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Two-step fabrication of nanoporous copper films with tunable morphology for SERS application

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\textbf{Highlights}

\begin{itemize}
  \item Facile fabrication of the uniform nanoporous copper is presented.
  \item SERS performance is examined by R6G with a detection limit of $10^{-9}$ M.
  \item The enhancement factor of $4.71\times10^{7}$ is comparable to some Au and Ag systems.
\end{itemize}

\textbf{Abstract}

It is an important issue to design and fabricate nanoporous metals (NPMs) with the optimized microstructures for specific applications. In this contribution, nanoporous coppers (NPCs) with controllable thicknesses and pore sizes were fabricated via the combination of a co-sputtering of Cu/Ti and a subsequent dealloying process. The effect of dealloying time on porous morphology and the corresponding surfaced-enhanced Raman scattering (SERS) behaviors were systematically investigated. Transmission electron microscopy (TEM) identified that both the gaps formed
between ligaments and the nanobumps on the nanoparticle-aggregated ligament surface were likely to contribute as the “hot spots” for electromagnetic enhancement. The optimal NPC film exhibited excellent SERS performance for Rhodamine 6G (R6G) with a low limiting detection (10^{-9} M), along with good uniformity and reproducibility. The calculated enhancement factor of ca. 4.71 \times 10^7 was over Au substrates and comparable to Ag systems, promising the proposed NPC as a cheap candidate to be a high-performance SERS substrate.

**Keywords**: Nanoporous copper, Co-sputtering, Dealloying, Surface-enhanced Raman scattering

1. Introduction

Surface-enhanced Raman scattering (SERS) of pyridine adsorbed on a rough silver surface was firstly reported by Fleischmann et al. in 1974 [1]. SERS, featuring with superior surface sensitivity and specificity, has become a very powerful technique in considerable sensing fields such as pollutant detection of water, air and soil [2, 3], *in vitro* [4, 5] and *in vivo* drugs tracking [6, 7], and *in-situ* monitoring of chemical reactions [8, 9]. Two major explanations, electromagnetic enhancement and chemical enhancement, are responsible to the exponential increase of Raman intensity. The former depends on the localized surface plasmon resonance (LSPR) enhancement, which is thought to play a more important role, and the latter is attributed to the molecular polarization [10-13]. Electromagnetic enhancement is typically generated between nanogaps or junctions, i.e. hot spots, on roughened and nanostructured coinage metals (Ag, Au, and Cu), leading to morphology-dependent SERS behavior [14-16]. Therefore, various nanostructured metallic materials with excellent SERS effect have been synthesized, e.g. nanoparticles in the form of three-dimensional (3D) structures [17, 18], hybrid nanowires [19], and ordered arrays [20]. Flexible and uniform SERS substrates fabricated through simple and clean methods are desired for further applications. One group of the most promising candidates is 3D freestanding nanoporous metal substrates [20-24].

In comparison to the template method using anodized aluminum oxides (AAOs) or polystyrene spheres (PS) for porous SERS substrates, dealloying is a much simpler method omitting laborious preparation of high-quality templates. Dealloyed nanoporous metals present characteristic
bicontinuous and homogenous porous structures and high surface-to-volume ratios, providing significant “hot spots” to absorb target molecules [21, 24-26]. For example, L. Qian et al. have found that smaller pore size and higher roughness of nanoporous gold (NPG) led to more active sites for molecules absorption and stronger electromagnetic field enhancement [27]. L. Zhang et al. reported increased SERS ability of NPG through wrinkling NPG film to produce plenty of microcracks and sharp tips as “hot spots” for electromagnetic enhancement [28]. Meantime, nanoporous silver (NPS) has also been prominently developed for SERS application. H. Qiu et al. prepared NPS integrated silver nanoparticles via dipping NPS ribbons into Ag colloidal solution, revealing that the excellent SERS performance was a result of the tradeoff between the content of residual Al and roughness [29]. R. Li et al. employed electrochemical dealloying of melt-spun Ag-Mg-Ca ribbons for NPS, which showed high SERS signals due to numerous nanocrystals on the ligaments [30].

