

Highly rough tapered gold and silver tips for polarization-controlled TERS performance

V E Vasilchenko¹, S S Kharintsev¹ and M Kh Salakhov^{1,2}

¹ Department of Optics and Nanophotonics, Institute of Physics, Kazan Federal University, 420008, Kremlevskaya St, 16, Kazan, Russian Federation

² Tatarstan Academy of Sciences, 420111, Bauman St, 20, Kazan, Russian Federation

E-mail: valeriya.vasilchenko@kpfu.ru

Abstract. This paper describes an electrochemical method for producing rough silver and gold taper tips for polarization-controlled TERS performance. This method allows to explore the directional intrinsic properties of the sample due to different dipole moment orientations at the tip apex. We give recommendations for fabricating rough silver and gold tips.

1. Introduction

Investigation of optical antennas [1,2] properties and parameters resulted in considerable advances of tip-enhanced Raman scattering (TERS) [3-7]. TERS tool utilizes a metallic tip (antenna) that is coupled to the incident light. Due to the resonant excitation of the localized surface plasmon polaritons (LSPPs) at the tip apex, a strongly enhanced and confined light field is created near the tip apex, which provides extremely high spatial resolution in TERS measurements. TERS provides the yield of the spectroscopic information of single objects and structures at nanometer scale and with high detection sensitivity. Tip geometry and material are two of the most important aspects in fabricating tips to generate localized field enhancements. For plasmonic implementations, in particular TERS, silver and gold are the most popular materials. Silver tips have a higher enhancement than gold tips in the visible range, because the imaginary part of its permittivity is much smaller than that of other metals in the visible range [8] and, thus, the damping of the plasmon polaritons is smaller. Unfortunately, the silver probes have such disadvantage as a fast oxidation. One observed that the enhancement of the Ag tips decreased over half a day [9]. The authors relate this decreasing to oxidation.

A new method of polarization-controlled TERS is a powerful tool to investigate directional properties of samples [10]. For performing polarization-controlling TERS one needs tips with nanoparticles with different directions of dipole moments. Polarization-controlled TERS can give information about molecular orientation of molecules at the nanoscale. For example, the tip dipole generates substantially polarization in its oscillation direction, so the SWNTs oriented in the direction of a dipole oscillation were strongly excited [10]. Shapes of random nanoparticles at the tip apex which cause dipole orientation cannot be controlled by existing techniques, but the authors of Ref. 10 offered to measure the direction of the dipole moment of given tip before TERS experiments. This knowledge can provide more information about specimen, because different directions of dipole oscillations can enhance different modes of oscillations of molecular structures. In their study the authors utilized atomic force microscopy (AFM) tips covered by silver. The influence of the dielectric under silver can reduce the optical performance of the coated AFM probes [11] so the solid tips are preferable.

We presented the electrochemical method for preparing tips with rough surface because such structures can help to visualize the samples more precisely. We made solid tapered tips from gold and silver, the most popular materials for plasmonic implementations.

2. Results and discussion



For preparing silver and gold tapered tips we used the electrochemical method [12]. In both cases of gold and silver, a wire was positioned in the center of a gold ring counter electrode of 10 mm in diameter made from 2 mm gold wire. A glass beaker utilized in our etching setup was similar to the previous studies [13]. The etching was carried out at the room temperature and the volume of an etchant in the beaker of 160 ml.

A 250 μm Ag wire had been used for preparing silver tips. At our early experiments perchloric acid HClO_4 with ethanol had been used as an etchant, but prepared tips were very blunt with apex radii ~ 5 microns. After few attempts we decided to use nitric acid. The etching solution consisted of HNO_3 and distilled water in proportion of 1:1. It is known that nitric acid wet etches Ag as follows:



applied voltage accelerates this reaction [11]. The wire was dipped into the solution for the magnitude of 1.5 mm. For precision positioning and pulling out prepared tips we used a nanomanipulator NM3D (DTI, USA). Tips were etched at a dc voltage of 1.5 V, the voltage was supplied with a commercial potentiostat μ -Autolab III (Autolab, The Netherlands). Etching time was in the range of 100-110 seconds. When the etching process comes to an end and the lower part of the wire dropped off, the prepared tip was retrieved from the solution. After that the probes was rinsed with distilled water and explored firstly by optical microscopy and scanning electron microscopy (SEM). SEM images of the three of prepared tips is shown in figure 1. Rough surface structure took place. In the inset we can see a tip apex. The tip is covered by nanoparticles, we suppose that the tips with similar structure can help to yield more information about directional properties of specimen, because of different dipole moment of the nanoparticles on its apex.

