Transferable low-attenuation scaffold based on transparent conductive oxide nanoparticles for nanoplasmonics and optical metamaterials

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Abstract

We report on functionalized freestanding membrane-based plasmonic structures transferable to various substrates, including curved and flexible surfaces, biological tissues, etc., but also usable as freestanding, self-supported media. The functionalized membranes consist of a supporting layer with a thickness of the order of tens of nanometers, to which additional layers containing doped transparent conductive oxide nanoparticles were deposited. The supporting layer provides mechanical strength to the structure, while the additionally deposited layers impart plasmonic functionality. Carbon nanotubes were utilized for the reinforcement of the supporting layer. Indium tin oxide and aluminum-doped zinc oxide nanoparticles produced by nonaqueous route were utilized as fillers to impart plasmonic functionality, their losses at near infrared being lower than those of usual plasmonic metals. Dip coating and drop coating were chosen as the deposition methods for the functionalized layers. The obtained plasmonic-dielectric-plasmonic multilayer scaffold is a candidate structure for further tailoring, for instance by forming a 2D array of nanoholes in it.

1. Introduction

Metamaterials for optical frequency range and generally (nano) plasmonics represent a vastly expanding and extremely promising field [1]. Among the most important problems hindering their more widespread application are the complex production technologies necessary to fabricate artificial media with nm-range characteristic dimensions and high absorptive losses connected with the necessity to use highly dissipative materials. Such problems become more severe with increasing operating frequency. An approach to decrease absorptive losses is the application of alternative materials instead of the customary plasmonic metals [2, 3]. Materials with lower attenuation of surface plasmons polaritons (SPP) include doped transparent conductive oxides (TCO), some alloys and inter-metallic, carbon-based materials like graphene, etc. [2].

Concerning the production technologies of metamaterials and nanoplasmonic structures, one of the possible approaches is the application of nanomembranes [4, 5] – freestanding, nm-thick structures with giant aspect ratio. They represent a medium with full electromagnetic symmetry, useful for e.g. long-range SPP applications. At the same time, nanomembranes are transferable to various substrates, ensuring possible combination of otherwise technologically incompatible materials. The substrates may be curved, stretchable or foldable and can even include biological tissues. Also useful is the pos-

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sibility to stack multilayer of different nanomembranes on top of each other in order to fabricate more complex photonic and plasmonic structures [6], thus ensuring an additional degree of design freedom. It is also possible to dynamically tune nanomembrane guides by stretching and folding. Planar metamaterial structures based on nanomembranes were reported in [7].

A combination of two alternative approaches, that of nanomembrane-based nano/meta photonics and low-loss alternative materials may furnish tailorability necessary to use advantages of the both concepts. The main challenges in this direction are technological ones: nanomembranes can be processed either while still attached to sacrificial substrate, in which case releasing procedure (etching) may destroy sensitive functionalization together with the sacrificial substrate; or they can be processed as freestanding structures, in which case many thin film deposition methods are not applicable for functionalization since they are too energetic for the delicate nm-thin freestanding structures.

We present here our work on the fabrication of nanomembrane-based scaffolds for nanoplasmonic and metamaterial applications, functionalized by doped TCO nanoparticles. A nonaqueous method for nanoparticle fabrication was applied, while the nanoparticle suspension was deposited by either drop coating or dip coating. Both methods are "gentle" enough not to damage the delicate membranes.

2. Approach

Transparent conductive oxides represent Drude-type plasmonic materials having lower losses compared to those of good plasmonic materials in the same frequency range. The TCO plasma frequency is in the near-infrared, and can be shifted by changing the doping level [8]. We chose two TCO materials, aluminum-doped indium oxide (ATO) and zinc oxide doped with aluminum (AZO). Both materials were prepared from nonaqueous sol-gels, where organic solvents were simultaneously used as reacting substances and stabilizing agents. Fig. 1 shows a schematic presentation of a nanomembrane structure functionalized by TCO.