However, nanoporous copper (NPC) has been laggingly studied. Recent research revealed that nanostructured Cu substrates could reach the same enhancement level of Ag and Au substrates [23, 31]. There is growing interest on the design of reasonable nanostructured Cu as efficient SERS substrates to compete with Au and even Ag. During the dealloying of Cu alloys, less noble metal atoms are selectively dissolved and residual Cu atoms are rearranged on the surface, leading to nanoporous copper (NPC) with significant hot spots [32]. The conventional precursors for dealloy are alloy ribbons (e.g. Cu/Ti, Cu/Al) obtained from melt-spin. The practical SERS applications of NPC ribbons are limited, as they are usually thick and narrow, lacking the plasticity [33-36]. As an effective approach, magnetron sputtering has been recently used to fabricate large scale, continuous and ultrathin NPM precursors [37-40]. To the best of our knowledge, co-sputtering derived NPCs for efficient SERS are barely reported.

Herein, by a simple controllable co-sputtering and dealloying method, we fabricated bicontinuous and flexible NPC films integrated on the Cu foil showing excellent SERS effect. A Cu/Ti system is chosen and Ti is selectively dissolved. The effects of precursor compositions and dealloying conditions on nanostructures of NPC films are studied in detail. Porous structure dependent SERS behavior is proposed. The optimal NPC shows the highest enhancement factor among reported Cu
substrates as far as we know.

2. Experimental

2.1 Chemicals and materials

Hydrochloric acid (HCl, 37%), sulfuric acid (H₂SO₄, 98%), hydrofluoric acid (HF, 40%) were supplied by Shanghai Sinopharm Chemical Co., Ltd (China). Acetone and absolute ethyl alcohol were obtained from Tianjin Fuyu Fine Chemical Co., Ltd (China). Rhodamine 6G (R6G, 99%) was purchased from Aladdin (China). Nitrogen gas (N₂, 99.999%) and argon gas (Ar, 99.999%) were from Jinan Deyang Special Gas Co., Ltd (China). All the chemicals were used as received without further purification. Ultrapure water with a resistivity of 18.25 MΩ•cm from a UPH-IV ultrapure water purifier (Chengdu Ultrapure Technology Co., Ltd, China) was used. Copper foil (99.95 wt.%) of 20 µm thickness, Cu target (99.99%) and Ti target (99.99%) both with a diameter of 60 mm and a thickness of 4 mm were purchased from Goodwill Metal Co., Ltd (China).

2.2 Fabrication of Cu/Ti alloys on Cu foil and the dealloying process

Cu/Ti films with different compositions were prepared by co-depositing Cu and Ti using a magnetron sputtering machine (TRP-450, SKY Technology Development Co., Ltd, CAS) (Scheme 1A). Copper foil (5 cm × 5 cm × 20 µm), washed with 1 M HCl, acetone and absolute ethyl alcohol subsequently and dried with N₂ flow, was used as the substrate for sputtering. Cu and Ti targets were both connected to DC power suppliers. The distance between both targets and the substrate was 11 cm, with an angle of 30°. Deposition of Cu and Ti was performed at the same time for 30 min. The composition of Cu/Ti film was tuned by varying the sputtering power of Ti and keeping Cu target at 30 W. Accordingly, three types of Cu/Ti film with atom ratios of \(~75:25\), \(~65:35\) and \(~48:52\) were fabricated from the sputtering power of Ti at 100, 140 and 220 W. After deposition, the substrate was annealed at 400 °C for 3 h.

To perform dealloy, Cu/Ti film precursors were immersed in the deaerated 0.03 M HF aqueous solution at 30°C for certain durations. As-dealloyed samples were cleaned with ultrapure water and absolute ethyl alcohol, subsequently. The precursors (Scheme 1B) and as-dealloyed samples (Scheme 1C) were all kept in a vacuum desiccator to avoid oxidization and damp.
2.3 Morphology characterization

