



# Carbon fiber cloth-supported Au nanodendrites as a rugged surface-enhanced Raman scattering substrate and electrochemical sensing platform



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## ABSTRACT

A carbon fiber cloth (CFC)-supported Au nanodendrite (CFC-AuND) prepared by simple electrodeposition of Au onto CFC has been demonstrated. The motivation of employing CFC was to fully incorporate its useful characteristics of flexibility, porosity, and conductivity in the development of substrates versatile for both surface-enhanced Raman scattering (SERS) and electrochemical measurements. To improve sample representation in SERS measurement, a wide area coverage (WAC) scheme able to cover an area of 28.3 mm<sup>2</sup> (illumination diameter: 6 mm) was used to compensate for the variation in Raman intensities of analytes adsorbed at different locations on the substrate. When a 1 nM 2-naphthalenethiol sample was measured using CFC-AuND, the corresponding Raman peaks were clearly observed and the substrate-to-substrate reproducibility of five separately prepared substrates was acceptable, with the relative standard deviation (RSD) of 8.5%. In addition, since the substrate was physically flexible, its SERS performance was not seriously degraded even after moderate bending. Next, the CFC-AuND substrate was used for the electrochemical detection of Hg(II) in aqueous samples by means of stripping voltammetry. The limit of detection (LOD) was 0.09 ppb and the substrate-to-substrate reproducibility was also superior, with RSDs below 3.6%. Overall, the results of the present work demonstrate the potential of CFC-AuND as a rugged, field-usable, cost-effective substrate for SERS and electrochemical measurements.

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## 1. Introduction

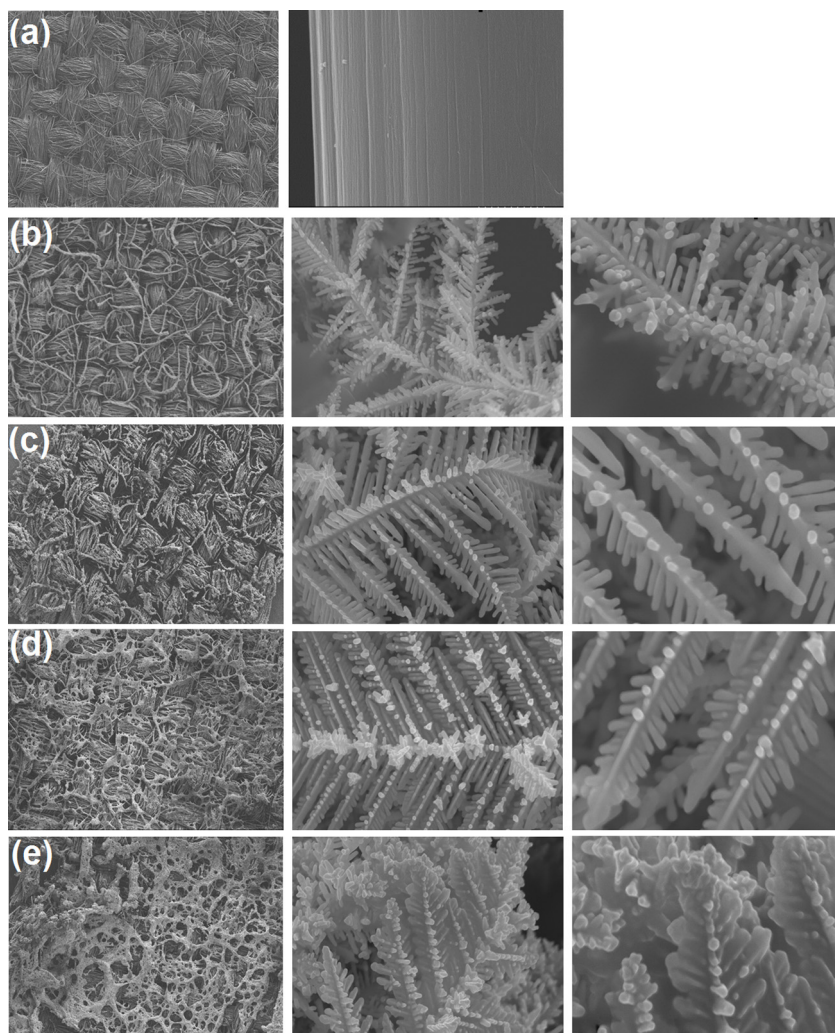
Recently, diverse metallic nanostructures have been developed for use as electrochemical sensing platforms, surface-enhanced Raman scattering (SERS) substrates, and catalysts. The motivation behind these material developments was to take advantage of the attractive characteristics of nanostructures for various applications, such as large surface area, enhanced optical/electrochemical properties, and efficient catalytic activity. As one effort in exploring novel nanostructures, our group has demonstrated nanodendrites composed of either Au only [1] or the multiple metals of Au/Ag [2] and Au/Ag/Pt [3]. The reported nanodendrites possessed a hierarchical structure with numerous terraces and edges, making a large number of active sites available that were beneficial for enhancement of SERS and catalytic activity. All these structures

