Characterization of the copper surface optimized for use as a substrate for surface-enhanced Raman scattering

A. Kudelski a,*, J. Bukowska a, M. Janik-Czachor b, W. Grochala a, A. Szummer c, M. Dolata b

a Department of Chemistry, University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland
b Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44 / 52, 01-224 Warsaw, Poland
c Department of Materials Science, Technical University of Warsaw, Narbutta 85, 02-053 Warsaw, Poland

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Abstract

A new electrochemical procedure of roughening of a copper surface was developed, producing a surface with a high surface-enhanced Raman scattering (SERS) activity. The surface morphology and composition was characterized by energy dispersive/wavelength dispersive/X-ray microprobe analysis and compared to the Cu electrodes roughened by the commonly used oxidation–reduction reactions. The morphology of such a surface was completely different from those produced by traditional electrochemical procedures. Moreover, X-ray microprobe analysis revealed that our new surface remained unoxidized in contrast to the other SERS active Cu surfaces. The potential profiles of SERS intensity of the ring breathing mode of pyridine adsorbed on these surfaces were discussed and interpreted in terms of charge-transfer (CT) effect. © 1998 Elsevier Science B.V.

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1. Introduction

Since it was discovered that Raman scattering from molecules adsorbed on certain surfaces is extremely enhanced, surface-enhanced Raman scattering (SERS) has become a well established technique for studying adsorbates on metal surfaces such as copper [1,2], gold [3,4] and silver [4–8]. Strong SERS spectra have also been observed for some of the alkali metals including sodium and potassium [9].

The enhancement of surface Raman spectra of molecules adsorbed on ‘smooth’ metal surfaces are negligible [10] or weak [11,12]. The observation of the strong SERS effect, with enhancement of scattering by a factor of approximately $10^5 \div 10^6$, requires the presence of submicron roughness on the metal surface. Therefore, some kind of surface preparation is required in order to obtain SERS-active systems.

Several activation methods have been reported, e.g. preparation of metal colloidal particles [13,14], subjection of metal to oxidation–reduction cycle (ORC) [15,16], evaporation of SERS-active metal on rough substrate [17–19], preparation of lithographically produced metal structures [20] and chemical etching treatment [2,21].
The most common metal used as a SERS-active substrate is silver because it exhibits the largest enhancement among all the metals, and its surface plasma resonance condition is reached for the wide range of visible light. However, silver substrate was found to be very unstable in time even if covered with a film of another metal [22]. On the contrary, the intensity of the SERS spectrum of molecules adsorbed at some copper surfaces remains constant in time [16,23–25]. It means that in some cases copper surfaces can be a better substrate for SERS measurements than silver.

The morphology of a roughened metal surface, its SERS-stability and the enhancement factor achievable, are extremely sensitive for the conditions of the roughening procedure [16]. Therefore, since the SERS discovery, a particular attention has been devoted towards an improvement of the roughening procedure and towards a development of more suitable substrates for the SERS investigations. Moreover, an attempt was made to understand the effect of surface morphology on SERS origin.

The aim of this paper is to characterize the surface morphology of copper substrates roughened by the typical electrochemical oxidation–reduction procedures as compared to a copper surface roughened according to a new procedure developed recently: a rapid anodic dissolution of Cu in an acidic electrolyte accompanied by a disproportionation of the dissolving Cu⁺, thus produced at the electrode, to Cu²⁺ and Cu⁰. Implications of the new surface morphology and chemistry for SERS are analyzed.

2. Experimental

2.1. Instruments and experimental configuration

Raman spectra were recorded with a Cary 82 spectrometer equipped with a Lexel model 98 krypton ion laser ($\lambda_{exc} = 647.1$ nm). The laser power at the sample surface was restricted to 40 mW. The spectral band pass of the Raman spectrometer was 4 cm⁻¹. We used the 90° configuration, with an angle of incidence on the metal surface during SERS measurements of ca. 60°.