The morphology and chemical composition of Cu/Ti and NPC films were characterized by scanning electron microscopes (SEM, SU-70 and FEI QUANTA FEG 250), equipped with an energy dispersive X-ray spectroscopy (EDX) system. The microstructure of NPC was further examined using a high-resolution transmission electron microscope (HR-TEM, JEM-2100) at an acceleration voltage of 200 kV. The roughness factor (Rf) of NPC was obtained based the comparison of the electrochemical-double-layer capacitance (EDLC) of NPC and the copper foil. Cyclic voltammetry (CV) was conducted on a CHI 660E electrochemical workstation (Shanghai CH Instruments Co., China) with a conventional three-electrode system, in which 5 × 5 mm² NPC films or copper foils were used as working electrodes, a Pt wire as the counter electrode, and a Ag/AgCl reference electrode. Potential was scanned from -0.11 to -0.05 V, where no faradaic reaction occurring, at a scan rate of 20 mV/s in 0.05 M H₂SO₄.

2.4 SERS test

R6G aqueous solutions with different concentrations from 10⁻⁶ to 10⁻¹⁰ M were prepared. The NPC films were attached on glass slides (Scheme 1D). Prior to usage, the sample was washed in 0.25 M HCl for 1 min to remove oxide on the surface. The immersion in R6G solutions for 4 h permitted sufficient molecule adsorption on the NPC surface, allowed to be dried. SERS spectra were collected on a Renishaw InVia Raman Microscope equipped with RL532C (Class 3B, continuous wave, diode-pumped solid-state laser) operating at 532 nm. All the Raman spectra were obtained from an area with a diameter of 2 µm with a laser power of 0.25 mW. Exposure durations of 10 and 1 s were adopted for the single point test and line-mapping mode, respectively. To test the storage stability, samples with a dealloy time of 1.5 h were kept in a desiccator with granular desiccant silica gel for nine months.

3. Results and discussions

3.1 Fabrication of Cu₇₅Ti₂₅ film on the Cu foil

Fig. 1A and 1B show the surface morphology of a Cu foil supported Cu₇₅Ti₂₅ film fabricated by
magnetron sputtering and subsequent annealing. Streaks were observed on the alloy film, while not seen on a smooth Si wafer (Fig. S1). It implied that the streaks originated from the native fluctuations of Cu foils (Fig. S2). A closer observation revealed that the Cu75Ti25 film was composed by nanoparticles with an average diameter of 15.7±2.7 nm confirmed by AFM imaging (Fig. S3). EDX analysis verified the presences of both Cu and Ti, and their homogenous distribution (Fig. 1C and Fig. S4). The cross-section view SEM image of the Cu75Ti25 film (30 min deposition) on a Si wafer after annealing shows a thickness of ca. 335 nm (Fig. S5a and S5c). The sputtering rate of Cu75Ti25 film was determined to be 11.3±0.2 nm/min when the sputtering power of Cu and Ti was 30 and 100 W (Fig. S5b). In other words, the thickness of the precursor can be easily tuned by changing the co-sputtering time.

3.2 The effect of dealloying time on the corresponding porous structure

The morphology of the porous structure was significantly influenced by dealloying conditions, which was explored here by control experiments. Fig. 2 shows SEM images of as-dealloyed NPCs obtained by dealloying Cu75Ti25 in 0.03 M HF at 30 °C for various durations. Ti atoms are preferentially dissolved from the Cu/Ti alloy in HF [33]. EDX analysis (Fig. S6b) indicates the complete removal of Ti from the thin alloy film after 1.5 h immersion. During dealloying, the remaining Cu atoms can reorganize into clusters at beginning and form connected islands instead of spreading over the surface, leading to uniform porous Cu structures [41]. The average pore sizes increased from 33.0±9.6 to 57.0±9.3 nm with the dealloying time prolonging from 0.5 to 5 h (Fig. 2H). This type of morphology transformation is mainly due to the rearrangement of Cu atoms on ligaments with time [33, 42].

NPC in Fig. 2A showed many cracks with hundreds of nanometers in length. They originated from the crevice-rich precursor (Fig. 1A and B) and the volume contraction introduced stresses during dealloying. The later phenomenon has been widely observed for nanoporous gold obtained from glass or Si supported Au/Ag precursors [38, 43], in contrast to the crack-free nanoporous structure obtained from self-supporting Au/Ag leaves [27, 44]. Pores grew larger with dealloy time and
occupied the original space of these cracks, leading them to be narrowed and shortened. After 3 h dealloy, the cracks became inconspicuous from pores because of the rearrangement of Cu atoms on ligaments (Fig. 2E and F). The cross-section SEM image shows no collapses on the thickness after dealloying (Fig. S5d). Besides, there was no detachment of the NPC film from the Cu substrate because the annealing process promoted the adhesion between the Cu foil and alloy.