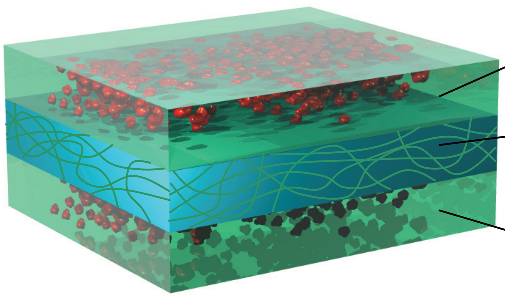

Fig. 1: Schematic presentation of the cross-section of the nanomembrane structure functionalized from both sides with layers containing TCO nanoparticles. Some of the supporting layers were reinforced by carbon nanotubes.

3. Results and discussion

We worked with two distinct types of freestanding substrates. One of them were chromium-containing, metal-composite nanomembranes [9] with a thickness 8-20 nm and with lateral dimensions 2-3 mm. Another kind of substrates included 50 nm-thick nanomembranes from woven carbon nanotube (CNT) sheets (CNT transparent sheets or "webs") [10].

The nanomembranes were functionalized with TCO nanoparticles using drop and dip coating techniques. The basic manufacturing steps are presented in Fig. 2a. The deposition of TCO was done using a capillary syringe to ensure accurate control the amount of the dropped nanoparticle suspension. After the deposition, the mixture is left to settle, allowing nanoparticles to self-assemble on the substrate, Fig. 2a bottom. Finally the liquid completely evaporates, leaving only binder material. By controlling the nanoparticle concentration in the suspension, one is able to tailor the thickness of the final thin film. Fig. 2b shows the dip coating method. Measured infrared spectral reflection of the formed mesoporous nanoparticulate films are shown in Fig. 2c, together with an SEM image of an AZO film.

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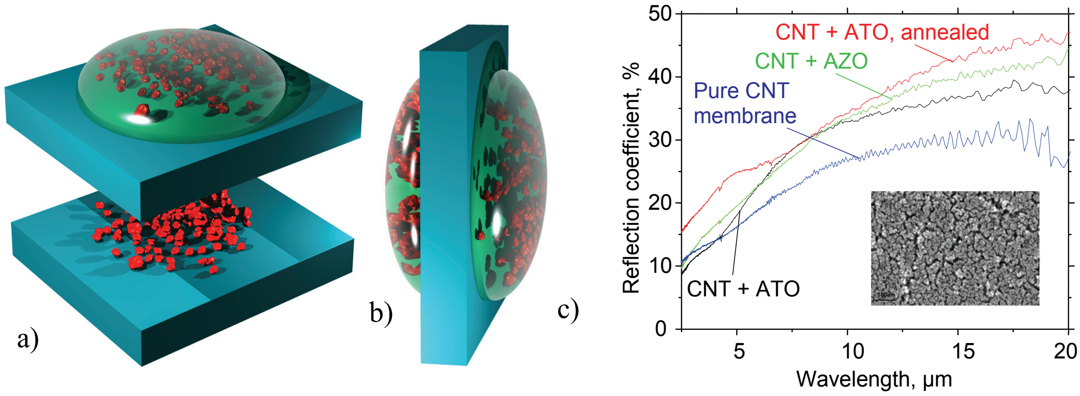

Fig. 2: a) Deposition of TCO nanoparticles from drop-coated nonaqueous suspension; b) dip-coated nanomembrane; c) infrared reflection of pure CNT membranes and those functionalized by Al-doped SnO2 (ATO) non-annealed and annealed at 400^0C and by AZO: inset: SEM image of AZO nanoparticle film

4. Conclusion

We applied Al-doped tin oxide and zinc oxide nanoparticles to form functionalizing layers on both sides of freestanding CNT-containing nanomembranes. Such a plasmonic scaffold has lower SPP attenuation at near-infrared, is highly tailorable, and can be transferred to a very wide range of different substrates. Albeit nm-thin, the structures are very robust and enable simple handling.

Acknowledgments

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