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Etchant-based design of gold tip apexes for plasmon-enhanced Raman spectromicroscopy

Sergey Kharintsev [a,b,*], Alexander Alekseev [c,d], Joachim Loos [e]

[a] Department of Optics and Nanophotonics, Institute of Physics, Kazan Federal University, Kremlevskaya, 16, Kazan 420008, Russia
[b] Tatarstan Academy of Sciences, Baumana str., 20, Kazan 420111, Russia
[c] National Laboratory Astana, Nazarbayev University, Kabanbay batyr ave., 53, Astana 01000, Kazakhstan
[d] STC NMST, Moscow Institute for Electronic Technology, Moscow, Russia
[e] DSM Resolve, 6167 RD Geleen, The Netherlands

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ABSTRACT

In this paper, we gain insight into the design and optimization of plasmonic (metallic) tips prepared with dc-pulsed voltage electrochemical etching gold wires, provided that, a duty cycle is self-tuned. Physically, it means that etching electrolyte attacks the gold wire equally for all pulse lengths, regardless of its surface shape. Etchant effect on the reproducibility of a curvature radius of the tip apex is demonstrated. It means that the gold conical tips can be designed chemically with a choice of proper etchant electrolyte. It is suggested to use a microtomed binary polymer blend consisting of polyamide and low density polyethylene, as a calibration grating, for optimizing and standardizing tip-enhanced Raman scattering performance.

1. Introduction

Optical spectroscopy based on tip-enhanced Raman scattering (TERS) has paved a new way to visualize and chemically characterize single molecules, quantum dots, thin films and other nano-patterned materials with nanometer spatial resolution [1–3]. Initially, it has become possible due to combination of Raman spectroscopy and scanning probe microscopy [4–6] – an emerging nanoscale chemical mapping method. Here, a major challenge is to couple laser light and a tip apex of an AFM cantilever or an optical antenna, in which highly localized surface plasmons (LSP) are excited. For this purpose, the optical antenna material should necessarily be plasmonic. The highest enhancement factors have been achieved with bulk plasmonic materials (gold and silver in the visible region) [7]. Therefore, the design of optical antennas and optimization of their parameters such as curvature radius, aspect ratio etc., play a crucial role in enhanced optical spectromicroscopy. Accessing to non-propagating (confined) optical fields, the antenna empowers us to go beyond the Abbe's diffraction limit and capture diffraction-free optical images of a sample under study. Being within the mainstream, the optical antennas are widely used as plasmonic biosensors [8], waveguides [9] and meta-material constituents [10].

Basically, the bulk metallic antennas are fabricated with electrochemical etching [1,11–13] and focused ion beam milling [14]. With the methods, considerable progress has been achieved for shaping mesoscopic surfaces of the optical antennas [15], whereas the reproducibility and reliability of well-defined tip apexes remain ambiguous [16]. In this context, under design of the optical antennas, the morphology of their mesoscopic surface is commonly understood; in particular, one deals with nanoparticles, nanorods, conical tips, self-similar antennas, bow-tie gap antennas, tip-on-aperture antennas and others [17–23]. Creation of the tip apex acting as a hot spot for effectively coupling/decoupling optical near- and far-fields is a task of high priority. One should distinguish the reproducibility of an antenna's mesoscopic structure from that of its tip apex and, therefore, we can introduce a concept for *controlled design* of the tip apexes, in our case, by tuning their curvature radii. It means that the reproducibility of the tip apex with the given parameters plays a more important role compared to fabricating apical tips with curvature radii as small as possible. Imperfect geometry

* Corresponding author at: Department of Optics and Nanophotonics, Institute of Physics, Kazan Federal University, Kremlevskaya, 16, Kazan 420008, Russia.
E-mail address: skharint@gmail.com (S. Kharintsev).

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of the tip apex and its orientation in respect to incident irradiation may impede LSP excitation in metallic nanostructures. Therefore, tip-enhanced Raman scattering with bulk plasmonic gold or silver probes is still a delicate tool for probing nano-sized materials. Frankly speaking, the application of the TERS tool is not widespread, especially in biology and surface chemistry, since a number of suitable materials, which might be probed, is rather limited. On the other hand, this nano-spectroscopic instrument is not routinely utilized in practice by virtue of low reproducibility of plasmonic antennas. Nowadays, there are no testing instruments to standardize TERS performance. For this purpose, carbon-containing materials such as carbon nanotubes, graphene and others are basically used [24,25].

In this paper, we demonstrate the etchant effect on the reproducibility of a curvature radius of the gold tip apex with a dc-pulsed voltage electrochemical etching method in which a duty cycle is self-controlled. For this purpose, we have developed an advanced dc/ac voltage controller equipped with a three-electrode electrochemical cell. Bent gold tips are attached to tuning fork sensors for performing top-illumination TERS measurements in tapping mode under normal conditions. This approach allows us to give a new interpretation for design of optical antennas and optimization of their parameters. A figure-of-merit of the electrochemical fabrication is introduced to evaluate its efficiency. To facilitate TERS measurements in practice we have developed a calibration grating based on a microtomed binary polymer blend consisting of polyamide and low density polyethylene.