TEM images of the as-dealloyed NPC further confirm that the bicontinuous nanostructure comprising inter-connected pores and ligaments (Fig. 3A). The pore size distributes from less than ten nanometers to more than fifty nanometers. There exist obvious cracks with several hundred nanometers in length and tens of nanometers in width, consistent with cracks in Fig. 2C. Ligaments are a few tens of nanometers to more than one hundred nanometers in width. Rough ligaments consist of many nanoparticles, as confirmed by high-magnification TEM images (Fig. 3B, C and D), contribute as “hot spots”.

Selective area electron diffraction (SAED) verified the polycrystalline feature of inter-connected ligaments. The SAED pattern (Fig. 3F) shows distinctive diffraction rings that are corresponding to the fcc Cu (111), (200), (220) and (311). EDX spectrum (Fig. S6b) and the thin layer with low contrast on ligaments (Fig. S6c) verified the formation of oxidation layer on NPC. The weak rings are identified as Cu$_2$O (110), (111), (200), (220) and (311) reflections (Fig. 3E), arising from the oxidation of Cu atoms on the outer surface of NPC ligaments as a consequence of the exposure to air during sample preparation. [33, 35]

Cu/Ti precursors with other different atom ratios (Cu$_{48}$Ti$_{52}$ and Cu$_{65}$Ti$_{35}$) were also dealloyed. Fig. S7 shows microstructures of NPCs obtained by dealloying these precursors in 0.03 M HF for 1 h and 2 h at 30°C. There were lots of granular aggregates attached on the Cu foil after 1 h dealloy (Fig. S7a). However, after 2 h dealloy, the resulting NPC presented isolated islands with partial Cu foil substrate exposed (Fig. S7b). The significant difference on structure from that of Cu$_{75}$Ti$_{25}$ derived NPC is due to the larger ratio of Ti. For both cases, the longer dealloying resulted in larger pores.
These results reveal that both the atom ratio of precursor and dealloy time are decisive parameters to control the structure of NPC.

### 3.3 SERS performance of the NPC film

As previously reported on NPS and NPG substrates [27, 29], SERS performance of the substrates is sensitive to the porous structure. To demonstrate the structure-dependent behavior, the Raman spectra of R6G were collected on NPCs obtained by dealloying Cu$_{75}$Ti$_{25}$ with different time (Fig. 4). It is obvious that all samples showed efficient enhancement for R6G with an optimal dealloy time of 1.5 h. As shown in Fig. 2 and Fig. 4, the shorter dealloying time led to smaller pore size, and larger specific surface area/Rf. L. Qian et al. have showed that NPG substrate obtained from Au/Ag alloy with small pores/high surface area favored SERS enhancement. However, rather high residual Ti content in NPC film obtained with short dealloy time could bring degradation to SERS effect, which caused a lower SERS signal on the NPC with smaller pore size [29, 32]. By dealloying less than 1.5 h, higher Ti content NPC with shorter time inhibited the SERS activity, so that we saw the increased SERS signal with dealloy time. By dealloying more than 1.5 h, the specific surface area played a prominent role, so that we saw the decreased SERS activity with dealloying time [41]. The optimal sample obtained by 1.5 h dealloying is the result of the negligible Ti content and the high Rf. We also observed that ligaments became smoother with time, leading to the declined population of the “hot spot” (Fig. 2C and F, Fig. S8). Besides this, the increased pore size is also likely to weaken SERS signals by reducing localized electromagnetic fields [27, 30]. In conclusion, 1.5 h was chosen as the appropriate dealloy time for further study.