were electrochemically constructed either on planar Pt or Ti substrates.

To develop rugged and practical nanostructure-based substrates employable for routine analysis, the supporting material itself must be durable without physical degradation, easily tailorable for application needs, and cost-effective. In addition, if it is also a conductor, the substrate will be further applicable for electrochemical sensing and electrocatalysis. In this sense, carbon fiber cloth (CFC) could be a promising candidate because it is an inexpensive conducting fabric with good physical flexibility and durability. The flexibility of CFC enables the design of substrates with diverse shapes and sizes, and the porous structure allows fast absorption of analytes, enabling rapid analysis. Also, CFC is chemically stable and cheap. Due to these advantages, several nanostructures constructed on CFC have been reported and applied for various applications; examples include electroless plating of Ag nanoparticles onto CFC for SERS measurements of Rhodamine 6G [4], and one-dimensional ZnO functional nanostructure loading onto CFC for removal of copper ions [5]. Demonstrations of CFC-supported catalysts have included Pd–Au

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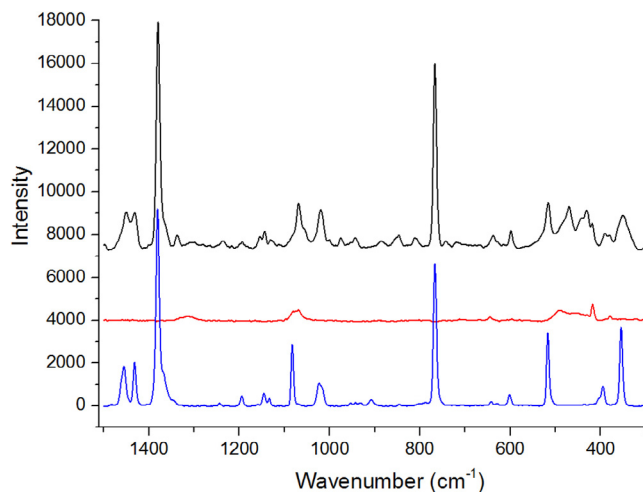
E-mail address: [hoeil@hanyang.ac.kr](mailto:hoeil@hanyang.ac.kr) (H. Chung).



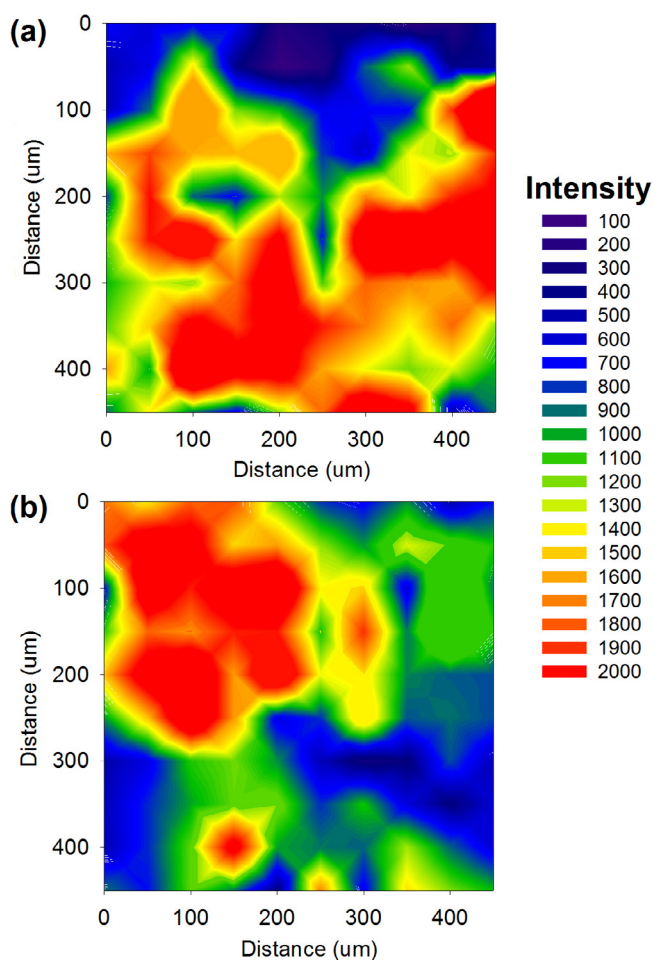
**Fig. 1.** SEM images of CFC-AuNDs prepared by using various electrodeposition durations: (a) 0 s (bare CFC), (b) 180 s, (c) 240 s, (d) 300 s, and (e) 360 s. Images in the left, center, and right columns respectively cover the areas of  $4.19 \text{ mm} \times 3.04 \text{ mm}$ ,  $4.33 \mu\text{m} \times 3.11 \mu\text{m}$ , and  $1.81 \mu\text{m} \times 1.33 \mu\text{m}$ .

