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# Copper nanowire coated carbon fibers as efficient substrates for detecting designer drugs using SERS

Vladimir Halouzka[a,c,1], Barbora Halouzkova[b,1], David Jirovsky[a], Dusan Hemzal[d], Peter Ondra[c], Eirini Siranidi[e], Athanassios G. Kontos[e], Polycarpos Falaras[e], Jan Hrbac[b,*]

[a] Department of Analytical Chemistry, Palacky University, Faculty of Science, 17. listopadu 12, 771 46 Olomouc, Czechia
[b] Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, 625 00 Brno, Czechia
[c] Department of Forensic Medicine and Medical Law, University Hospital Olomouc, Hnevotinska 3, 775 09 Olomouc, Czechia
[d] Department of Condensed Matter Physics, Faculty of Science, Masaryk University, Kotlarska 2, 611 37 Brno, Czechia
[e] Institute of Nanoscience and Nanotechnology, NCSR "Demokritos," 15310 Agia Paraskevi Attikis, Athens, Greece

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ABSTRACT

Miniature Surface Enhanced Raman Scattering (SERS) sensors were fabricated by coating the carbon fiber microelectrodes with copper nanowires. The coating procedure, based on anodizing the copper wire in ultrapure water followed by cathodic deposition of the anode-derived material onto carbon fiber electrodes, provides a "clean" copper nanowire network. The developed miniature (10 μm in diameter and 2 mm in length) and nanoscopically rough SERS substrates are applicable in drug sensing, as shown by the detection and resolving of a range of seized designer drugs in trace amounts (microliter volumes of $10^{-10}$–$10^{-12}$ M solutions). The copper nanowire modified carbon microfiber substrates could also find further applications in biomedical and environmental sensing.

## 1. Introduction

Fabrication of substrates for Surface Enhanced Raman spectroscopy (SERS) belongs to intensely researched topics as SERS is a promising, rapid and non-destructive technique, that allows for probing trace amounts of molecular species, in special cases even down to the single molecule level [1]. SERS active substrates contain nanoscopic metal material (predominantly silver, gold or copper [2–4]) with features size-matched to the wavelength of the exciting laser light. The target molecules, when brought into contact with SERS substrate, experience strong electromagnetic fields of the excited surface plasmons in which the probability of Raman transitions is increased. Very intense local-fields (SERS hotspots) occur if neighboring nano-features exist at distances in the order of 1–2 nm [1].

Although a low-cost option, copper is less frequently employed as SERS active metal due to its tendency to surface oxidation. It was, however, shown that the intensity of the SERS spectrum of molecules adsorbed at copper surfaces can remain constant in time [5,6] and that nanostructured copper can compete with the frequently used silver and gold, providing similar values of SERS enhancement factors (EF) [7]. Recently, Guo et al. [8] developed Cu-based SERS substrates employing electrochemical roughening of smooth copper sheet in 1 M sulphuric acid by square wave potential pulses (0÷−1.4 V vs. Ag/AgCl at 10 Hz for 5 s) and registered the SERS spectrum of pyridine on this substrate immersed to 0.05 M aqueous pyridine solution. Irregular nanostructured features, fabricated onto copper sheets by ultrafast laser ablation in aqueous medium [9] provided SERS substrates capable to record spectra of 5-amino-3-nitro-1,2,4-triazole and 2,4,6-trinitrotoluene after evaporating 10 μL aliquots of $10^{-6}$ M solutions. Nanowires, thanks to their tendency to form bundles and networks, may provide increased number of hotspots located on crossings of individual nanowires and nanowire branches. Twinned copper nanowires prepared using polyoil synthesis were employed for SERS detection of 4-mercaptobenzoic acid (MBA) [10]. A suspension of Cu nanowires was allowed to dry on a silicon plate, the resulting SERS substrate was immersed into $10^{-4}$ M solution of MBA followed by SERS spectra acquisition after evaporating the solvent. The employed synthetic procedure, however, was tedious requiring heating the mixture of CuCl with oleylamine at 170 °C for 60 h. Xu et al. demonstrated electrochemical preparation of Cu nanowires on quartz glass by electrochemical reduction of $Rb_4Cu_{16}Cl_{13}I_7$ ionic conductor and showed the resulting SERS substrate as capable to provide Raman spectrum of rhodamine 6 G after evaporating 10 μL drop of its $10^{-11}$ M solution on the substrate [11].

* Corresponding author.
[1] The authors contributed equally to this work.

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In this work an innovative, facile and green procedure for coating copper nanowires over carbon fiber microelectrodes (CFME) is presented and the high efficiency of these microelectrodes acting as miniature (10 μm in diameter×2 mm in length) SERS substrates is demonstrated. To our best knowledge, there is no report in the literature concerning the use of carbon fiber as a support for SERS active metal nanostructure immobilization. To assess the advantage of the developed SERS substrates we have decided to test their capability to provide SERS spectra of trace amounts of the designer drugs. Designer drugs are substances that are related to the structure of controlled drugs and cause similar effects, but are not listed among illegal substances [12–14]. Most often, their effects are similar to the effects of 3,4-methylenedioxymethamphetamine (Ecstasy), cocaine and/or substances of amphetamine group. Common designer drugs include 4-mephedrone (4-methylmethcathinone, 4-MMC), methylone (3,4-methylendioxy-N-methylcathinone, bk-MDMA, MDMCAT, MDMC), butylone (β-keto-N-methylbenzodioxolyl-propylamine, bk-MBDB) and naphyrone (1-(naphthtalen-2-yl)–2-(pyrrolidin-1-yl)pentan-1-one). The aforementioned compounds have, however, been already included in the list of illegal substances. The still "legal" drugs are buphedrone, products containing 1-benzyl-4-methylpiperazine (MBZP), para-methoxyphenylpiperazine (MOPP) and 4′-Methoxy-α-pyrrolidinopropiophenone (MOPPP).

