Cu-Pd Bimetal and CuPt Alloy Nanotubes Derived from Cu Nanowires: Novel Amplification Media for Surface-Enhanced Raman Spectroscopy

Eva Bozo, Aron Dombovari, Melinda Mohl, Vesa K. Virtanen, Simo Saarakkala, Robert Vajtai and Krisztian Kordas

Abstract—Surface-plasmons of metals have been utilized to enhance the Raman spectra of various adsorbed moieties for over decades. While amplification of the spectral intensity takes place on most of the metals, due to their superb properties, Au, Ag and Cu surfaces represent the benchmark in surface-enhanced Raman spectroscopy. In this paper, we show that Cu-Pd bimetal and CuPt alloy nanotubes derived from Cu nanowires by simple galvanic exchange reactions are suitable for the efficient enhancement of Raman spectra when dispersed on Si surfaces. Amplification factors of 120× on Cu nanowires, 150× on Cu-Pd bimetal nanotubes and 250× on CuPt alloy nanotubes in reference to the factors of 120× on Cu nanowires, 150× on Cu-Pd bimetal exchange reactions are suitable for the efficient enhancement of SERS on most of the metals, due to their superb properties, Au, Ag and Cu surfaces represent the benchmark in surface-enhanced Raman spectroscopy in the future.

Index Terms—SERS, Cu nanowires, galvanic exchange reaction, CuPt alloy, Cu-Pd bimetal.

I. INTRODUCTION

Surface-enhanced Raman spectroscopy (SERS) is a powerful analytical tool to detect and quantify a broad range of chemicals even in trace quantities, and thus it has been widely employed in analytical chemistry [1], environmental monitoring [2], [3], biomedical diagnostics [4]-[7], food security [8], and even in forensic investigations [9], [10].

Enhancement of the Raman spectra are due to two primary reasons. On the one hand, the electric field in the proximity of resonant surface plasmons is amplified, which then enhances polarization of the adsorbate and increase Raman intensity (electromagnetic effect). On the other, (partial) charge transfer between adsorbed molecules on metal surfaces can result in the change of polarizability thus contributing to an enhanced polarization in the electric field (chemical or charge-transfer effect) [11].

Although SERS was discovered in the 1970s [12], there is still an immense interest in finding newer and affordable materials as amplification media other than the traditional gold or silver surfaces. Platinum group metals, although also very expensive, are particularly interesting because their catalytic and electrocatalytic properties make the follow up of chemical reactions possible by observing adsorbed reactants and intermediates [13], [14]. As demonstrated experimentally [14]-[16] and confirmed theoretically [22], common metals (e.g. Fe, Co, Ni, Al, Sn) show reasonable Raman enhancement although less efficient than the noble metals. Furthermore, not only pure metals but their various alloys, bi- and tri-metallic compositions [18], [19] and multi-layered structures [20], [21] and hybrids with semiconductors [5], [7], [22] have been reported to improve SERS efficiency of less active metals because of multiple effects. One is based on the extended range of increased electric field on the surface of a metal or semiconductor near a highly SERS active particle or film (borrowed SERS activity) [23]. The other effect is associated with plasmonic hot electron injection from the metal to the semiconductor [24], which inherently results in different local fields and can alter the metal-molecule complex thus influencing both electromagnetic and chemical sensing mechanisms. In addition to the above processes, also the geometry, morphology, and size of particles influence SERS, as the local field is a function of surface curvature [25]-[29] and semiconductor near a highly SERS active particle or film (borrowed SERS activity) [23].

Recently, we have shown that Cu nanowires are suitable for SERS, in particular, when dispersed on Au thin films [30]. Although rapid oxidation of common metals may influence the

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local field and thus spectral amplification, in the case of Cu, the native surface oxides [31] do not seem to degrade SERS quality [30], [32]. In this paper, our aim is to extend our SERS studies on Pt and Pd derivatives of Cu nanowires. Our strategy follows the idea of combining highly and less SERS active metals into a synergic system by using very simple and easy-to-scale synthesis routes, which include hydrothermal growth of Cu nanowires [30], [31], [33] followed by a partial exchange of Cu with Pd and Pt in galvanic replacement reactions [34]. We show that the as-made hybrid nanostructures are having superior Raman enhancement as compared to Cu nanowires making them promising new candidates for SERS applications.

II. MATERIALS AND METHODS

Cu nanowires were synthesized by a hydrothermal route, [30], [31], [33] whereas their Pd and Pt modified derivatives were obtained by galvanic replacement reactions [34] similar to those as we reported earlier.

A. Synthesis of Cu nanowires

1.4 g of CuCl₂·H₂O and 3.2 g of D-glucose were dissolved in 640 mL distilled water, then while stirring, 11.5 g hexadecylamine was slowly added to the solution. After 4 hours of stirring, the light blue solution was inserted into a Teflon lined autoclave (Parr Instrument) to facilitate hydrothermal synthesis in 120 °C at autogenic pressure (~1.2 bar) for 24 hours (stirring at 35 rpm). After the reaction, the products were collected, and washed with distilled water, hexane and ethanol (each repeated three times). The purified product was kept in ethanol until further use.