To evaluate the sensitivity of the selected NPC as the SERS substrate, the Raman intensities of the R6G adsorbed on the NPC surface were collected. Fig. 5A shows that the characteristic peaks of R6G at 1182, 1312, 1362, 1507, 1579, 1601 and 1651 cm$^{-1}$ are discernible when concentration down to $10^{-9}$ M, but not identified in $10^{-10}$ M (Fig. S10). The detect limitation of $10^{-9}$ M is lower than most of the reported Cu substrates (Table 1) [32, 45]. The enhancement factor (EF) was calculated based on the peak density of 1651 cm$^{-1}$ by the following equation [46, 47]:

\[
\text{EF} = \frac{I_{\text{SERS}}}{I_{\text{Raman}}} 
\]
Where \( C_{\text{SERS}} \) and \( I_{\text{SERS}} \) are the concentration and peak intensity of Raman under SERS conditions, respectively, and \( C_0 \) and \( I_0 \) are the concentration and peak intensity of the normal Raman measurement, with a 0.01 M R6G aqueous solution on the Si wafer and on copper foil used for substrate of sputtering. EFs of Cu foil and Si wafer supported NPCs could be calculated to be as high as \( 4.71 \times 10^7 \) and \( 5.28 \times 10^6 \), separately (Fig. S11). The EF of \( 4.71 \times 10^7 \) is outstanding over previously reported Cu based materials (Table 1). Such EF is higher than those of gold substrates presenting EFs in the order of magnitude of \( 10^5-10^6 \)\cite{27, 48}, and comparable to silver systems up to \( 10^7-10^{10} \)\cite{24,29,30,50,51}. 

Fig. 5B shows concentration-dependent SERS intensities. The prominent peaks at 1651, 1362 and 1182 cm\(^{-1}\) were chosen as the intensity standard. The intensities of the related bands increased with the concentration of the R6G aqueous solution. A relatively good linearity was obtained in the range of \( 10^{-6} \)M to \( 10^{-9} \)M. The log-log plot of the concentration-dependent SERS intensity presented excellent linear relationships. The slopes at 1651 cm\(^{-1}\), 1362 cm\(^{-1}\), 1182 cm\(^{-1}\) were calculated to be 0.727, 0.708, and 0.665, respectively, with \( R^2 \) of 0.976, 0.992, and 0.973, qualified for the quantitative detection of analytes absorbed on the NPC surface.

Excellent SERS enhancement from NPMs, including NPG, NPS, and NPC, are owing to the chemical enhancement and electromagnetic enhancement \cite{10, 11}. For metallic nanostructures, electromagnetic enhancement is thought as the main enhancement mechanism \cite{52, 53}. Raman “hot spots” for the enhancement of the electromagnetic effect are believed to be attributed to the crevices and junctions between neighboring nanoparticles \cite{14-16} and nanostructures with sharp corners or tips \cite{28, 54}. For the optimal NPC we fabricated, there exist two kinds of structures that can act as “hot spots”. One is the pores or gaps formed between ligaments marked with red circles in Fig. 3 with an average size of 41.6±9.2 nm, which is a distance that can generate Raman enhancement under laser irradiation \cite{27}. Another one is on the rough ligaments presenting large number of nanobumps and nanotips, identified with blue cycles in Fig. 3. Previous reports \cite{29, 39} showed that NPM with rough ligaments displayed high SERS capability even with larger pores as
metal particles on the ligaments can generate more “hot spots”, which is also applicable in this work. Besides this, 3D nanoporous structures provide abundant locations for these “hot spots” for electromagnetic enhancement than plat substrates.

