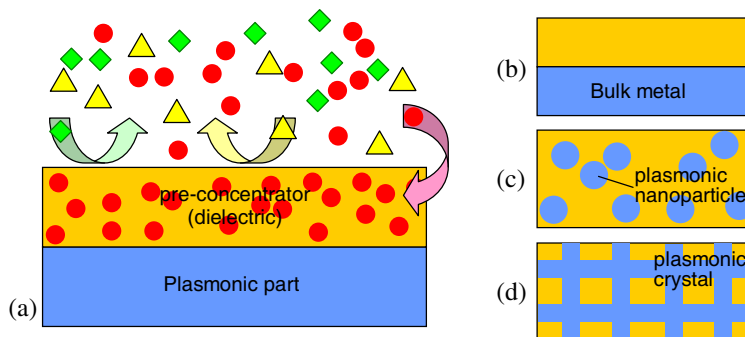


Figure 1: Use of multifunctionalized membrane for enhancement of plasmonic devices. (a) Dielectric membrane as pre-concentrator; (b) application of porous membrane to conventional surface plasmon resonance structure using bulk metal; (c) nanoparticle-based structure; membrane is dielectric host; (d) plasmonic metamaterial case; membrane is the dielectric part of plasmonic crystal.

This approach can be applied to all three main groups of plasmonic devices. The first one is represented by the conventional surface plasmon resonance structure where the plasmonic part is bulk noble metal, usually gold or silver (Fig. 1(b)); the membrane is simply placed or deposited on the metal surface. The second one is a membrane with incorporated plasmonic nanoparticle fillers, which ensures localized plasmon functionality (Fig. 1(c)). Finally, in the most general case, membrane may form a plasmonic metamaterial structure through combination with plasmonic material in an ordered fashion. In these metamaterials the membrane forms the dielectric part of a plasmonic crystal used for dispersion tailoring and having a desired group velocity that may be superluminal (“fast light”), subluminal (“slow light”) or negative (“left-handed light”) [12]. Such a plasmonic crystal may have a simple 1D form where thin sheets of metal and multifunctionalized membrane alternate, 2D form (functional surface) where a pattern of metal structures is defined on a dielectric membrane or even a full 3D structure.

Figure 2(a) shows the function of the multifunctionalized membrane as a pre-concentrator of a targeted agent. The inclusion of functional groups (shown as red “Y” forms at the interior surfaces of the pores) ensures the possibility that the membrane binds a targeted species or a range of species only. The inclusion of pores increases the effective surface for adsorption. Thus a larger quantity of the targeted species is captured within the membrane, exactly in the position of the SPP field maximum. The additional functionalization is done through inclusion of nanoparticles.

Nanoparticles are introduced throughout the membrane volume, and a proportional amount of these nanoparticles will be localized at the interior surfaces of the pores and thus exposed to external species. If these particles are plasmonic, then the freestanding membrane itself is a convenient medium for localized plasmon function. They can also be catalyst nanoparticles

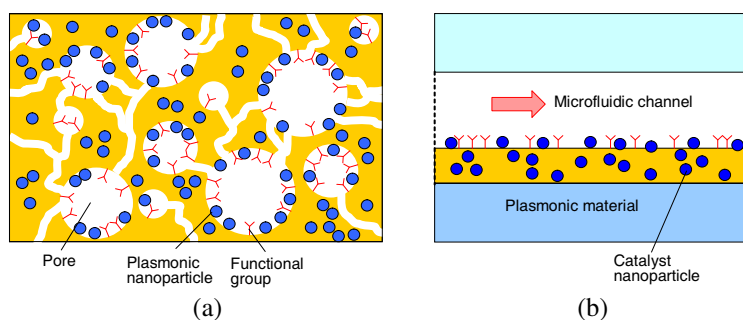


Figure 2: Schematic of membrane multifunctionalization principle (pores, functional groups and embedded nanoparticles). (a) Use as pre-concentrator for a plasmonic sensor; (b) plasmonic enhancement of photocatalytic processes in microfluidic channel of a microreactor.

(Fig. 2(b)), ensuring the applicability in photo-enhanced catalysis. Here the SPP field serves as photo-enhancer, since its intensity can be several orders of magnitude higher than that of a wave propagating in the free space. Such electromagnetic field is obviously evanescent and bound to the surface, but a microfluidic channel shape can be tailored to coincide with the SPP wave. It should be mentioned that instead of pore formation the equivalent functionality can be enabled by the use of the solution-diffusion mechanism in non-porous membranes.

3. EXPERIMENTAL

In order to obtain porosity in GMA-based membranes, we started from polyethersulfone (PES) matrix [13]. GMA was incorporated into PES polymer solution, combined with trimethylolpropane trimethacrylate (TMPTMA) crosslinker. The prepared solutions were cast on a glass plate and placed in an experimental enclosure blanketed with nitrogen gas. Photoinduced copolymerization was done by UV radiation for 10 minutes before the immersion precipitation and final solidification. The exposure dose, mainly in the UVA region, was 4.5 J/cm^2 , measured by YK-35UV radiometer.