B. Synthesis of bimetallic Cu-Pd and alloy CuPt nanotubes

1 mL of Cu nanowire suspension was first diluted in ethanol (1 mg/mL) and then sonicated for at least half an hour then centrifuged at 3200 rpm and washed with dimethyl sulfoxide (DMSO). The copper nanowires were then dispersed in DMSO (5 mL) under N₂ atmosphere in a 50 mL flask. Aliquots of noble metal salt solutions (1 mM of potassium tetrachloropalladate or potassium tetrachloroplatinate in DMSO) were then added slowly to the copper nanowire dispersions (at 189 °C) and kept under reflux until its color became stable (typically 10 min). Thereafter the product was centrifuged and washed with ethanol and kept in ethanol.

C. Materials characterization

The morphology, microstructure and composition of the products were characterized by field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus, 15 kV, samples were drop cast on chips of a Si wafer), transmission electron microscopy and electron diffraction (EFTEM, Jeol FS 2200, 200 kV, samples were drop cast on Ni grids) and energy dispersive X-ray spectroscopy (EDX installed in both SEM and TEM). For crystal structure analysis we used powder X-ray diffraction (XRD, Bruker D8 Discovery, Cu Kα, with 2θ scans between 5° and 90° at a rate of 0.01 °s) of each sample drop cast on the surface of glass slides.

D. Surface-plasmon enhanced Raman spectroscopy analysis

Surface-plasmon enhanced Raman spectroscopy (SERS) measurements of rhodamine 6G (R6G) and methyl violet (MV) model compounds were carried out on random networks of the nanomaterials. The NWs of Cu and NTs of Cu-Pd or CuPt were drop cast from their corresponding dispersions in ethanol on pristine Si and Au coated chips (laser cut to 10×10 mm² size from the corresponding wafers). After drying, aqueous R6G or MV (both 10⁻⁴ M) were drop cast on the NW and NT coated chips and dried in air before analysis using Raman microscopy (ThermoFisher DXR2xi Raman Imaging Microscope) with the following parameters: 100× objective, λ = 532 nm, laser power 2 mW, exposure time 0.02 s, number of scans 1000×, full range resolution grid, slit aperture 50 µm and laser spot size 0.6 µm. (Representative SEM images of Cu NWs and Cu-Pd NTs on Si and Au surfaces are shown in Supplementary information, Fig. S1.)

III. RESULTS AND DISCUSSION

According to scanning electron microscopy (SEM) analysis, the hydrothermally grown Cu nanowires have a length between 10 and 50 µm, and an average diameter of ~50 nm. The nanowires are straight, and only some kinks may be seen in their structure due to crystal twinning (Fig. 1a). After the partial galvanic replacement with Pd or Pt, the overall nanowire structure changed for tubular due to the consumption of Cu and simultaneous deposition of Pd or Pt, respectively (Fig. 1b,c). In addition, the originally smooth surface of the nanowires turned rough and highly nanostructured. About half of the Cu atoms are replaced with either Pt or Pd as measured by energy dispersive X-ray spectroscopy (EDX).

The surfaces of the nanotubes are polycrystalline and have a grain size of 5 to 10 nm of the corresponding noble metal. Under these metal nanoparticles, the crystal structure of the nanotubes is different as suggested by high-resolution transmission electron microscopy (TEM) (Fig. 1d-I), EDX (Fig. 1g,h) and X-ray diffraction (XRD) (Fig. 1i). The Pt replaced Cu seems to be a bimetallic alloy rather than a mixture of individual Cu and Pt crystals hence the notation CuPt. On the other hand, for Cu replaced by Pd, we find X-ray reflections from separate crystals of the two metals in the corresponding pattern thus the material is noted as Cu-Pd.
Fig. 1. SEM images of (a) Cu nanowires as well as (b) Cu-Pd and (c) CuPt nanotubes. Scale bars are 500 nm. TEM images and corresponding electron diffraction patterns (insets) of (d) Cu nanowires, (e) Cu-Pd and (f) CuPt nanotubes. The sub-panels (d1-f2) are magnified parts of the respective samples indicated by the white rectangular areas. (d1) Cu$_2$O crystals covering the surface of the Cu NWs. (d2) Cu crystal and its (100) and (110) planes. (e1) Polycrystalline Pd nanoparticle on the surface of the Cu-Pd nanotube identified by the (111) planes of Pd. (e2) Wall of the Cu-Pd nanotube. (f1) and (f2) Pt nanoparticles and their identified (200), (110) and (100) planes. Scale bars are 5 nm. Panels (g) and (h) show bright-field scanning TEM images of Cu-Pd and CuPt nanotubes, and their corresponding EDX elemental maps in the sub-panels. Scale bars are 200 nm. (i) XRD patterns of the nanostructures. Inset: resolved reflections of Pd and CuO.