bimetallic catalysts for direct  $\text{H}_2\text{O}_2$  synthesis [6], Au nanoflowers for ethanol electrooxidation [7], and Au nanodendrites for  $\text{H}_2\text{O}_2$  electroreduction/electrooxidation [8]. Relatedly, Co–Ni layered double hydroxide nanoflakes [9] and  $\text{NiFe}_2\text{O}_4$  nanoparticles on CFC [10] have been suggested as flexible supercapacitors. Also, a CFC-supported  $\text{Co}_3\text{O}_4/\text{PbO}_2$  core–shell nanorod array has been evaluated as an electrochemical glucose sensor [11].

This paper reports a dual-functional CFC-supported Au nanodendrite (CFC-AuND) versatile for both SERS and electrochemical measurements. Its fabrication was easily accomplished by simple electrodeposition of Au on CFC and the variation of Au nanodendrite structures resulting from varying the electrodeposition duration was examined. SERS is a highly localized event and the measured intensity of an analyte sensitively varies depending on the surrounding plasmonic conditions [12–14], so measurement reproducibility is a critical concern when SERS-based quantitative analysis is desired [15]. One reliable and practical approach to acquire reproducible and quantitatively representative SERS spectra could be the use of a scheme enabling bulk Raman sampling covering a large area on a SERS substrate in spectral acquisition, such as the wide area coverage (WAC) scheme covering an area of  $28.3 \text{ mm}^2$  (illumination diameter:  $6 \text{ mm}$ ) [15,16]. In this way,



**Fig. 2.** SERS spectrum of 2-NpSH adsorbed on CFC-AuND (black), compared with normal Raman spectra of bare CFC (red) and 2-NpSH powder (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** SERS mapping images showing the intensity of the  $1378\text{ cm}^{-1}$  band, acquired from two different locations on a CFC-AuND sample. Each image covers the area of  $450\text{ }\mu\text{m} \times 450\text{ }\mu\text{m}$ . Redder and bluer colors respectively indicate higher and lower SERS intensities. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

varying Raman intensities of an analyte emanating from different locations on a substrate can be leveraged, as the intensity over a wide area is more quantitatively representative and reproducible. To match the size of the illumination area, a CFC was cut into a  $0.6\text{ cm} \times 0.6\text{ cm}$  piece and Au nanodendrites were constructed on it by electrodeposition in the presence of iodide as a co-reagent as previously reported [1]. The fabricated CFC-AuND was then used to measure 2-naphthalenethiol (2-NpSH) samples of different concentrations and the corresponding variations in intensity were investigated. In parallel, 5 separately prepared CFC-AuNDs were employed to measure each sample and the substrate-to-substrate reproducibility was assessed. Finally, the durability of the substrate was tested by repeatedly folding a 2-NpSH-bound substrate in half and unfolding it, and observing its Raman spectra after various numbers of folding cycles up to 100.