The copper surfaces were characterized by optical microscopy and X-ray electron microprobe analyzer Cameca SEM probe SU 30 equipped with an energy dispersive spectrometer/wavelength dispersive spectrometer (EDS/WDS) facility.

2.2. Materials and sample preparation methods

The copper samples were prepared from Cu 99.99% sheet 0.5 mm thick or Cu 99.998% rod 6.35 mm diam. (Aldrich). H₂SO₄, CuSO₄, CuCl₂, KCl and LiCl were all of analytical reagent grade and were used as received. Pyridine (Ubichem, analytical-reagent grade) was distilled before measurements. The water was purified by triple distillation.

Electrochemical roughening of Cu surface was carried out in a typical 3-electrode potentiostatic system. A platinum sheet was used as the counter electrode and a saturated calomel electrode (SCE) as the reference. All potentials are reported with respect to SCE.

Before spectroscopic measurements the polycrystalline copper surfaces were subjected to the following roughening procedures:

(i) 50 successive positive–negative scans at 20 mV s⁻¹ from −0.55 to +0.05 V in 0.2 M LiCl and 0.01 M CuCl₂ solution.

(ii) 50 successive positive–negative scans at 20 mV s⁻¹ from −0.50 to +0.13 V in 0.1 M KCl solution.

(iii) Anodic ‘active’ dissolution in 0.2 M CuSO₄ + 0.4 M H₂SO₄ at $E = E^{0} + 0.4$ V and $i = 1$ A cm⁻² during 30 s, where $E^{0}$ is a reversible electrode potential of Cu metal in the above solution ($E^{0} = +0.07$ V vs. SCE).

The samples were then carefully rinsed in triply distilled water and dried in air.

3. Results and discussion

There is a variety of electrochemical roughening procedures used to activate copper substrate for SERS experiments. In general, they can be divided into three groups, regarding the electrolyte used during roughening.

(a) copper salts or copper containing salts mixtures (e.g. CuCl₂)
The main disadvantage of copper surfaces roughened according to the typical electrochemical procedures (i) and (ii) is a considerable contamination of the surface with copper oxides, which may quench the SERS signal. Therefore, an attempt was made to develop a new roughening procedure (iii) resulting in an unoxidized surface.

Surface morphology after the procedure of a rapid anodic dissolution of Cu accompanied by a disproportionation of dissolving Cu⁺ (iii) looks completely different than these after the procedures commonly used. The grains are etched and there are longitudinal strips within each grain (see Fig. 6). On the top of some strips small ‘particles’ of redeposited Cu with a size below 1 · 10⁻⁴ mm are visible. X-ray microprobe with EDS/WDS do not reveal any O, which implies that the whole surface remains unoxidized (see Fig. 7).

The SERS spectrum of pyridine adsorbed on cop-
Fig. 2. EDS/X-ray microprobe spectra showing presence of O, Cl and C at Cu surface after the pretreatment in LiCl + CuCl₂ solution. (a) analysis at an ellipsoidal ‘particle’; (b) analysis at an underlaying metal surface (compare Fig. 1).
per surface roughened according to this new pretreatment (iii) is presented in Fig. 8. A careful inspection of the measured SERS spectrum reveals that it is of an excellent quality with a high signal to noise ratio. Because all SERS spectra were recorded under identical conditions, our results (Figs. 5 and 8) confirm that the enhancement factor is higher (about $5 \div 20$ times) for this new surface than for the copper surfaces pretreated according to commonly used procedures (i) and (ii).

Fig. 5. SERS spectra of pyridine adsorbed from 0.05 M pyridine + 0.1 M KCl solution on a copper electrode after the pretreatment (i) in LiCl + CuCl$_2$ solution (a) and after the pretreatment (ii) in KCl solution (b). $E = -0.6$ V; $\lambda_{exc} = 647.1$ nm.

Figs. 5 and 8 show that SERS band at 1013 cm$^{-1}$ recorded at Cu surface after the new pretreatment is considerably narrower ($\Delta v_{1/2} = 10$ cm$^{-1}$) than the band recorded at the typical Cu surfaces ($\Delta v_{1/2} = 14$ cm$^{-1}$). This suggests that Cu surface after the new pretreatment (iii) is certainly more homogeneous than those after the commonly used pretreatments (i) and (ii).