Motivated by the promising SERS results we obtained lately using Cu nanowires to detect rhodamine 6G dye, it appeared to be a natural step to extend our research to its galvanic replaced Pt and Pd derivatives. The synthesized CuPt and Cu-Pd nanotubes as well as Cu nanowires were dispersed on Si and Au surfaces, and then coated with solutions of rhodamine 6G (R6G) and methyl violet (MV) dyes. After drying, we collected Raman spectra of the dyes from several locations of each sample populated with large number of nanowires or nanotubes. For reference, we use Si and Au surfaces coated only with either of the dyes (Fig. 2). As expected, on Si surface (without any NWs or NTs), we can hardly observe the spectra of the dyes. On Au surface, we see the spectra of both dyes but the intensity of peaks is low and not resolved entirely. In the presence of Cu NWs, we find the spectra are well resolved but with moderate peak intensities. On the other hand, the intensity of peaks improves significantly on surfaces covered with CuPt or Cu-Pd NTs (Fig. 2). The overall amplification factors for both types of dyes as compared to the corresponding substrates are approximately 15× (Cu), 30× (Cu-Pd) and 60× (CuPt) on Au and 120× (Cu), 150× (Cu-Pd) and 250× (CuPt) on Si. The smaller substrate to NW (or NT) amplification on Au surface is due to the already ~10-fold Raman intensities as compared to the Si surface.

Fig. 2. Raman spectra of R6G and MV on Cu NWs, Cu-Pd and CuPt NTs dispersed on (a) and (c) Si and (b) and (d) Au surfaces. The dyes were cast from 10$^{-4}$ M aqueous solutions. Each spectrum correspond to the best performing surface areas covered by networks of nanowires or nanotubes. The reference spectra correspond to Si and Au substrates coated only with either of the dyes. (Instrument: ThermoFisher DXR2xi Raman Imaging Microscope, 100× objective, λ = 532 nm, P = 2 mW, τ = 0.02 s, 1000× scans, slit aperture: 50 μm and laser spot: 0.6 μm.)
The Raman intensities show proportionality to the concentration of the analytes (Fig. 3). The spectrum of MV can be resolved well for $10^{-5}$ M, and we observe reasonable peak intensities even at $10^{-6}$ M comparable to that obtained using Ag NWs with a detection limit of $10^{-7}$ M for MV [35].

It is important to point out here, that significant improvement (5 to 40-fold) of the Ag NWs enhanced spectrum of 4-mercaptobenzoic acid was shown on Ag-Au nanowires [36], and as reported very lately. Also, Ni templated Ag-Au nanocages [18] helped detection of R6G at $10^{-10}$ M limit of analyte concentration. Furthermore, as Ag nanoparticles grown on semiconducting NWs of Si [37] and GaN [38] showed even better detection limits ($10^{-14}$ M and $10^{-12}$ M, respectively) for R6G. These results suggest that implementing Ag or Au on Cu NWs instead of Pd or Pt; or combination with semiconducting nanoparticles/surfaces could probably provide better spectral amplifications and thus shall be assessed in detail in the future.

To demonstrate the robustness of the measurements, we collect spectra at several locations of NW or NT coated surfaces and calculate the intensity statistics for the characteristic Raman peaks (Fig. 4). The results show some minor scattering of the peak intensity data measured in different locations; however, the typical amplification factors show a consistent trend. It is worth pointing out, that even individual NWs or NTs induce reasonable Raman amplification. Furthermore, it is also interesting to note, that the Raman peak intensities measured on Au surfaces in the proximity of NWs or NTs (blank areas) show rather high values for both types of dyes. We do not observe such high intensities on Au wafers without NWs or NTs, and we do not see either a similar effect on blank areas of Si wafers otherwise coated with NWs or NTs. Such a phenomenon fits well the „borrowed SERS activity” model.

Fig. 3. Raman spectra of methyl violet adsorbed on CuPt NTs (dispersed on Au surface) from solutions of different concentrations (from $10^{-4}$ M to $10^{-6}$ M).

Fig. 4. Raman peak intensity statistics for (a-f) R6G and (g-l) MV on Cu NWs, Cu-Pd NTs and CuPt NTs dispersed on Si and Au surfaces. Each plot displays the intensities measured on networks of NWs or NTs as well as on individual particles. Empty area data correspond to peak intensities measured on locations in the proximity of NWs or NTs. The dyes were drop cast from $10^{-4}$ M aqueous solutions.
In closing, we studied surface-plasmon enhanced Raman spectroscopy using Cu-Pd bimetal and CuPt alloy nanotubes synthesized by a partial galvanic exchange of Cu nanowires. Significant amplification of the Raman spectra of rhodamine 6G and methyl violet was demonstrated on Si or Au surfaces with a detection limit of 10^−6 M. The improved Raman intensity enhancement of nanostructured CuPt and Cu-Pd nanotubes in reference to smooth Cu nanowires suggests that their corrugated surfaces facilitate local field enhancement (shape effect) and the presence of Pd and Pt nanoparticles on the surface extend the range of increased electric field adjacent to the particles (borrowed SERS activity).

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