Thus processed, the GMA-based membrane develops an asymmetric structure, with smallest pores near the top and gradually spreading to reach the largest dimensions at the bottom of the structure.

In order to obtain targeted functional groups in GMA, the epoxide groups were treated with diethylene triamine under alkaline conditions, thus opening their rings and transforming them into amine functionality. SEM analysis of the structures was performed using a JEOL JSM-6610 L instrument. Fig. 3(a) shows SEM micrographs of the bottom of the GMA-based membrane, while its cross-section is presented in Figs. 3(b)–(d). The asymmetry across the membrane thickness is clearly visible. One can also notice a fine structure of pores beyond the macroscopic level; the GMA-based functionalized membranes retain a “foamy” structure.

Our further experiments dealt with the introduction of silver nanoparticle fillers into GMA-based membranes. We started from a polished Si wafer functionalized with (3-aminopropyl) trimethoxysilane. A thin layer containing GMA, 2-hydroxyethyl methacrylate (HEMA) or polyvinylpyrrolidone (PVP), and trimethylolpropane trimethacrylate (TMPTMA) and 2% AgNO_3 solution in *N*-methyl pyrrolidone (NMP) was deposited over it. UV radiation was used to generate silver nanoparticles and simultaneously perform polymerization forming a GMA-containing hydrogel nanocomposite membrane. The final samples were $7 \mu\text{m}$ thick, as measured by Talystep profilometer.

Figure 4 shows the measured absorbance spectra of glycidyl methacrylate hydrogel with Ag nanoparticle fillers. UV-vis spectra were made by a Thermo Scientific Evolution 60 spectrometer, while FTIR-ATR spectra were recorded by Nicolet 6700 spectrometer equipped with a Smart ATR Diamond accessory. Fig. 4(a) shows spectra with added HEMA (top two curves) or PVP (bottom curve). Absorbance maximum is approximately at 415 nm, which corresponds to a mean diameter of spherical silver nanoparticles of about 30 nm. Fig. 4(b) shows FTIR absorbance spectra of a GMA-HEMA-TMPTMA sample in $(5\text{--}16.6) \mu\text{m}$, i.e., $(2000\text{--}600) \text{ cm}^{-1}$ range. The spectrum shows peaks corresponding to carbonyl groups at 1720 cm^{-1} and the epoxy group at 906 cm^{-1} , which is related with GMA.

The experiments showed that GMA can be readily functionalized by three different properties of interest for plasmonics. Each of them can be separately optimized — i.e., the pore size and distribution can be tailored, epoxy groups can be functionalized toward one or more different

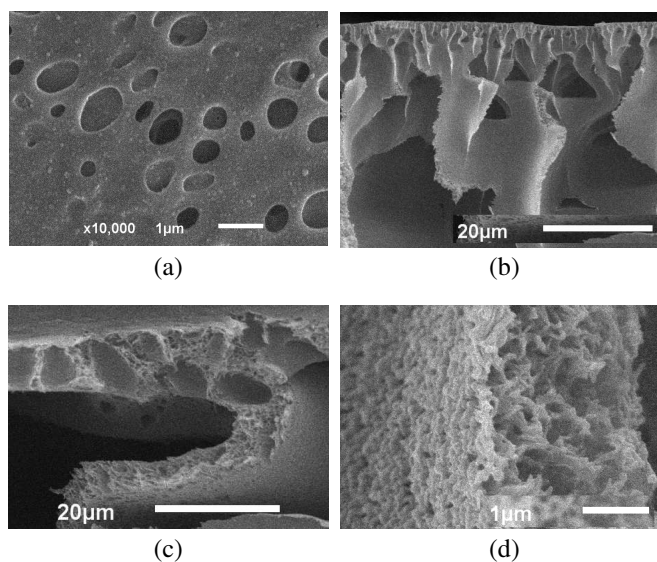


Figure 3: SEM images of precursor asymmetric PES membranes with adsorbent particles of crosslinked glycidyl methacrylate copolymer. (a) Bottom view of the membrane; (b) membrane cross-section near the top; (c) membrane cross-section near the bottom; (d) enlarged cross-section near the bottom.

