

## Detection of Trace Copper Metal at Carbon Nanotube Based Electrodes Using Squarewave Anodic Stripping Voltammetry

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We investigate sensitivity and limit of detection (LOD) of trace copper (Cu) metal using pristine carbon nanotube (CNT) and acidified CNT (ACNT) electrodes. Squarewave based anodic stripping voltammetry (SWASV) is used to determine the stripped Cu concentration. Prior to performing the SWASV measurements, its optimal conditions are determined and with that, effects of potential scan rate and  $\text{Cu}^{2+}$  concentration on stripping current are evaluated. The measurements indicate that (1) ACNT electrode shows better results than CNT electrode and (2) stripping is controlled by surface reaction. In the given  $\text{Cu}^{2+}$  concentration range of 25-150 ppb, peak stripping current has linearity with  $\text{Cu}^{2+}$  concentration. Quantitatively, sensitivity and LOD of Cu in ACNT electrode are  $9.36 \mu\text{A} \mu\text{M}^{-1}$  and 3 ppb, while their values are  $3.99 \mu\text{A} \mu\text{M}^{-1}$  and 3 ppb with CNT electrode. We evaluate the effect of three different water solutions (deionized water, tap water and river water) on stripping current and the confirm types of water don't affect the sensitivity of Cu. It turns out by optical inspection and cyclic voltammetry that superiority of ACNT electrode to CNT electrode is attributed to exfoliation of CNT bundles and improved interfacial adhesion occurring during oxidation of CNTs.

**Key Words :** Copper trace metal, Anodic stripping voltammetry, Carbon nanotube, Surface reaction controlled, Acidified carbon nanotube

### Introduction

Recently, as a global industry has made progress, concerns about environmental contaminations that were concomitant with such an industrial development have been getting high. In particular, in Korea, efforts for appropriate management and quality control of drinking water to alleviate the water contamination by pollutants such as heavy metals have made as a form of nationally supported project like "four river refurbishment project", which is associated with quality improvement of the four main Korean river waters.<sup>1,2</sup>

Quality of drinking water is closely linked to that of river water. For the effective quality controlling of the drinking water, development of appropriate sensor for on-site monitoring of the interesting heavy metal pollutants in predetermined multiple detecting points around the river is important. Such a sensor should have an excellent sensitivity and detectability for identification of the heavy metals although a portion of heavy metal occupied in the water is infinitesimal.

As one of typical heavy metals affecting the water quality and contamination, copper (Cu) can be considered. The Cu causes blood and kidney problems for humans, while it makes the growth of plants retard as a form of shortened root length, fewer leaves and decline in the plant biomass. Also, Cu is known for its interfering role when included with the other trace metals.<sup>3-6</sup>

The maximum acceptable containment level of Cu established by the World Health Organization (WHO) is ~1 ppm in drinking water.<sup>3</sup> With this standard Cu concentration regulation, to date, there have been many attempts to detect

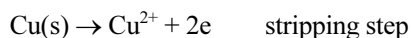
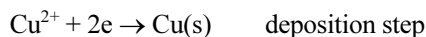
properly the trace Cu metal that include methods using spectrophotometry, inductively coupled plasma mass spectroscopy, solid-phase extraction, atomic absorption spectroscopy and hydride generation atomic fluorescence spectroscopy.<sup>7-10</sup> However, the abovementioned methods have the drawbacks like use of expensive equipment, time consuming pretreatment and high operation cost.<sup>7-11</sup>

Unlike the conventional methods, electrochemical analysis using squarewave based anodic stripping voltammetry (SWASV) can address the problems created by the other methods because its cheap cost, portability and faster processing time. Furthermore, the SWASV can detect even to the low concentration of heavy metals.<sup>12-15</sup>

The SWASV mainly consists of deposition and stripping steps. During the initial deposition step, predetermined potential is imposed to working electrode over the predetermined time for depositing the corresponding metal atoms on the electrode. Metal ions that are included in the solution at first are reduced to the metal atoms by electrochemical reduction reaction when the potential is applied. Following the deposition step, stripping step is carried out. During the stripping step, the metal atoms deposited on the electrode are oxidized into metal ions by linear sweep voltammetry and they are stripped from the electrode, producing current. Such a current is called as a stripping current and detected in the potentiostat. Intensity of the stripping current is supposed to depend on metal concentration while the peak potential is uniquely displayed with the corresponding metal because the metal itself has its own standard electrode potential.<sup>16,17</sup>

In our study, standard electrode potential of Cu is 0.142 V

vs Ag/AgCl and the following deposition and stripping reactions take place over the whole process.<sup>18</sup>



In the early stage of SWASV use, several types of mercury electrodes (*i.e.*, mercury hanging and dropping) have been used due to easy procuring of reduced metal, good reproducibility and easy cleaning of electrode surface. However, in the viewpoint of environmental and human health, toxicity of mercury made continuous usage of the mercury electrode difficult. To overcome the toxicity problem related to mercury electrode and to maintain the positive features of SWASV, new electrode should be developed.<sup>17,19,20</sup>

As a replacement of the mercury electrode, electrodes using noble metals like nanosized platinum (Pt) and gold (Au) have been proposed.<sup>4,13,21,22</sup> Although the metal electrodes have advantages like fast mass transfer, enhancement in sensitivity and activation of catalytic reaction, their expensive cost makes their commercialization difficult.

