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Free-Standing Large-Area Nanoperforated Gold Membranes Fabricated by Hopping Electrodeposition

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A room-temperature two-step cost-effective electrochemical technology is proposed for the preparation of free-standing Au nanomembranes. A thin Au film with the thickness less than 100 nm was deposited by pulsed electroplating on a GaAs substrate in the first step, while electrochemical etching was applied in the second technological step to introduce porosity into the GaAs substrate underneath the Au film. It has been shown that detachment of the film from the substrate occurs at optimized parameters of anodic etching. Scanning electron microscopy imaging of the deposited Au film revealed its nanoparticulate structure generated via the mechanism of hopping electrodeposition, i.e. the film proved to consist of a monolayer of Au nanoparticles with the mean diameter around 20–30 nm. It was found that nanoholes with the diameter controlled by the duration of negative voltage pulses can be introduced into the Au film during electroplating. The purity of the detached Au nanomembranes was demonstrated by the energy dispersive X-ray analysis. The flexibility, nanoparticulate structure along with possibilities to transfer the prepared nanomembranes to various substrates make them promising for new optical, plasmonic and electronic applications.
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Membrane technologies have been widely used for gas separation processes, for example, for the hydrogen separation from hydrotreaters in refineries, oxygen/nitrogen separation, and separation of CO_2 from natural gas.[1] Particularly, composite polymer membranes became used in large-scale industrial gas separation technologies. The purification of hydrogen via selective permeation through a membrane has been considered to be one of the most promising approaches for the production of high-purity hydrogen, as compared to energy intensive pressure swing adsorption and cryogenic distillation processes.[2] Apart from polymeric membranes, inorganic zeolite, rare earth oxide, pure-metal and metal-alloy membranes have been reported to produce rather pure hydrogen from CO_2-rich stream.[2] Among metallic membranes, palladium membranes have been exploited for both hydrogen production and hydrogen purification.[3–5] A number of polymeric, inorganic and ceramic materials was also used to form membranes applied to water and wastewater treatment.[6] In spite of the fact that inorganic membranes are more expensive than organic polymeric ones, they offer some advantages such as temperature stability, resistance towards solvents, narrow pore size distribution, and the opportunity for more sterilization options.[7]

Inorganic membranes have been prepared from materials such as metals (e.g., Pd, Ag, and their alloys, and steel), carbon, silica, zeolite, and various oxides (e.g., Al_2O_3, TiO_2, ZrO_2), nitrides, carbides and similar materials, many of which are semiconducting.[8] Metal membranes are usually prepared by three methods: chemical vapor deposition, physical sputtering or electroless plating, among which the last one is the most versatile. Porous metal membranes have recently received increasing attention, and significant progress has been achieved in their preparation and characterization, which resulted in their applications in a number of key industries including wastewater treatment, dairy processing, wineries, and biofuel purification.[9] In particular, the application of porous metal filters and membranes with special wettability (superhydrophobic–superoleophilic) for oil–water separation has been reviewed recently.[10]

Apart from these traditional applications, metallic nanomembranes, especially those of noble metals, significantly expanded their areas of applications over the last decade due to their specific catalytic and plasmonic properties. The occurrence of long-range surface plasmons was disclosed as a phenomenon inherent to metal nanomembranes.[11] Plasmonic nanomembranes self-assembled from metallic nanocrystals with highly ordered nanoscopic structures allowed one to control their programmable multifunctionality by adjusting the morphology, composition and size of constituent nanoparticles, as well as by engineering packing order of lattice structures, which proved to be of great practical significance for bottom-up built plasmonic devices and circuits.[12] Note that the optoelectronic and nanoelectronic applications are also boosted by the dimensional confinement and quantum effects inherent to nanostructures. Particularly, self-supported nanomembranes exhibit electrical and thermal conductivities which are fundamentally different from their bulk counterparts.

Among noble metals, gold outperforms both palladium and platinum as catalysts for many applications.[13,14] Gold is also advantageous from the point of view of its plasmonic properties, since the resonance wavelength of nanostructured gold lies in the red and near-infrared spectral range,[11,15–17] which is important for optical and fiber-optic applications. A new electron transport regime was found in a gold-nanoparticle-based suspended nanomembrane due to the plasmon-assisted electron transport at the nanoscale, which opened possibilities for future combinations of plasmonics and nanoelectronics.[15] Even greater potential for the next generation of plasmonic sensors, color filters and planar nano-lenses has been provided by nanoperforation of gold nanomembranes.[16] Large-area free-standing 100 nm thick gold nanomembranes perforated with nanohole arrays have been recently prepared using a template transfer technique with a replication-releasing procedure.[17] An extremely narrow plasmonic resonance with a record figure-of-merit of 240 was found to occur in such nanomembranes, which made them usable as high-performance plasmonic refractometric sensors.

Nowadays, different fabrication techniques at the nanoscale are elaborated to obtain artificial nanoporous membranes. It is worth to mention focused ion beam (FIB) milling as one of the most accurate and high-precision techniques.[18–20]

Over the last two decades, it has been demonstrated that electrochemistry is one of the most accessible and cost-effective approaches for nanostructuring semiconductor materials in a controlled fashion. Combining two methods, namely electrochemical etching and electrochemical deposition, one-dimensional nanostructures such as nanowires, nanotubes and their networks have been successfully fabricated.[21–24] Besides, electrochemistry proved to be an indirect tool for the characterization of semiconductor materials. The non-uniformity of

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