Fig. 6. Typical morphology of Cu surface after the roughening according to the new procedure of rapid anodic dissolution of Cu accompanied by a disproportionation of the dissolving Cu$^+$. See text for details.
Fig. 7. EDS spectrum of the surface shown in Fig. 6 with no O signal at 524.9 eV detectable.

(ii). This inhomogeneity is undoubtedly connected with the presence of copper oxides at the surfaces (i) and (ii). Pyridine molecules adsorbed on Cu$_2$O contribute to quite different SERS spectrum consisting of two bands at 1024 and 1005 cm$^{-1}$ [26], thus introducing some asymmetry and widening of the 1013 cm$^{-1}$ band contour.

Fig. 9 shows the normalized SERS intensity of the 1013 cm$^{-1}$ band of pyridine adsorbed at all copper surfaces under investigation plotted as a function of a potential. As can be seen from Fig. 9 the maximum of the SERS intensity is attained at $-0.85$ V in the case of Cu surface activated by our new roughening procedure (iii) and at $-1.0$ V for the electrodes roughened by the typical ORC cycles according to procedures (i) and (ii).

The simplest possible explanation of the shift of this maximum is that the SERS intensity is mainly determined by the surface coverage factor and that the potential at which the maximum of surface coverage is achieved depends on surface morphology.

However, as it was observed for silver, gold and copper surfaces, bands of pyridine exhibit enhancement due to photon-driven charge transfer (PDCT) process [27–29]. In such a case the potential at which the maximum of SERS intensity is observed...
Fig. 8. SERS spectrum of pyridine adsorbed on a copper surface, after the new pretreatment (iii), from 0.05 M pyridine + 0.1 M KCl solution. $E = -0.6$ V; $\lambda_{ex} = 647.1$ nm.

($E_{max}$) is correlated to the best fitting of the PDCT process. PDCT occurs between the Fermi level of the metal and unoccupied level of the adsorbed pyridine molecule. Therefore, the difference between $E_{max}$ may be explained in terms of the shift of acceptor levels of pyridine upon adsorption on these various types of surfaces, or alternatively by the shift of Fermi level for these surfaces.

The first explanation may be correlated to the atomic inhomogeneity of the surfaces under investigation and to various interactions between adsorbed pyridine molecules and different atomic scale creatures created on the surface. If there is a higher rise of acceptor levels of pyridine for molecules adsorbed on the one kind of the Cu clusters (caused, for example, by different orientation of the adsorbed molecules) than for molecules adsorbed at the other Cu clusters, the potential necessary to provide resonance conditions would be more negative for surface exhibiting higher number of Cu cluster of the first type.

The second explanation of the discussed location of $E_{max}$ may be correlated to the presence of oxygen ions at the surface of an electrode roughened by a typical ORC procedure. As it was suggested for halide ions, anions adsorbed at the metal surface induce a positive charge in the metal. Thus, to obtain the same position of the Fermi level as for the electrode uncovered with anions, and to provide PDCT-resonance conditions, more negative potential has to be applied to the first type of the electrode [30]. We may expect that the similar reasons have to be considered in the case of oxidized and unoxidized copper surfaces. This leads to the conclusion that maximum of PDCT occurs at the more negative potentials for the surface partially covered with oxygen ions (or OH⁻) than for an electrode obtained with our new procedure and providing an unoxidized metal surface.

However, the explanation of the difference in location of $E_{max}$ for various surface pretreatments remains still unclear and further investigations of the above phenomenon are in progress.