The uniformity and reproducibility of the NPC film are other vital factors for SERS applications. To test the substrate’s uniformity, we collected SERS spectra of $10^{-7}$ M R6G from the line-mapping test of 50 points covering a length of 150 µm. The intensities of the R6G Raman vibrations at 1651 cm$^{-1}$, 1362 cm$^{-1}$, 1182 cm$^{-1}$ were selected (Fig. 6A, B and C) displaying relative standard deviations (RSD) of 8.73%, 9.51%, and 9.67%, respectively, which were all less than 10%. The reproducible Raman spectra implies that the interesting areas with a diameter of 2 µm, which is much bigger than pores size and ligaments size, contained almost the same number of “hot spot”. Moreover, the proposed route for NPC fabrication is repeatable. Fig. 6D shows that peak intensities of the five samples at 1182 cm$^{-1}$ exhibited a RSD of 9.27%. Overall, the excellent activity, uniformity and reproducibility of NPC SERS substrates, along with the cost-efficient materials and fabrication, allow the potential application in detection fields. Fig. S12a shows the Raman spectra of $10^{-7}$ M R6G on the optimal NPC film after nine-month storage in air with acid washing. Characteristic peaks of R6G at 1362, 1507, 1579, and 1651 cm$^{-1}$, were still discernible, although the intensity at peak 1651 cm$^{-1}$ decreased by 43.6% (Fig. S12b). The signal decline was attributed to the decreased surface roughness by 26.6% (from 4.9 to 3.6, Fig. S12b) as a result of the removal of oxidation layer by acid washing. SEM examination (Fig. S12c and S12d) showed that it preserved the bicontinuous porous structure, displaying nanobumps on ligaments (as pointed by red arrows in Fig. S12d). The above observation implies that the sample was still active to low concentration of R6G.

4. Conclusions

We have developed a type of low-cost and mass-producible NPC SERS substrates with high sensitivity and uniformity through the co-sputtering Cu/Ti and subsequent dealloy. The dealloy conditions determined the resulting porous structure and the corresponding SERS activity. The ultrathin NPC film with 3D bicontinuous nanostructure presented significant “hot spots” on the ligaments. The enhancement factor of the optimal substrate is as high as $4.71 \times 10^7$, the highest among reported Cu substrate as far as we know. Besides SERS, the NPC film fabricated by this
method has practical potential in catalysis and energy storage field with easy adjustment of the NPC structure to meet different requirements.

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References


Figures and captions

**Figure 1.** SEM images of a Cu$_{75}$Ti$_{25}$ film integrated on Cu foil at a low (A) and high magnification (B) and the corresponding EDX spectrum (C).

**Figure 2.** SEM images of NPCs obtained by chemically dealloying Cu$_{75}$Ti$_{25}$ in 0.03 M HF for A: 0.5 h, B: 1 h, C: 1.5 h, D: 2 h, E: 3 h, F: 5 h. The Cu and Ti content profile with dealloy time (G). The evolution of pore size with dealloy time (H).

**Figure 3.** TEM images of the NPC obtained by dealloying Cu$_{75}$Ti$_{25}$ in 0.03 M HF for 1.5 h at 30°C (A-D) and the corresponding selected-area electron diffraction (SAED) patterns (E). Red circles represent nanogaps and nanopores, and blue circles represent nanotips or nanobumps on ligaments in this film.

**Figure 4.** The dependence of the intensity of 1651 cm$^{-1}$ Raman band (red line) and roughness factor (blue line) on dealloy time.

**Figure 5.** Raman spectra on the optimal NPC film in various concentrations of R6G (A); Log-log plot of the Raman intensity peak of at 1651, 1362 and 1182 cm$^{-1}$ versus the R6G concentration (B).

**Figure 6.** Intensities of three main Raman vibrations (A: 1182 cm$^{-1}$; B: 1362 cm$^{-1}$; C: 1651 cm$^{-1}$) obtained in 10$^{-7}$ M R6G on 50 spots of the NPC film. D: Reproducibility of the NPC tested by recording intensities at 1182 cm$^{-1}$ of Raman spectra on five different samples.

**Scheme 1.** (A) Fabrication process of the NPC film. Digital photos of the flexible Cu/Ti film on Cu foil (B), the NPC film integrated on Cu substrate (C) and the glass slide supported NPC for SERS study (D).
Figure A: Raman shift (cm⁻¹) vs. intensity (a.u.) for different concentrations of RG. The peaks at various Raman shifts correspond to the different concentrations.