CFC-AuND is potentially useful for electrochemical measurements due to its high surface-to-volume ratio, which provides a large electro-active surface, and its porous structure, which facilitates analyte diffusion inside the material. Its utility was examined by measuring Hg(II) in a low concentration range (1–100 ppb) using stripping voltammetry, and assessing the resulting analytical performance with respect to sensitivity and substrate-to-substrate reproducibility. Finally, a diffusional electrode area ( $A_{\text{diff}}$ ) of the substrate was calculated.

## 2. Experimental

### 2.1. Construction of Au nanodendrites on CFC

All reagents necessary for the construction of Au nanodendrites and subsequent measurements,  $\text{HAuCl}_4$  (99.999%), KI,  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ , and 2-NpSH, were purchased from Sigma-Aldrich. CFC ( $20\text{ cm} \times 20\text{ cm} \times 0.36\text{ cm}$ ) was obtained from Nara Celltech Corp. (Seoul, Korea). For the preparation of CFC-AuND, a precursor solution of  $20\text{ mM HAuCl}_4$ ,  $0.5\text{ M H}_2\text{SO}_4$ ,  $1.0\text{ mM KI}$ , and  $5\text{ M NH}_4\text{Cl}$  was prepared. A  $6\text{ mm} \times 6\text{ mm}$  piece of CFC was immersed in this solution and a current of  $50\text{ mA}$  was applied using a galvanostat to carry out the electrodeposition, following a previously reported experimental protocol [1]. The electrodeposition duration was varied from 180 to 360 s (interval: 60 s), and the resulting structures of Au nanodendrites that formed on the CFC under each condition were examined. SEM images of CFC-AuNDs were acquired using a Hitachi S-4800 SEM.

### 2.2. Raman and electrochemical measurements using CFC-AuND

For each SERS measurement,  $10\text{ }\mu\text{L}$  of a  $10\text{ }\mu\text{M}$  2-NpSH solution was dropped onto a CFC-AuND sample and the 2-NpSH was allowed to adsorb onto the Au surface for 1 min. Then, triplicate Raman spectra of this sample were collected using the WAC scheme, allowing laser illumination over a circular area of  $28.3\text{ mm}^2$  with the diameter of  $6\text{ mm}$  ( $\lambda_{\text{ex}}$ :  $785\text{ nm}$ , PhAT probe, Kaiser Optical System). The triplicate spectra (resolution:  $4\text{ cm}^{-1}$ ) were collected by randomly positioning the substrate before each measurement and each spectrum was acquired using the exposure time of 50 s. Baseline correction of spectra was performed using Matlab version 7.0 (The MathWorks, Inc., MA, USA).

All electrochemical measurements were performed at room temperature using a three-electrode system in which Ag/AgCl and Pt wire were used as reference and counter electrodes, respectively. The working electrodes used in this study were CFC-AuNDs prepared using various electrodeposition times for comparison. The three-electrode system was connected to a custom-made multifunction potentiostat/galvanostat manufactured at the Vietnam Academy of Science and Technology (Hanoi, Vietnam). It was equipped with a 12-bit analog–digital converter (ADC) and the signal was amplified by two operational amplifiers equipped with an active filter. Noise was reduced using a custom-written noise reduction algorithm. Overall, the system provided current resolution down to  $0.008\text{ nA}$ , suitable for sensitive electrochemical measurements. Data acquisition was performed using a custom software developed by our group.