It is interesting to note that the full-width-at-half maximum (FWHM) of the SERS intensity vs. $E$ profiles in Fig. 9 depends on the pretreatment of the Cu electrode. Comparable half-widths are observed for the Cu activated by ORC in KCl solutions and for Cu roughened by a rapid anodic dissolution (about $0.55 \div 0.60$ V). Considerably narrower profile is found for Cu activated by ORC in presence of CuCl₂ (about 0.35 V). These FWHM values expressed in V corresponds to the width of charge-transfer (CT) profiles expressed in eV. The width of

Fig. 9. Normalized SERS intensity of the ring breathing mode of pyridine adsorbed at Cu vs. electrode potential. Cu after the new pretreatment (iii) (●); Cu activated in CuCl₂ + LiCl solution (i) (■); Cu activated in KCl solution (ii) (▲). Measurements in 0.1 M KCl and 0.05 M pyridine. $\lambda_{ex} = 647.1$ nm.
the CT band $\Delta(h\omega)$ can be calculated from the formula given by Furtak [30]:

$$\Delta(h\omega) = (d\Delta E/dV_{app}) \cdot \Delta V$$

where $d\Delta E/dV_{app}$ is the slope of a plot of excitation energy $\Delta E$ vs. potential for which a maximum of SERS intensity is observed ($V_{app}$); $\Delta V$ represents FWHM of the potential profile.

Assuming that $d\Delta E/dV_{app}$ is 1.85 eV/V for Cu-pyridine + 0.1 M KCl$_aq$ system [29] one obtains 1.11 eV and 0.65 eV, respectively, for our two types of profiles. This considerable narrowing of the CT band for the surface activated in presence of CuCl$_2$ suggests that, in this case, the sites responsible for CT effect are exceptionally homogeneous. It is worth to mention that the width of the CT profiles for the other surfaces roughened according to (ii) and (iii) (1.11 eV) is the same as that reported by Pemberton et al. [29] for Cu electrode activated in KCl in the presence of pyridine.

There is also an additional weak maximum on the discussed CT profiles observed between $-0.4$ and $-0.6$ V (see Fig. 9). We suppose that it is due to the presence of Cu$_2$O on the electrode surfaces. Apparently the SERS spectrum of pyridine adsorbed on copper oxide surfaces exhibits CT maximum at $-0.5$ V [26]. As seen in Fig. 9 the second CT maximum (at $-0.5$ V) is distinct only for profiles observed at electrode surfaces produced by common procedures. Our new roughening procedure resulting in Cu$_2$O free surface causes that this additional CT maximum is hardly visible.

In order to check stability of the SERS signals on our electrodes the intensity of the 1013 cm$^{-1}$ ring breathing vibration band of pyridine adsorbed at all copper surfaces under investigation was monitored at a constant electrode potential of $-1.2$ V for 1 h (Fig. 10). As follows from Fig. 10, SERS intensity remains nearly constant in time. Because recording usually started after two minutes, it was necessary to estimate the possible intensity change during the first two minutes after applying the potential $-1.2$ V. Thus, the following experiment was performed. The band at 1013 cm$^{-1}$ was recorded at an open circuit potential, then the potential $E = -1.2$ V was applied for 2 min and again the spectrum at the starting potential was measured. It appeared that the intensity of the second spectrum was equal, within the limit of an error, to that of the first spectrum. This implies that the copper surface roughened according to the new pretreatment (iii) is also very stable in time.

4. Conclusions

In summary one should emphasize that the new procedure of activation of the Cu electrode results in:

- a superior, particularly active SERS substrate
- a surface morphology which is very different from those produced by the common roughening procedures.

A question, however, still arises about the relative contributions of various factors to SERS on these new surfaces. It appears that both electromagnetic and CT effects may be changed after this new pretreatment procedure. This new surface is very rough with a quite developed morphology. Recent AFM/STM work [18] suggests that the overall enhancement factor on Ag could be partitioned into two contributions: one connected with metal ‘particles’ in the 5–30 nm range and the second (smaller) due to larger scale structures (about 500 nm). Our results imply that on our newly obtained Cu surface there is a great variety of ‘particles’ of different sizes which may be SERS active as well.
More detailed studies with AFM and Raman imaging techniques are needed in order to determine more quantitatively the relationship between the surface structure and SERS enhancement.

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