2. Experimental setup

Dc, dc-pulsed, ac voltage electrochemical etching is commonly used as a low-cost, simple and reliable nanofabrication tool for designing plasmonic optical conical tips with a high yield of >90% [9,18]. A drawback of this method is a lot of parameters such as the chemical nature of etching electrolyte, electrode arrangement, applied voltage shape and cutoff current, which should be necessarily optimized. Fig. 1(a) shows a schematic circuit of an electrochemical arrangement developed for dc, dc-pulsed and ac voltage etching gold wires. The home-built voltage controller is equipped with a three-electrode cell with an internal bottom-free glass beaker, as shown in Fig. 1(b). Unlike the setup developed in [26], the three-electrode arrangement is favored to meet all electrochemical cell designs equally. The developed potentiostat allows us to automatically monitor the etching current with a time resolution of ~10 μs. A heart of this setup is a microcontroller STM32F417VG that supplies a voltage to a working electrode (WE), that is a 100 μm gold wire (purity: 99.99%, GoodFellow, UK), and monitors a current cutoff event. A gold counter ring 2 mm thick electrode (CE) with a diameter of 15 mm is entirely submerged by a depth of 10 mm into etchant electrolyte (Fig. 1(b)). The volume of the etchant is 160 ml and is maintained at a room temperature of 22 °C.

In order to take a true voltage value applied to the WE one introduces a the Ag/AgCl (~0.22 V) reference electrode (RE). A nanomanipulator NM3D (DTI, USA) positions the WE symmetrically into the beaker by a magnitude of 1.5 mm in depth with a precision of 125 nm and lifts up the gold tip as the drop-off event comes into reality. Data exchange between a computer (PC) and remote facilities is performed with using a TCP/IP protocol. As etching electrolyte, we used well-established a triple mixture of HCl/Isopropanol/Water with different volume proportions [16]. Such a composition allows us to easily handle a meniscus shape, which is formed around the gold wire, due to a strong difference in surface tensions of their constituents. Instead of isopropanol, used as a buffer constituent, other alcohols such as ethanol or butanol can be exploited equally [16].

The anodic dissolution of the gold wire in highly acidic solution includes oxidation, complexation and diffusion [11–13]. A corrosion mechanism for gold comes into play at voltages of ~1.5 V and ~1.68 V which launch the following reactions: $Au \leftrightarrow Au^{3+} + 3e^-$ and $Au \leftrightarrow Au^{+} + e^-$, respectively [11,12]. Oxidizing agents Cl^- are supplied into the etchant due to the complete dissociation of HCl in the aqueous environment. Chlorides Cl^- attack the gold surface and ultimately chloroaurate complexes $AuCl_{4-x}[OH]_x^-$ form. This passivation results in the formation of a double electric layer which blocks an access for Cl^- anions to the gold wire surface. Etching at the meniscus takes place due to a disturbed balance of surface tension and gravity close to its vicinity. Concentration gradients of Cl^- ions results in their migrating through the formation of vortexes towards the interface to decrease the surface free Gibbs energy [28]. Thinning of the gold wire at the meniscus is produced due to complexation, since this process prevents the reassembly of oxidized gold atoms back into the bulk metal. On the other hand, gold corrosion products slow down the electrochemical etching because of depletion of chloride anions near the gold surface. Diffusion of chloroaurate complexes close to the meniscus plays a crucial role in shaping the tip morphology and dramatically influences on its apex because of strong fluctuations of etching current at a final stage [28].

3. Etchant effect on the reproducibility of curvature radius

A more simple and popular method for fabricating gold tips is dc electrochemical etching, which has been widely used over the last decades. As was shown by many research groups [11–13] the reproducibility of the size and the shape of the tip apexes produced with wet chemistry leaves much to be desired. Nevertheless, this can be considerably improved, for example, with the help of varying an applied voltage, moving a gold wire or adding an organic buffer layer onto etchant surface [28]. In all cases, underlying physical mechanism is related to the meniscus shape and its motion. Alternatively, the chemical nature of the etchant provides the same effect but it requires optimization for its surface tension $\sigma(E)$ as a function of applied potential E. As was reported in Ref. [16], water affects strongly the meniscus shape due to higher surface tension of ~72 N/m at room temperature, it leads to concave-like conical tips. Adding water into the etchant leads to an extra height-of-rise of its meniscus under applied voltage. In our experiment,

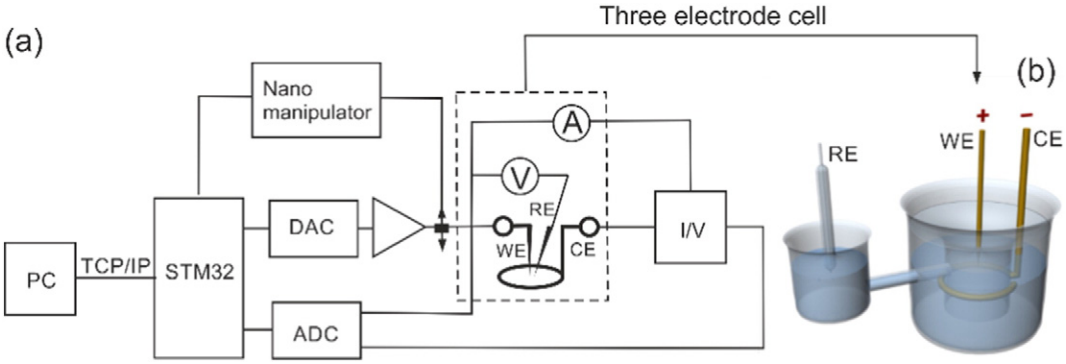

Fig. 1. Schematic circuit of an electrochemical arrangement (a), a three electrode electrochemical cell (b).