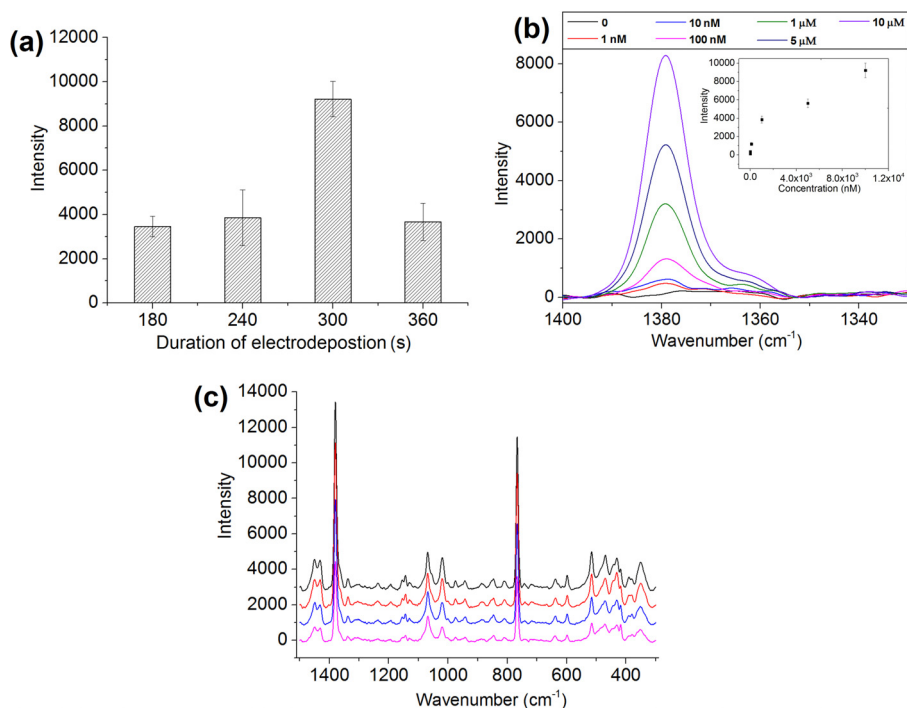
Hg(II) sample solutions were prepared by using a standard mercury solution (1000 ppm) purchased from Merck. The supporting electrolyte used for voltammetric experiments was mixture of  $0.1\text{ M KCl}$  and  $\text{HCl}$  at pH 3.0. Diluted sample solutions of desired concentrations were freshly prepared using the stock solution before measurement. The determination of Hg(II) was accomplished using anodic stripping voltammetry (ASV). Initially, a potential of  $0.0\text{ V}$  (vs. Ag/AgCl) was applied to a sample with stirring over 180 s, and after 10 s quiescence, a stripping voltammogram was acquired over the scan range from  $0.0$  to  $+1.0\text{ V}$ .

## 3. Results and discussion

### 3.1. Characterization and evaluation of CFC-AuNDs for SERS measurement

Fig. 1 shows SEM images of bare CFC and CFC-AuNDs prepared with the electrodeposition durations of 180, 240, 300, and 360 s.





**Fig. 4.** (a) Intensities of the 2-NpSH peak at  $1378\text{ cm}^{-1}$  obtained for CFC-AuND samples prepared using four different electrodeposition durations. (b) Raman spectra ( $1400\text{--}1330\text{ cm}^{-1}$  range) of six 2-NpSH samples ranging in concentration from  $1\text{ nM}$  to  $10\text{ }\mu\text{M}$ , measured using the CFC-AuND substrates (300 s electrodeposition). (b, inset) Variation of peak intensities at  $1378\text{ cm}^{-1}$  in the spectra. (c) Raman spectra of a 2-NpSH-adsorbed substrate subjected to 0 (black), 10 (red), 50 (blue), and 100 (pink) cycles of folding/unfolding. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In images of bare CFC before electrodeposition (Fig. 1a), the woven carbon fibers (left) and clear CFC surface (right) can be observed. After electrodeposition of 180 s (Fig. 1b), Au deposition on the fibers was apparent (left) and the formation of nanodendrites was evident in magnified images (center and right); however, the growth of terraces was immature. With longer electrodeposition periods, the Au nanodendrites that formed were denser (Figs. 1c–e, left column) and the dendrite structure became more distinct (center and right columns). The 300-s electrodeposition produced nanodendrite structures with terraces well aligned along the column and the distances between two adjacent terraces were very small (Fig. 1d); this structure was potentially useful for generating SERS hotspots. However, after the longer electrodeposition period of 360 s, the overall shape of the nanodendrites became less characteristic and included blunt edges, which would degrade SERS efficiency.

