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Toward Robust High Resolution Chemical Imaging

Carlos A. Barrios, Andrey V. Malkovskiy, Alexander Kisliuk, Alexei P. Sokolov, Mark D. Foster

Department of Polymer Science, The University of Akron, Akron, OH, 44325-3909

Resonant plasmon excitations at the surface of noble metals can localize and amplify an electromagnetic field in a very small volume and are the enabling element of surface enhanced optical microscopies [1]. Tip enhanced Raman spectroscopy (TERS) combines scanning probe microscopy (SPM) with Raman spectroscopy, taking advantage of this enhancing mechanism [2]. So far a 20 nm lateral resolution in chemical imaging of a surface has been achieved. Unfortunately, pure noble metal nanostructures, the most active plasmon materials known, are fragile, and prone to mechanical, chemical, and morphological degradation (Fig 1). Means of protecting and extending the lifetime of these surfaces are key for making the plasmon-based high resolution chemical imaging a robust characterization technique.

Usually, a very rough noble metal nanostructure at the apex of a sharp SPM tip, also known as the plasmonic nanostructure, provides the signal amplification required for high resolution chemical imaging. Plasmonic structure characteristics such as roughness, shape, and radius determine the spatial resolution and signal enhancement. Successful extension of the probe's active life requires stopping degradation processes while minimizing unfavorable influences on the optical response. Controlled physical vapor deposition (PVD) of aluminum can be used to create an ultrathin Al_2O_3 protective layer of a few nanometers on silver-coated SPM tips that dramatically improves chemical stability and wear resistance without sacrificing initial TERS efficiency [3]. Such a coating completely prevents decay in plasmonic activity over 40 days of use (Fig 2). A similar SiO_x protective coating provides some lifetime improvement, but fails to completely stop degradation [4].

The plasmonic/air interface is not only the heart of the plasmon resonance enhancement, but also the focus of the degradation. Two flat plasmonic surfaces prepared at the same time, but in different ways, one protected with a 3nm thick Al_2O_3 layer and the other unprotected, were used to determine how chemical degradation, principally generated by sulfur containing gases in the atmosphere and promoted by atmospheric humidity, is affected by the presence of the ultrathin Al_2O_3 layer. XPS spectra measured after 2 months of storage under ambient conditions show sulfidation, one of the main reactions of silver tarnishing, but also contamination of the unprotected tip by water, carbonaceous material and chlorine (Fig 3). The spectrum for the protected surface shows no sulfidation, no chlorine, and a lower concentration of carbon, evidencing how the ultrathin Al_2O_3 layer drastically minimized chemical degradation.

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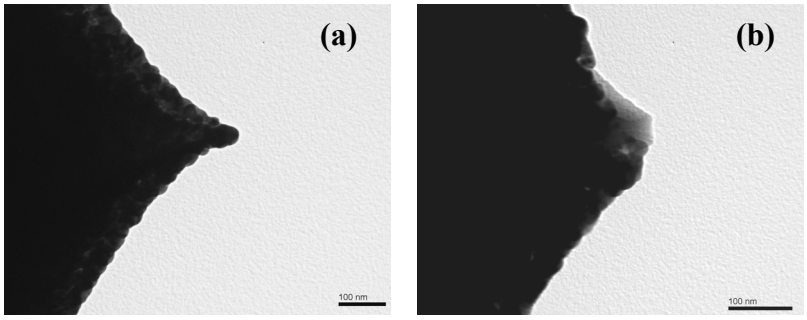


Figure 1. Transmission Electron Microscopy (TEM) images of an unprotected silver-coated SPM tips (a) before and (b) after scanning a polymer thin film three times. Mechanical degradation of the plasmonic structure by wearing is evident in Fig 1b. Scale bar is 100nm. Electron beam accelerating voltage = 120kV.

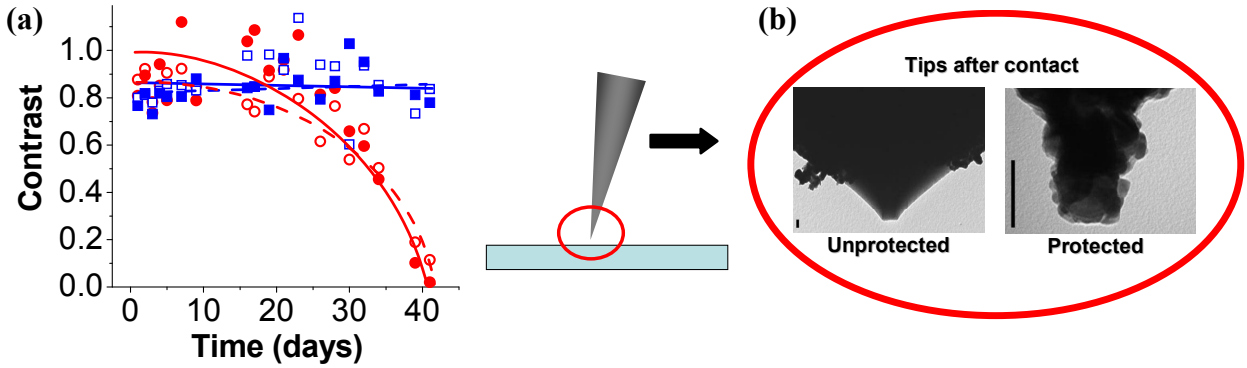
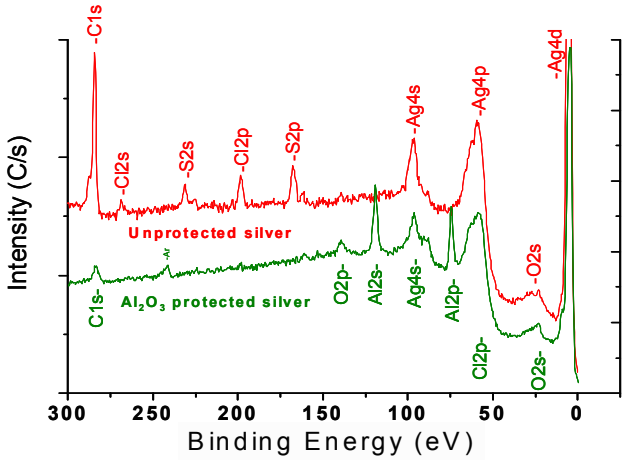


Figure 2. (a) TERS contrasts (measured at wave number 1450 cm^{-1}) as a function of time for a 50 nm thick PEDOT/PSS film for unprotected silver-coated Si_3N_4 tips (circles) and silver-coated Si_3N_4 tips protected by a 3nm thick Al_2O_3 thin layer (squares). Some tips were stored under ambient conditions (open symbols) and some inside a plastic desiccator under vacuum (filled symbols). (b) TEM images of an unprotected and a protected silver-coated SPM tip after scanning a polymer thin film three times. Scale bar is 50nm. Electron beam accelerating voltage = 120kV.

Figure 3. X-ray photoelectron spectra of silver plasmonic structures created on flat substrates after two months stored under ambient conditions: unprotected(upper curve) or protected by a 3nm thick ultrathin Al_2O_3 coating (lower curve). The lower concentrations of carbon, sulfur, and chorine species evidence how the ultrathin Al_2O_3 layer drastically reduces chemical degradation.



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