DC-pulsed voltage electrochemical method based on duty cycle self-control for producing TERS gold tips

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Abstract. This paper presents a modified dc-pulsed low voltage electrochemical method in which a duty cycle is self tuned while etching. A higher yield of gold tips suitable for performing tip-enhanced Raman scattering (TERS) measurements is demonstrated. The improvement is caused by the self-control of the etching rate along the full surface of the tip. A capability of the gold tips to enhance a Raman signal is exemplified by TERS spectroscopy of single walled carbon nanotubes bundle, sulfur and vanadium oxide.

1. Introduction
Over the last decade, optical microscopy and spectroscopy have reached the nanoscale through techniques that use optical antennas [1, 2]. Extra information on properties of materials at the nanoscale is obtained by combining scanning probe microscopy and optical spectroscopy. In the case of Raman scattering this approach is often referred to as tip-enhanced Raman spectroscopy (TERS) [3]. In the TERS method a sharp metal tip is illuminated with a laser light in such a way to excite localized surface plasmon waves at the tip apex that concentrate the light energy within of several nanometers. This enables to probe a specimen under study with high spatial resolution, extremely less than the Abbe's diffraction limit, and a giant sensitivity up to several molecules [4]. In general, a tip squeezes the electromagnetic field within a subwavelength volume due to both the lightning rod effect and the plasmonic effect [2]. Based on the latter TERS is a powerful tool for non-destructive chemical analysis of nanometer-sized structures with the spatial resolution of several nanometers [3, 5, 6] and single molecule sensitivity [4] under normal conditions. There is a number of geometrical parameters to be necessarily optimized, namely: curvature radius and cone angle. Tip material is also crucial since it strongly affects plasmon resonances excitation [2]. For the sake of simplicity we used gold wire because of its high performance. In order to produce TERS-active gold tips we utilized a low-cost and reliable electrochemical etching method [6, 7].

In this paper we developed a dc-pulsed low voltage electrochemical method based on a self-adjustable duty cycle for producing TERS active gold tips with a high yield of >90%. Unlike the approach developed in Ref. [9], in our approach in-situ cutoff current control is not used. The capacity of gold tips to probe specimen of interest on the nanoscale is demonstrated with near-field Raman measurements of single-walled carbon nanotubes bundle, vanadium oxide and sulfur.
2. Results and discussion

For producing gold tips we used 100 µm gold wire (purity 99.99%) immersed into a solution of fuming hydrochloric acid (HCl, 37%) and ethanol (C₂H₅OH, 96%) in a volume proportion of 1 : 1. A counter-electrode is 10-mm gold ring positioned around the inner bottom-free glass beaker (figure 1(a)) [9]. A sketch of a home-built electrical circuit for etching a gold wire is given in figure 1(b). Microcontroller STM32f415 sets a voltage between the working electrode (WE), which is the gold wire, and the counter electrode (CE) and controls the current cut-off event with a sampling rate of 0.7 µs.

The voltage driven corrosion of pure gold in highly acidic solutions incorporates three processes: 1) oxidation, 2) complexation and 3) diffusion [9]. The complete dissociation of HCl supplies chloride anions Cl⁻ into the solution which react with a gold wire producing chloroaurate complexes AuCl₄⁻[OH]ₓ [10]. The most strong etching takes place at the meniscus where Cl⁻ concentration gradients occur [9]. The presence of chloroaurates prevents the returning of oxidized gold atoms back into the bulk metal. Besides chloroaurates create a double electric layer which blocks an access of Cl⁻ anions to the surface of the gold wire. One of the ways to attack a passivation layer is mechanical mixing at the meniscus with dc-pulsed voltage. The underlying mechanism is related to change in the meniscus height with applied voltage. For this purpose a voltage square wave is normally utilized. Evidently, such wave parameters as voltage values of \( V_{down} \) and \( V_{up} \), a pulse duration of \( \tau \), and a duty cycle of \( D = \tau/T \) (where \( T \) is a period of the square wave) should be optimized. The greater the difference \( \Delta V = V_{up} - V_{down} \) the greater the extra height of the meniscus \( \Delta h(t) = h(V_{up}) - h(V_{down}) \) [11].

A value of \( V_{up} \) is determined in the vicinity of the plateau, as shown in figure 2(b), where the etching current abruptly drops because of the passivation layer. A choice of \( V_{down} \) is not limited and it might even be zero to maximize the voltage difference. However, small values of \( V_{down} \) lead to vanishing currents and current cutoff event comes true prior to detachment of the lower part of the gold wire. Therefore we choose a value of \( V_{down} \) on the plateau which is as far from the value of \( V_{up} \) as possible. For the gold wire in hydrochloric acid these values lie in the range of 1.4 V and 2.0 V, as follows from figure 2(b).