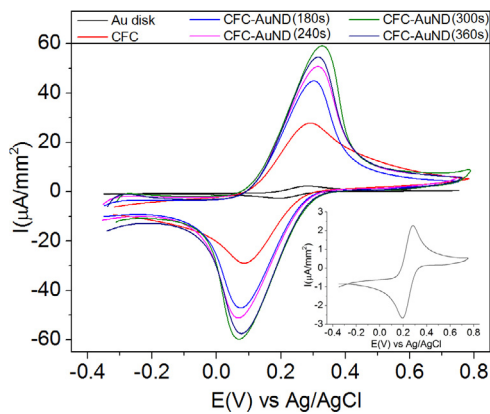
Fig. 2 shows Raman spectra of 2-NpSH-adsorbed on CFC-AuND (black, prepared with 300-s electrodeposition), pure 2-NpSH powder (blue) and bare CFC (red). In the 2-NpSH SERS spectrum, two major bands were observed at  $1378$  and  $764\text{ cm}^{-1}$ , assigned respectively to ring stretching and ring deformation [17]; these were also observed in the 2-NpSH powder spectrum, but the intensities were slightly stronger in the sample spectrum. This clearly indicated that the substrate enhanced the intensities of the 2-NpSH peaks. The CFC peaks were much simpler and less intense than the 2-NpSH peaks; this low background signal of CFC could be advantageous for spectroscopic analysis.

Although SERS is beneficial for analytical applications demanding sensitive measurement, its reproducibility is of great concern, especially when quantitative analysis is desired. Because SERS is a highly localized event, Raman intensities of an adsorbed analyte would sensitively vary depending on its surrounding plasmonic environment. Moreover, the porous structure of the CFC could exacerbate the fluctuations in SERS intensity, because a decrease of intensity is expected when the laser illuminates a void space in

the CFC during spectral acquisition. For examination of potential intensity variation, the CFC-AuND used in Fig. 2 was chosen again for study. A  $10\text{ }\mu\text{L}$  solution of  $10\text{ }\mu\text{M}$  2-NpSH was dropped on the substrate, and was nearly instantaneously absorbed into the substrate due to its porous fabric structure. Raman mapping of this sample was performed over an area of  $450\text{ }\mu\text{m} \times 450\text{ }\mu\text{m}$ , and the variation of peak intensities in the mapping was investigated. The mapping interval was  $50\text{ }\mu\text{m}$  in both the  $x$  and  $y$  directions, and a total of 100 spectra were collected. The mapping was performed twice at different locations.

Fig. 3 shows two maps of the intensity of the  $1378\text{ cm}^{-1}$  band on the 2-NpSH-adsorbed substrate; this band was chosen because it was the strongest band for 2-NpSH. In both cases, the intensity variation over the mapped area was substantial; very low-intensity areas (smaller by a factor of about 20 than the highest intensity) were observed as expected. The relative standard deviations (RSDs) of the intensities over the 100 mapping points in the mappings shown in Fig. 3a and b were 54.6 and 47.6%, respectively. Thus, to use this substrate for quantitative analysis, a method to minimize the intensity fluctuation was needed. Obviously, small-area sampling for acquisition of Raman spectra was undesirable, such as that achieved by using a microscope.

One simple and effective approach to minimize the effects of intensity fluctuation and to produce more quantitatively representative SERS spectra was large-area sampling in spectral acquisition. A WAC scheme covering more than 95% of the substrate area was suitable for this purpose. To evaluate the substrate-to-substrate reproducibility, 5 CFC-AuNDs were prepared for each electrodeposition duration and triplicate SERS spectra of 2-NpSH adsorbed on the substrates were acquired as described above. Fig. 4a shows the average intensities of the  $1378\text{ cm}^{-1}$  band acquired using the 5 substrates prepared at the 4 different electrodeposition durations. The intensity was maximized when the electrodeposition duration of 300 s was used; this was attributed to the more perfect



**Fig. 5.** CVs of  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  acquired using an Au disk, bare CFC, and CFC-AuND substrates prepared using the electrodeposition durations of 180, 240, 300, and 360 s. (Inset) Enlarged view of the CV measured using the Au disk.