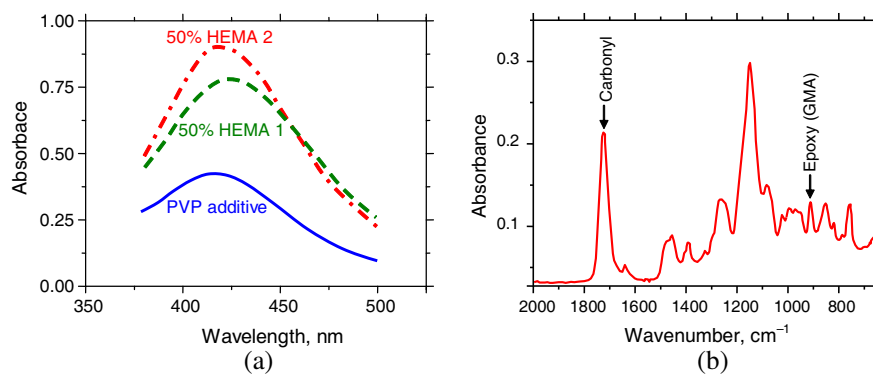


Figure 4: Absorbance spectra of glycidyl methacrylate copolymer hydrogel nanocomposite membrane incorporating silver nanoparticle fillers. (a) UV-vis absorbance; (b) IR absorbance.

analytes, and nanoparticle inclusions themselves can have different functionalities and even several different kinds of nanoparticles can be introduced simultaneously.

4. CONCLUSION

We presented a concept for multifunctionalization of membranes for the use in plasmonic sensors and plasmon-enhanced photocatalysis. The obtained platform can be implemented in the conventional SPR structures, nanoparticle-based devices and metamaterial structures based on plasmonic crystals. In our experiments we simultaneously imparted three different properties of interest to membranes based on glycidyl methacrylate: porosity giving an increase of effective surface for adsorption, target-selective functional groups and incorporated spherical plasmonic nanoparticles (silver with a 30 nm mean diameter). Our further plans include development of different functional groups to serve as pre-concentrators of targeted analytes, which includes oxides of sulfur and nitrogen and heavy metals pollutants. Multifunctionalized membranes are compatible with micro-electromechanical systems (MEMS) technologies and are readily transferable across platforms by simple mechanical means. Details on the technological procedure for membrane multifunctionalization are out of the scope of this conference and will be published elsewhere.

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REFERENCES

1. Barnes, W. L., A. Dereux, and T. W. Ebbesen, “Surface plasmon subwavelength optics,” *Nature*, Vol. 424, No. 6950, 824–830, 2003.
2. Jiang, C., S. Markutsya, Y. Pikus, and V. V. Tsukruk, “Freely suspended nanocomposite membranes as highly sensitive sensors,” *Nature Mater.*, Vol. 3, No. 10, 721–728, 2004.
3. Jakšić, Z., S. M. Vuković, J. Buha, and J. Matovic, “Nanomembrane-based plasmonics,” *J. Nanophotonics*, Vol. 5, 051818.1–20, 2011.
4. Berini, P. “Long-range surface plasmon polaritons,” *Adv. Opt. Photon.*, Vol. 1, 484–588, 2009.
5. Jakšić, Z. and J. Matovic, “Functionalization of artificial freestanding composite nanomembranes,” *Materials*, Vol. 3, 165–200, 2010.
6. Matović, J. and Z. Jakšić, *Bionic (Nano) Membranes; Biomimetics — Materials, Structures and Processes. Examples, Ideas and Case Studies*, P. Gruber, D. Bruckner, C. Hellmich, H.-B. Schmiedmayer, H. Stachelberger, I. C. Gebeshuber, Eds., 9–24, Springer, Berlin, 2011.
7. Jakšić, Z., S. M. Vuković, J. Buha, and J. Matovic, “Nanomembrane-based plasmonics,” *J. Nanophotonics*, Vol. 5, 051818.1–20, 2011.
8. Matović, J. and Z. Jakšić, *Nanomembrane: A New MEMS/NEMS Building Block*, in *Micro Electronic and Mechanical Systems*, K. Takahata, Ed., 61–84, In-Tech, Rijeka, 2010.
9. Kalal, J., F. Švec, and V. Maroušek, “Reactions of epoxide groups of glycidyl methacrylate copolymers,” *J. Polym. Sci. Part C, Polym. Sym.*, Vol. 47, 155–166, 1974.
10. Nastasović, A., Z. Sandić, L. Suručić, D. Maksin, D. Jakovljević, and A. Onjia, “Kinetics of hexavalent chromium sorption on amino-functionalized macroporous glycidyl methacrylate copolymer,” *J. Hazard. Mater.*, Vol. 171, 153–159, 2009.
11. Miletić, N., R. Rohandi, Z. Vuković, A. Nastasović, and K. Loos, “Surface modification of macroporous poly (glycidyl methacrylate-co-ethylene glycol dimethacrylate) resins for improved *Candida antarctica* lipase B immobilization,” *React. Funct. Polymers*, Vol. 69, 68–75, 2009.
12. Milonni, P. W., *Fast Light, Slow Light and Left-handed Light*, Taylor & Francis, Abingdon, Oxford, 2004.
13. Guillen, G. R., Y. Pan, M. Li, and E. M. V. Hoek, “Preparation and characterization of membranes formed by nonsolvent induced phase separation: A review,” *Ind. Eng. Chem. Res.*, Vol. 50, 3798–3817, 2011.

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