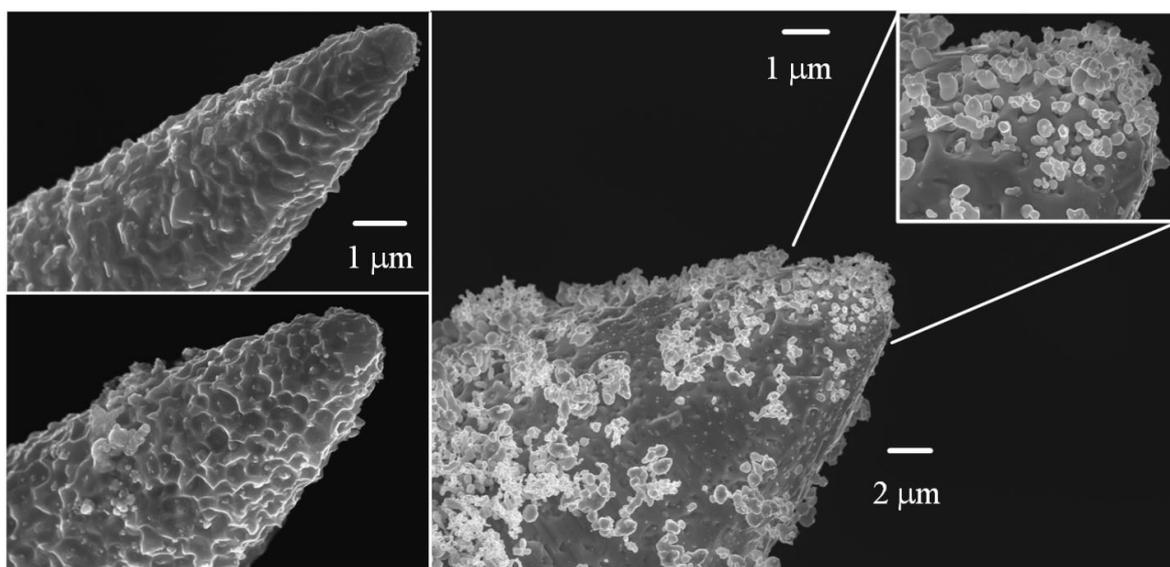


Figure 1. SEM image of prepared silver tips.

Gold tips were fabricated from 100 μm wire. The set up is similar to the one for fabrication of silver tips. We chose a hydrochloric acid with ethanol and water as etchant solution. Gold dissolution in hydrochloric acid is a well known process [13,14]. The fastest etching reaction is going in the liquid/solid interface i.e. in the meniscus on the wire. The gold etching occurs due to the following reaction:



The complexation occurs due to the reaction between chloride ions with gold 3+ ions. The solution was prepared in following proportions: HCl - 55%, ethanol - 25% and water - 20%. This proportion was chosen experimentally. Ethanol and water were used as solvents. Gold etching drives faster at the meniscus area because of migration of Cl^- ions from solution to the interface. This effect is caused by changing pH balance near the surface [13].

In our study tips were etched with a voltage of 1.7 V, that was taken from the voltamperogramm (figure 2).

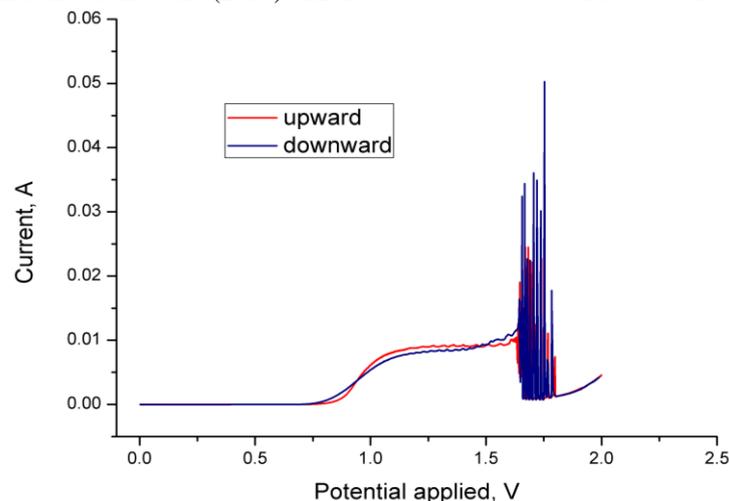


Figure 2. Cyclic voltamperometry of electrochemical cell with gold electrodes and etching solution (HCl - 55%, ethanol - 25% and water - 20%).

Figure 2 shows the voltamperogram of gold etching in the electrolyte. In the previous studies [15] we chose a potential from the range of 1-1.5 V to reduce bubbling and to obtain smooth and sharp tips. A current abruptly drops when a potential exceeds 1.7 V because of blocking an access of Cl^- ions to the wire, as shown in figure 2. An etching time is about 40-50 seconds. The wire was dipped into the solution by a magnitude of 1.5 mm. The shapes of prepared gold tips were explored by transmitting electron microscopy (TEM). As follows from the figure all the tips etched with the above mentioned method are rough.