Figure 1. A schematic of the electrochemical cell (a), a layout of an electric circuit for electrochemical etching with a self-tuned duty cycle (b).
The second parameter of interest is the pulse duration $\tau$ or the duty cycle $D$. Traditionally, this parameter is empirically found from a requirement to improve the reproducibility. However, it depends on a number of factors such as background electrolyte, tip material and electrochemical regimes. Besides, the electrochemical etching is assumed to be robust and uniform and, therefore, it makes the tip surface smooth and cone-shaped. Unfortunately, an etching rate along the immersed tip surface changes noticeably: convex areas on the surface dissolve stronger than concave ones do. For this purpose, we suggest an adaptive electrochemical method in which the duty cycle is self-tuned. It means that when the etching current at $V_{up}$ decays down to a threshold value $I_{th}$, the circuit (see figure 1(b)) triggers for $V_{down}$. As a measure for adaptive control, we introduce the parameter $\eta$

$$\eta = \frac{I_i - I^0_i}{I^\text{max}_i - I^0_i}$$

(1)

$$I_{th} = \eta I^\text{max}_i$$

(2)

where $I_i$ is the current in the $i$-th pulse at $V_{up}$, $I^\text{max}_i$ is the maximal current in the $i$-th pulse, $I^0_i$ is the current at $V_{down}$ (see figure 2(a)). A histogram of pulse durations is given in figure 2(c). From the figure, we observe three macro-regions which provide evidence that the gold wire is etched in a non-uniform fashion. It means that the tip shape is not conical, since a radius of the gold wire $r(t)$ diminishes with a variable etching rate. The etching current decay behavior is caused by sliding down the meniscus and thinning the wire due to gravity and corrosion, respectively. The second mechanism is strongly sensitive to small changes in the etching rate when the wire radius approaches the extent of several nanometers. It means that radius fluctuations at the tip apex are comparable with the ultimate curvature. The conical shape requires uniform etching in correspondence with $r(t) = r_0 - \nu t$ (where $r_0$ is an initial radius of the gold wire, $\nu$ is an etching rate). As a result, the homogeneous pulse durations distribution has to be observed.

TERS measurements are performed with a scanning probe nanolaboratory NTEGRA SPECTRA™ (NT-MDT, Russia) which includes a confocal scanning laser spectrometer, an optical microscope and a scanning atomic force/shear force microscope. Prepared tips were glued at the end of a quartz tuning fork driven by shear-force control mechanism (see figure 3(a)). The tip apex, shown in figure 3(b), is illuminated with a linearly polarized 632.8 nm wavelength light coming from a He–Ne laser. A 100xoil immersion objective with a high numerical aperture of 1.4 focuses a laser beam down to ~250 nm spot. An optical reflection image of the tip raster scanned over the pure glass has demonstrated the presence of longitudinal lobes at the rims of the laser spot (figure 3(c)). All spectra were recorded with an electron multiplying CCD detector (Andor, UK) cooled down to $-82^\circ\text{C}$. 

![Figure 2.](image-url)
Figure 3. A gold tapered tip glued to a tuning fork operating in the vertical mode (a), high-resolution transmission electron microscopy image of a tip apex (b), confocal optical image of the tip raster scanned over a laser spot (c).

Far- and near-field Raman spectra are exemplified with a single walled carbon nanotubes bundle (figure 4(a)), vanadium oxide (figure 4(b)) and sulfur (figure 4(c)). The results provide evidence that electrochemically etched gold tips, brought to the sample under study with shear force feedback control, operate as hot spots due to the plasmonic effect (average field enhancement factor values exceed 2).

Figure 4. Far (tip-off) and near (tip-on) Raman spectra of single walled carbon nanotubes bundle (a), vanadium oxide (b) and sulfur (c).

3. Concluding remarks
In this paper we have developed a home-built potentiostat which allows one to perform dc-pulsed low voltage etching with self-tuning the duty cycle. In other words, a pulse duration in the voltage square wave is automatically adjusted in the basis of etching rates at the meniscus region. This optimization provides a high yield (>90%) of gold tips with the given parameters when no in-situ cut-off current control is used, unlike the approach reported in Ref. [9]. Near-field Raman spectra confirm the presence of the plasmonic effect under illumination of gold tips with a tightly squeezed laser beam.

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