To overcome the drawback of metal electrodes, functionalized carbon materials such as carbon nanotube (CNT) have been recently suggested. It can offer merit such as cheapness, excellent electrocatalytic activity, good electrical and mechanical properties and large surface area.<sup>23,24</sup> In one step further, CNT oxidized by wet chemical can be more beneficial due to its superior exfoliation capability and purification impact that are increased during the oxidation process.<sup>23-25</sup>

In this work, we demonstrate how the CNT and the oxidized CNT (ACNT) electrodes have an influence on detecting trace Cu metal by SWASV in differently composed solution systems. In addition, the optimal parameter conditions for the SWASV measurements like deposition time, deposition potential, squarewave amplitude and squarewave frequency are determined. The sensitivity and limit of detection (LOD) of Cu<sup>2+</sup> ions in CNT and ACNT electrodes are measured. As the practical application of the CNT and ACNT electrode-based sensors, the sensitivity with low LOD is investigated in electrolytes consisting of tap water and river water as well as deionized (DI) water. In addition, in chemical prospect, our research will help establish a process window for electrochemical detection of the trace Cu metal and extension of applicability of the CNT-based electrodes.

## Experimental

**Reagents and Apparatus.** Sulfuric acid (95% H<sub>2</sub>SO<sub>4</sub>) was used as an electrolyte. In order to dilute pure H<sub>2</sub>SO<sub>4</sub> to the predetermined H<sub>2</sub>SO<sub>4</sub> concentration, three different waters are used - DI water, tap water and river water. The river water sample was prepared in JungRang Stream, Seoul. To remove the natural organic materials, the river water was filtered three times using filtering paper (Glass microfiber filter, 110 mmφ, Whatman international).

Stock solutions of various concentrations of Cu<sup>2+</sup> ions were also prepared from a 1002 mg/L Cu standard solution (Kanto Chemical, Japan) in 0.1 M H<sub>2</sub>SO<sub>4</sub> that was served as a supporting electrolyte for electrochemical experiments. Multi-walled CNT (MWCNT, > 90 wt % purity, diameter of 5-20 nm and length of ~5 μm) used as an electrode material was purchased from Carbon Nano-material Technology (Gyeongsangbuk-do, Korea).

For oxidation process of the CNT, nitric acid (60% HNO<sub>3</sub>) and sodium hydroxide (98% NaOH) were used while mineral oil (density of 0.83-0.89, liquid paraffin) was served as binder for making an electrode paste.

All the electrochemical measurements were implemented by an electrochemical analyzer ZIVE SP2 (Wonatech, Seoul) that was connected to a personal computer. A three electrode system was prepared with in-house CNT-based electrodes as a working electrode, Ag/AgCl (3 M KCl) as a reference electrode and Pt wire as a counter electrode. All the electrochemical experiments were operated at room temperature.

**Working Electrode Preparation.** For making in-house electrodes related to this research, we divided as received MWCNTs into two types - CNT and ACNT. For manufacturing CNT electrode, 1g of as received MWCNTs was washed and filtered three times and then dried at 60 °C for 12 h. The dried MWCNTs were mixed with 0.3 g of mineral oil in the mortar for 30 min. to form CNT paste. 0.03 g of the CNT paste was then filled with the bottom part of a capillary tube glass that has 1.1 mm diameter and 2 cm length. For the connection between CNT paste and external electrochemical analyzer, Cu wire that has 1 mm diameter and 3 cm length was put into the tube-filled CNT paste.<sup>26</sup>

For building ACNT electrode that is made by oxidation of CNT, 3 g of as received MWCNTs that were washed and filtered was mingled with 240 mL of H<sub>2</sub>SO<sub>4</sub> and 60 mL of HNO<sub>3</sub> in a 500 mL round bottom flask that was equipped with a condenser. In turn, the solution was refluxed at 60 °C for 5 h. Such refluxed solution was cooled to the room temperature and washed repeatedly until its pH reached neutral and then that was filtered. The CNT powders gained by the filtering were dried at 60 °C for 12 h. After that, 1 g of the dried CNTs was mixed with 0.3 g of mineral oil in the mortar for 30 min. to form ACNT paste. The next sequence is the same as the procedure of CNT electrode.

**Cyclic Voltammetry (CV) and Squarewave Based Anodic Stripping Voltammetry (SWASV).** Prior to performing SWASV measurement, all the electrodes were preconditioned (activated) in 0.1 M H<sub>2</sub>SO<sub>4</sub> by CV sweeping from -1 to 1 V at a scan rate of 100 mV s<sup>-1</sup>.<sup>27</sup> To evaluate the active surface areas of CNT and ACNT electrodes, CVs of the two electrodes were measured in “before Cu deposition” and “after Cu deposition” cases. In the CV measurements, applied potential sweeping range was from -0.3 to 0.3 V and potential scan rate was 100 mV s<sup>-1</sup>.