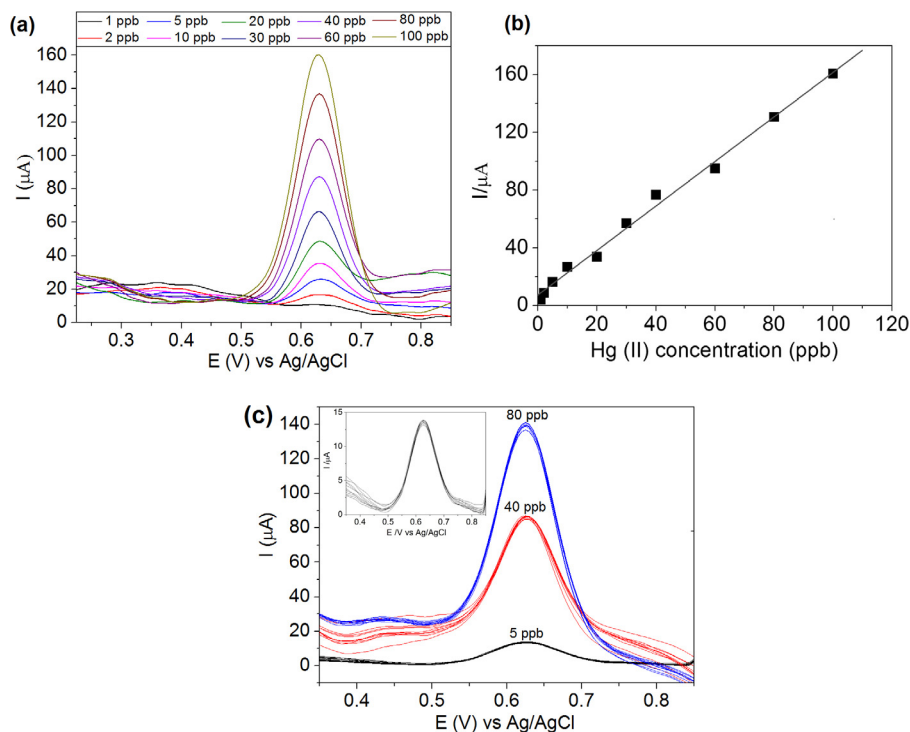
nanodendrite structure formed under this condition, possessing well-aligned terraces with small inter-terrace distances as shown in Fig. 1d. Also, the substrate-to-substrate reproducibility was good, with the relative standard deviation (RSD) of 8.5%. The RSD of the intensities of triplicate spectra acquired from one substrate was 1.5%. The use of the WAC scheme clearly contributed to the reproducibility of the SERS spectra, even among 5 separately prepared substrates. The calculated SERS enhancement factor [18] was  $4 \times 10^6$  relative to the intensity of a normal 2-NpSH spectrum (concentration: 300 mM). The decreased intensity resulting from the use of the substrate prepared with 360 s of electrodeposition was expected because of the less characteristic, blunt-edged structure of the nanodendrites formed under this condition. The degree of perfection of the nanodendrite structure was clearly related to SERS efficiency.

Fig. 4b shows Raman spectra of six 2-NpSH samples ranging in concentration from 1 nM to 10  $\mu\text{M}$ , measured using the substrates (300 s electrodeposition); the 1400–1330  $\text{cm}^{-1}$  range surrounding the 1378  $\text{cm}^{-1}$  peak is shown. Fig. 4b inset shows the variation of peak intensities at 1378  $\text{cm}^{-1}$  in the spectra, including error bars based on the measurements of 5 separate substrates for each condition. The peak intensities increased according to the elevation of concentrations with a typical pattern of intensity variation in SERS measurements, when the adsorption of a molecule on a substrate followed Langmuir isotherm [19]. In the measurement of the 1 nM 2-NpSH sample (the lowest concentration tested), the 1378  $\text{cm}^{-1}$  peak was still apparent. These results show that CFC-AuND is an effective SERS substrate that enables sensitive measurement with good reproducibility.

Next, the physical durability of the substrate was tested by evaluating the intensity variations of 2-NpSH-adsorbed substrate, after repeated folding it in half and unfolding up to 100 times. Fig. 4c shows Raman spectra of the 2-NpSH-adsorbed substrate acquired after folding and unfolding 0, 10, 50, and 100 times. Relative to the initial intensity, the intensity decreased by 12.5, 33.5, and 57.3% after 10, 50, and 100 folding cycles, respectively; the substrate was unbroken and still usable after this test. The observed decrease of intensity was due to the breakage of nanodendrites, mainly around the folded region, by the physical abrasion. The peak intensity was still strong after the 100 folding cycles. It was noteworthy that the folding carried out in this durability testing represented an extreme case; in reality, the folding of a substrate in half would not occur in the normal course of analysis. When the substrate was moderately bended by approximately 10–20°, the intensities remained nearly constant.

