Aluminum and copper nanostructures for surface-enhanced Raman spectroscopy: A one-to-one comparison to silver and gold

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In this work, we aimed at investigating how good or bad aluminum (Al) and copper (Cu) perform in plasmonic applications as compared to silver (Ag) and gold (Au). Contrary to our expectations, and to widely accepted misconceptions, our experimental and simulation results show that Cu and Al layers on nanospheres make efficient nanostructures for surface-enhanced Raman spectroscopy. In an unprecedented one-to-one comparison among all metal nanostructures, it is demonstrated that Al and Cu rival the conventionally used materials, Ag and Au, displaying similar enhancement. The enhancement capability was shown with the metal nanostructures exposed to air under room conditions showing that the oxide layers formed on Al and Cu do not affect their SERS performance significantly. This concise report further supports large-scale chemical sensing applications using low-cost metals compatible with mass-production fabrication in microelectronics as well as demonstrating an appropriate way to compare the electric field enhancement of different plasmonic materials.

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1. Introduction

From food industry, materials science, to health care and early cancer diagnosis, the capabilities in ultra-sensitive chemical detection can make the difference between life and death [1,2]. Raman spectroscopy possesses the unique ability to provide fingerprints of chemical compounds present in a sample, thus allowing improved reliability of diagnostics [3]. Until recently, one important drawback of Raman spectroscopy was its low sensitivity, due to the very inefficient nature of inelastic light scattering. However, since the late 1990s until now, the application of Raman spectroscopy experienced strong growth in chemical sciences. This renewed interest is also supported by the coupling with plasmonics that gave rise to surface-enhanced Raman spectroscopy (SERS) techniques [4]. In this way, a long-standing sensitivity limitation of Raman spectroscopy was broken, allowing scientific achievements such as single molecule detection [5]. The physical principle behind SERS is based on the collective photo-excitation of free electrons in metal nanostructures, the so-called localized surface plasmons (LSP). Plasmons excited in nanoparticles strongly amplify the electric field of the incident and scattered light, especially when resonance conditions are met. This interaction between plasmons and light results in an amplification of the Raman signal that is roughly proportional to the fourth power of the incident electric field $I \propto |E_0|^4$, the so-called electromagnetic enhancement mechanism [4]. Au and Ag nanostructures show LSP resonances (LSPR) in the visible spectral range thus providing maximum signal enhancements close to laser excitation wavelengths commonly used in Raman spectroscopy. Moreover, the optical properties (dielectric function) of Ag and Au lead to low losses. These characteristics make Ag and Au materials the undisputable top choices in many plasmonic applications, including SERS. In the 1980s and 1990s, copper was also used in SERS [6] and later on in surface-enhanced IR absorption [7]. Very recently, aluminum jumped onto the plasmonics stage not only for applications using UV excitation [8] but also in the near infrared range [9–14]. With improvements in sample preparation such as optimized deposition methods the scenario is starting to

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