In drug analysis, liquid and also gas chromatography with mass spectrometry (LC-MS, GC-MS) are the routinely used techniques [15,16]. Recent work by S. Bell et al. [17] demonstrates the SERS detection of four cathinone drugs (mephedrone, 4-methylmethcathinone, 4-chloromethcathinone and benzedrone) on hydroxyethylcellulose films with embedded silver nanoparticles. The sample loadings necessary to obtain high S/N SERS spectra (approx. 100 μg i.e. ~$1\times10^{9}$ molecules per $\mu m^2$ of the substrate) indicate that rather concentrated solutions of samples were needed, corresponding to 10 μL of ca. $10^{-2}$–$10^{-1}$ M solutions dried on their SERS substrates. In agreement with [17], we demonstrate here that SERS is a technique capable to securely distinguish among various structurally similar drugs, thus representing an alternative to LC/GC-MS based analysis while offering improved detection limits. Such an application perfectly fits the high needs in designer drugs detection, often distributed in the form of powder, capsules, caplets or tablets which usually contain only one active ingredient with high purity exceeding 95%. Although the SERS assay specificity is not strictly required for designer drug samples, it is possible to analyse simple mixtures e.g. using spectral deconvolution softwares [18–20] or following our singular value decomposition analysis (SVD) based protocol [21].

## 2. Materials and methods

### 2.1. Reagents and drug samples

Copper wire was purchased from Alfa Aesar (1 mm in diameter, 99.95% purity). Designer drugs samples (Table 1) were obtained from the Police of the Czech Republic. The identification of the samples was performed by LC-MS and GC-MS according to previously published protocols [22,23].

Working solutions of drug samples were prepared from powders by stepwise dilution in Millipore water and ethanol (Chromasolv, Sigma-Aldrich) mixture (50:50 v/v). In the case of tablets, the material was taken from their inner parts, which were finely filed and ca. 10 mg of the resulting powder suspended with 1 mL of ethanol. The mixture was filtered off and evaporated to dryness under stream of nitrogen. The post-evaporation residue was reconstituted with water-ethanol mixture (50:50 v/v).

### 2.2. Preparation of cylindrical carbon fiber microelectrode and its coating with copper nanostructure

A polyacrylonitrile-based carbon fiber (diameter 7 μm, Sigrafil C30) was obtained from a local distributor (GRM-systems, Czech Republic). The carbon fiber taken out from the bundle was glued using conductive silver epoxy (EC101, Polytec, Germany) onto a copper wire, the junction was then hardened at 130 °C for 10 min. The fiber with copper contact attached was fitted into a glass capillary and about 5 mm of the fiber was left protruding from its tapered end. Both ends of the capillary were sealed using low viscosity epoxy resin (L200, Havel Composites Inc., Czech Republic). The fiber end of the electrode was briefly sonicated in dichloromethane in order to clean the fiber. To prepare copper nanostructure onto CFME, a copper wire electrode (1 mm diameter, 2 cm length) was anodized in a two-electrode cell containing ultrapure water as the medium while the CFME was connected as a cathode, the interelectrode distance being 1 cm. Unless stated otherwise, the applied voltage was 30 V and deposition time 5 min. To ensure reproducibility of the coating procedure, each electrode was coated separately, after each coating the used water medium was discarded and the cell was refilled with ultrapure water. Cu coated CFMEs were dried in the air and used for SERS measurements within one week after the preparation.

### 2.3. Scanning electron microscopy and EDX spectroscopy

Scanning electron microscopy (SEM) images were obtained with a Vega 3 (Tescan, Brno, Czech Republic, SE image resolution 2 nm at 30 kV). The images were collected with a high voltage of 15 kV at a working distance ranging from 5 to 25 mm. The sample material (i.e. carbon fibers) was immobilized onto conductive carbon discs after cutting the fiber from the CFME. EDX spectra were collected using the Quantax EasyEDS module (Bruker) integrated into the SEM instrument. The analysis of EDX spectra was performed using EasySEM software with the One-Touch EDX tool.

### 2.4. Raman experiments

To acquire SERS spectra, copper nanostructure coated carbon fiber was cut-off from the microelectrode, placed onto a silicon plate and overlaid by a drop (5 μL) of the sample containing the tested drug. The droplet was spread to cover the fiber substrate using a micropipette tip. For standard samples, concentrations of $10^{-12}$, $10^{-11}$ and $10^{-10}$ mol/L were analysed. Gold SERS substrates (Silmeco, UK) were used in similar way, in typical experiment 5 μL of $10^{-7}$ mol/L sample was carefully pipetted onto the superhydrophobic surface of this substrate. After drying of the sample solution, Raman measurements were

**Table 1**
Tested drug samples.

| Sample | Physical form | Main compound | Alternative name(s) |
|---|---|---|---|
| P2 | Powder | (RS)-2-methylamino-1-(4-methylfenyl)propan-1-on | 4-mephedrone, 4-methylmethcathinone |
| P6 | Capsule | 2-(methylamino)-1-phenylbutan-1-one | Buphedrone |
| T9 | Powder | 1-benzyl-4-methylpiperazine | MBZP |
| T18 | Capsule | 1-(4-Methoxyphenyl)piperazine | MOPP |
| P5 | Powder | 1-(1,3-benzodioxol-5-yl)-2-(methylamino)butan-1-one | 3,4-butylone |