Figure B: Plot of log(I) vs. log(C) for RG concentrations. The linear fits show correlation coefficients (R²) of 0.976, 0.932, and 0.973 for different bands at 1651 cm⁻¹, 1362 cm⁻¹, and 1192 cm⁻¹, respectively.
Table 1. Comparison between the proposed NPC and previously reported SERS substrates

<table>
<thead>
<tr>
<th>Structure</th>
<th>Calculation method</th>
<th>EF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPS ribbon</td>
<td>$EF = \frac{(I_{SERS}/I_{bulk}) \times (N_{bulk}/N_{SERS})}{6 \times 10^{-4} g/mL}$ R6G</td>
<td>$7.5 \times 10^5$</td>
<td>[29]</td>
</tr>
<tr>
<td>NPS film</td>
<td>$EF = \frac{(I_{SERS}/I_{bulk}) \times (N_{bulk}/N_{SERS})}{10 \text{ mM 4-Mercaptobenzoic acid}}$</td>
<td>$6 \times 10^6$</td>
<td>[49]</td>
</tr>
<tr>
<td>NPG film</td>
<td>$EF = \frac{(I_{SERS}/I_{bulk}) \times (N_{bulk}/N_{SERS})}{10^{-8} M}$ R6G</td>
<td>$\sim 10^6$</td>
<td>[27]</td>
</tr>
<tr>
<td>NPG film decorated with Ag nanoparticles</td>
<td>$EF = \frac{(I_{SERS}/I_{0}) \times (C_0/C_{SERS})}{10^{-7} M}$ P-aminothiophenol</td>
<td>$1.4 \times 10^5$</td>
<td>[48]</td>
</tr>
<tr>
<td>Ag-nanorod arrays on alumina nanotip arrays</td>
<td>$EF = \frac{(I_{SERS}/I_{RS}) \times (N_{RS}/N_{SERS})}{10^{-10} M}$ R6G</td>
<td>$3.2 \times 10^7$</td>
<td>[24]</td>
</tr>
<tr>
<td>Ag-Cu nanoparticle-decorated graphene</td>
<td>$EF = \frac{(I_{SERS}/I_{0}) \times (C_0/C_{SERS})}{10^{-5} M}$ R6G</td>
<td>$2.5 \times 10^6$</td>
<td>[50]</td>
</tr>
<tr>
<td>Ag-nanoparticle-decorated ZnO nanoflowers</td>
<td>$EF = \frac{(I_{SERS}/I_{0}) \times (C_0/C_{SERS})}{10^{-6} M}$ R6G</td>
<td>$\sim 4 \times 10^7$</td>
<td>[51]</td>
</tr>
<tr>
<td>NPC ribbon</td>
<td>$EF = \frac{(I_{SERS}/I_{bulk}) \times (N_{bulk}/N_{SERS})}{10^{-5} M}$ R6G</td>
<td>$1.85 \times 10^5$</td>
<td>[32]</td>
</tr>
<tr>
<td>Thin NPC foil</td>
<td>$EF = \frac{(I_{SERS}/I_{0}) \times (C_0/C_{SERS})}{10^{-6} M}$ R6G</td>
<td>$2.52 \times 10^5$</td>
<td>[45]</td>
</tr>
<tr>
<td>Cu nanoparticles/Si wafer</td>
<td>$EF = \frac{(I_{SERS}/I_{0}) \times (C_0/C_{SERS})}{10^{-9} M}$ R6G</td>
<td>$2.29 \times 10^7$</td>
<td>[23]</td>
</tr>
<tr>
<td>Cu platform</td>
<td>$EF = \frac{(I_{SERS}/I_{bulk}) \times (N_{bulk}/N_{SERS})}{10^{-6} M}$ Malachite green isothiocyanate</td>
<td>$4.6 \times 10^7$</td>
<td>[31]</td>
</tr>
<tr>
<td>Cu nanoparticles/graphene/Cu foil</td>
<td>$EF = \frac{(I_{SERS}/I_{bulk}) \times (N_{bulk}/N_{SERS})}{0.5 \text{ nm Copper phthalocyanine}}$</td>
<td>$1.9 \times 10^7$</td>
<td>[46]</td>
</tr>
<tr>
<td>NPC film/Cu foil</td>
<td>$EF = \frac{(I_{SERS}/I_{0}) \times (C_0/C_{SERS})}{10^{-9} M}$ R6G</td>
<td>$4.71 \times 10^7$</td>
<td>this work</td>
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