### 3.2. Use of CFC-AuND for electrochemical detection of Hg(II)

The close distance between aligned terraces in a nanodendrite is advantageous in generating hotspots for SERS signal



**Fig. 6.** (a) Anodic stripping voltammograms of Hg(II) samples ranging in concentration from 1 to 100 ppb, measured using the optimal CFC-AuND and (b) relationship between Hg(II) concentrations and corresponding peak intensities. (c) Anodic stripping voltammograms acquired from Hg(II) samples of 5, 40, and 80 ppb, using ten separately prepared substrates in each case. (c, inset) Enlarged view of the voltammograms acquired from the 5 ppb sample.

enhancement, but may not be optimal for electrochemical measurements, in which diffusion of an analyte to the surface is one of the major factors governing the sensitivity. As a criterion to find an adequate substrate for electrochemical analysis, diffusional electrode area ( $A_{diff}$ ) was considered, based on the Randles–Sevcik equation [20] shown below. In this equation,  $A_{diff}$  actually corresponds to the effective surface area available for a given electrochemical reaction, estimated by considering the diffusion of an analyte.

$$i_p = 2.69 \times 10^5 n^3/2 D^{1/2} A_{diff} C v^{1/2} \quad (1)$$

Here,  $i_p$  is the peak current corresponding to the reduction of the redox species,  $n$  is the number of electrons transferred in the redox event,  $D$  is the diffusion coefficient of the analyte,  $C$  is the molar concentration of an analyte, and  $v$  is the scan rate in  $V s^{-1}$ . Initially, cyclic voltammograms (CVs) of the redox couple of  $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$  were recorded using the prepared CFC-AuNDs shown in Fig. 1. For comparison, a bare Au disk and bare CFC were also used to measure the same sample. The  $C$  and  $D$  values of  $K_3[Fe(CN)_6]$  used for the calculation were  $5 \times 10^{-3} M$  and  $7.5 \times 10^{-6} cm^2 s^{-1}$ , respectively.

Fig. 5 shows CVs of  $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$  acquired using the Au disk, bare CFC, and CFC-AuNDs prepared by electrodeposition over 180, 240, 300, and 360 s. In all cases, the reversible cyclic voltammograms were obtained. The peak current was highest for the CFC-AuND prepared using the electrodeposition duration of 300 s. As was observed previously in SERS measurements, the less characteristic nanodendrite structure produced by 360 s of electrodeposition degraded the sensitivity of electrochemical measurement. The more perfect nanodendrite structure prepared with the electrodeposition of 300 s was also the most effective for electrochemical analysis. The calculated  $A_{diff}$  values for the CFC-AuNDs prepared with the electrodeposition durations of 180, 240, 300, and 360 s were 1.89, 2.05, 3.31, and 2.24  $cm^2$ , respectively. The  $A_{diff}$  of bare CFC was 1.57  $cm^2$ .

Using the optimal CFC-AuND, Hg(II) samples in KCl/HCl (pH 3.0) with concentrations ranging from 1 to 100 ppb were analyzed using stripping voltammetry (Fig. 6a). The peak intensity apparently increased linearly with increasing concentration ( $R^2$ : 0.994; Fig. 6b). The calculated limit of detection was 0.09 ppb. Further, to evaluate the substrate-to-substrate reproducibility in electrochemical measurements, 3 Hg(II) samples of 5, 40, and 80 ppb were measured using ten separately prepared substrates in each case and the RSDs of the peak intensities were calculated. The stripping voltammograms acquired from these 3 samples are shown in Fig. 6c. The intensities of peaks were highly reproducible, with RSDs of 3.7, 2.8, and 1.1% for the measurements of 5, 40, and 80 ppb Hg(II) samples, respectively.

#### 4. Conclusions

The CFC-AuNDs demonstrated herein were rugged and versatile for both SERS and electrochemical analyses. The substrate-to-substrate reproducibility, a parameter governing practical applicability for routine analysis, was good for both analyses. Especially, the use of the WAC scheme in SERS analysis was a great aid in improving reproducibility. The physical flexibility of CFC made it useful in building durable CFC-AuND substrates. In addition, due to its fabric nature, the CFC provided high surface area and absorbed samples into the substrate easily. The construction of diverse multimetal nanostructures such as Au/Ag and Au/Ag/Pt on CFC is underway to develop substrates with enhanced SERS and catalytic efficiency, respectively. In addition, these substrates will be used to measure analytes in real biological and environmental samples.

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