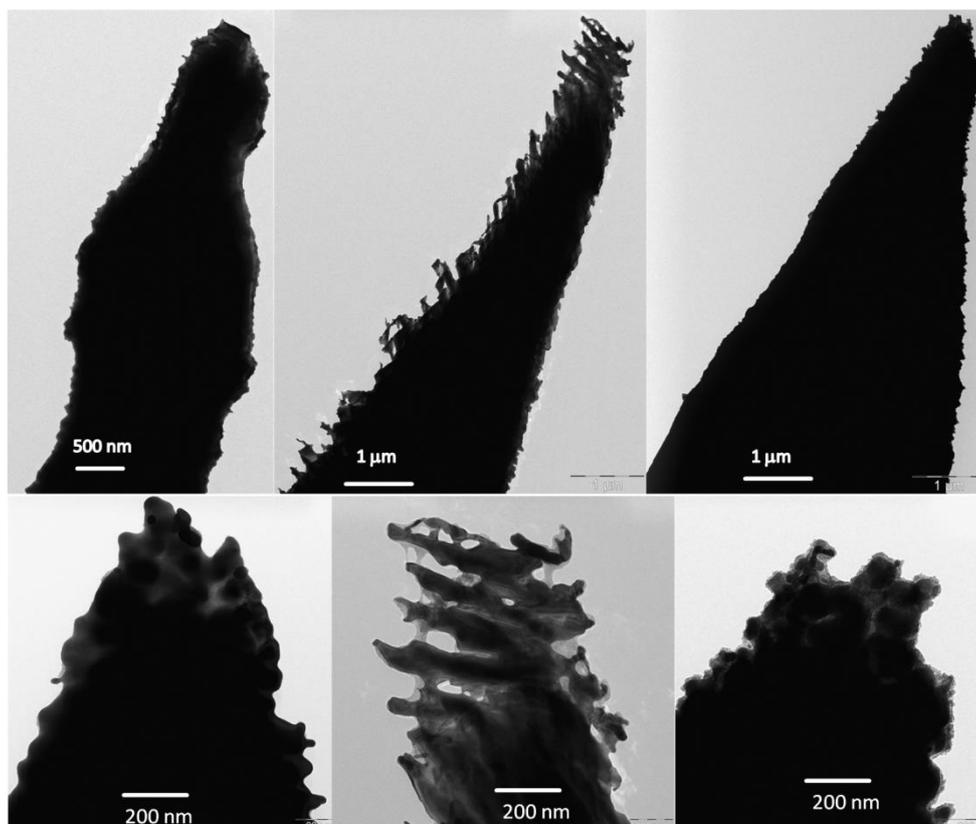


Figure 3. Prepared gold tips and their apices.

3. Concluding remarks

In this paper we have presented methods which allow one to prepare highly rough silver and gold tips for polarization-controlled TERS. For producing rough silver tips the nitric acid/water etchant should be utilized. Appropriate voltage regime of 1.5 V dc voltage was empirically found. For gold tips with high

surface roughness we used hydrochloric acid/ethanol/water etchant and 1.7 V dc voltage. Prepared tips were explored by scanning and transmitting electron microscopy.

References

- [1] Bharadwaj P, Deutsch B and Novotny L 2009 *Advances in Optics and Photonics* **1** 438
- [2] Novotny L and Hecht B 2006 *Principles of Nano-optics* (Cambridge: Cambridge University Press)
- [3] Kneipp K, Moskovits M and Kneipp H 2006 *Topics Applied Physics* **103** 217
- [4] De Angelis F, Das G, Candeloro P, Patrini M, Galli M, Bek A, Lazzarino M, Maksymov I, Liberale C, Andreani L C and Di Fabrizio E 2010 *Nature Nanotechnology* **5** 67
- [5] Mauser N and Hartschuh A 2014 *Chem. Soc. Rev.* **43** 1248
- [6] Yang Y, Li Z, Nogami M, Tanemurad M and Huang Zh 2014 *RSC Advances* **4** 4718
- [7] Kharintsev S S, Hoffmann G G, Fishman A I and Salakhov M Kh 2013 *Journal of Physics D: Applied Physics* **46** 145501
- [8] Johnson P B and Christy R W 1972 *Phys. Rev B* **6** 4370
- [9] Zhang W, Yeo B S Schmid and T Zenobi R 2007 *The Journal of Physical Chemistry C* **111** 1733-1738
- [10] Mino T, Saito Y and Verma P 2014 *ACS Nano* **8** 10 10187
- [11] Lloyd J S, Williams A Rickman R H, McCowen A and Dunstan P R 2011 *Applied Physics Letters* **99** 14 143108
- [12] Ren B, Picardi B and Pettinger B 2004 *Rev. Sci. Instrum.* **75** 837
- [13] Kharintsev S S, Noskov A I, Hoffmann G G and Loos J 2011 *Nanotechnology* **22** 025202
- [14] Busev A I and Ivanov V M 1973 *Analytical Chemistry of Gold* (Moscow: Nauka)
- [15] Kharintsev S S, Rogov A M and Kazarian S G 2013 *Rev. Sci. Instrum.* **84** 093106