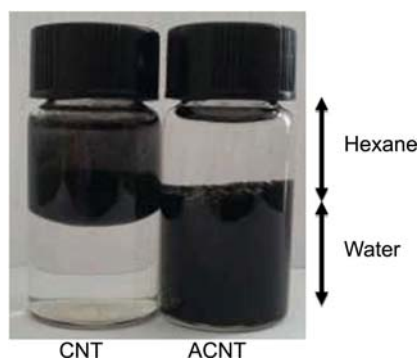
The SWASV measurements consist of two main steps; (1) deposition of Cu produced by reduction of Cu<sup>2+</sup> on the electrode and (2) stripping of the Cu deposited on the electrode by oxidation into Cu<sup>2+</sup>. The Cu<sup>2+</sup> ions were initially reduced

to Cu at  $-1.0$  V for the predetermined time and the reduced Cu was accumulated on the electrodes. Following the step, Cu was oxidized at around  $0.1$  V vs Ag/AgCl during the potential scan from  $-0.7$  to  $0.6$  V vs Ag/AgCl with the measurement of stripping peak current. Part of samples for the SWASV measurements applied to a background subtraction method, meaning that initial saving of the signal of reference (blank) solution and then subtracting it from the signal of interesting sample to attain actual signal.

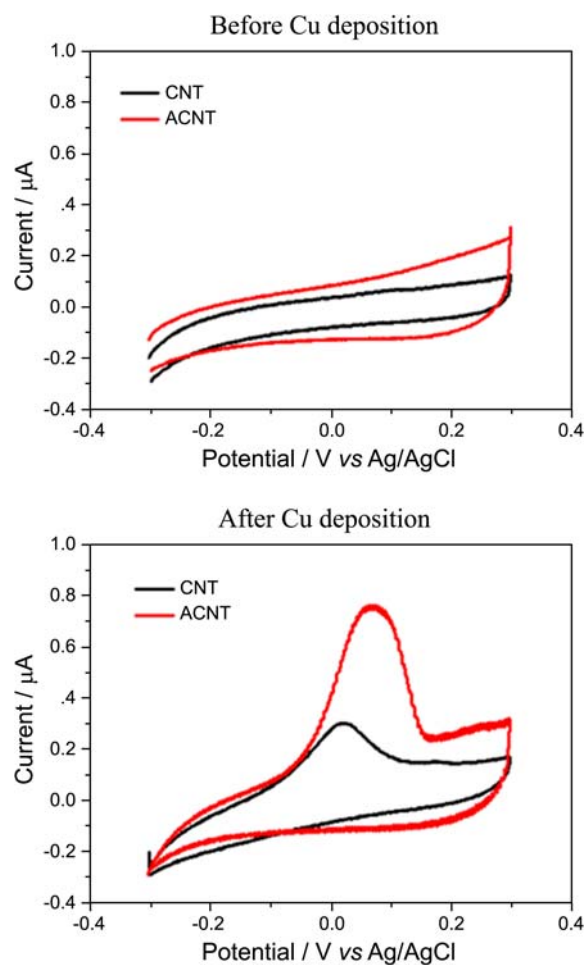
## Results and Discussion

**Structural Difference between CNT and ACNT Electrodes.** For evaluating structural difference between CNT and ACNT electrodes, two characterizations were carried out - measurements of hydrophobicity and CV measurement. The surficial states of CNT and ACNT electrodes were inspected by observing their dispersion in 50:50 mixture of water and hexane and Figure 1 displays the result. For the test, CNT and ACNT powders of the same mass were dispersed into the water (polar media)/hexane (non-polar media) mixture, respectively. The mixtures were then agitated for 30 sec. and the movements of both powders were observed. As shown in Figure 1, the CNT powder was stayed in the hexane side due to its intrinsic hydrophobicity, while the ACNT powder was moved in the water side. It indicates that surface property of the acid treated CNT powder was changed into hydrophilic mode due to water affinity (or solubility in polar media) increased by oxygen containing groups formed in CNT surface.<sup>24,25</sup> ACNTs that are surrounded with the oxygen containing groups prompt exfoliation of ACNT bundles and improve interfacial adhesion with other composites.<sup>28</sup> The exfoliation induces an increase in active surface area of ACNT, while the enhancement of interfacial adhesion makes the deposition of Cu on the CNT surface easier.

The CV curves were also measured in terms of “before Cu deposition” and “after Cu deposition” cases as shown in Figure 2. Here, “before Cu deposition” is defined as the initial state before implementing Cu deposition step, while “after Cu deposition” is determined as the state before performing Cu stripping step. In “before Cu deposition” case, ACNT electrode showed larger background current than CNT



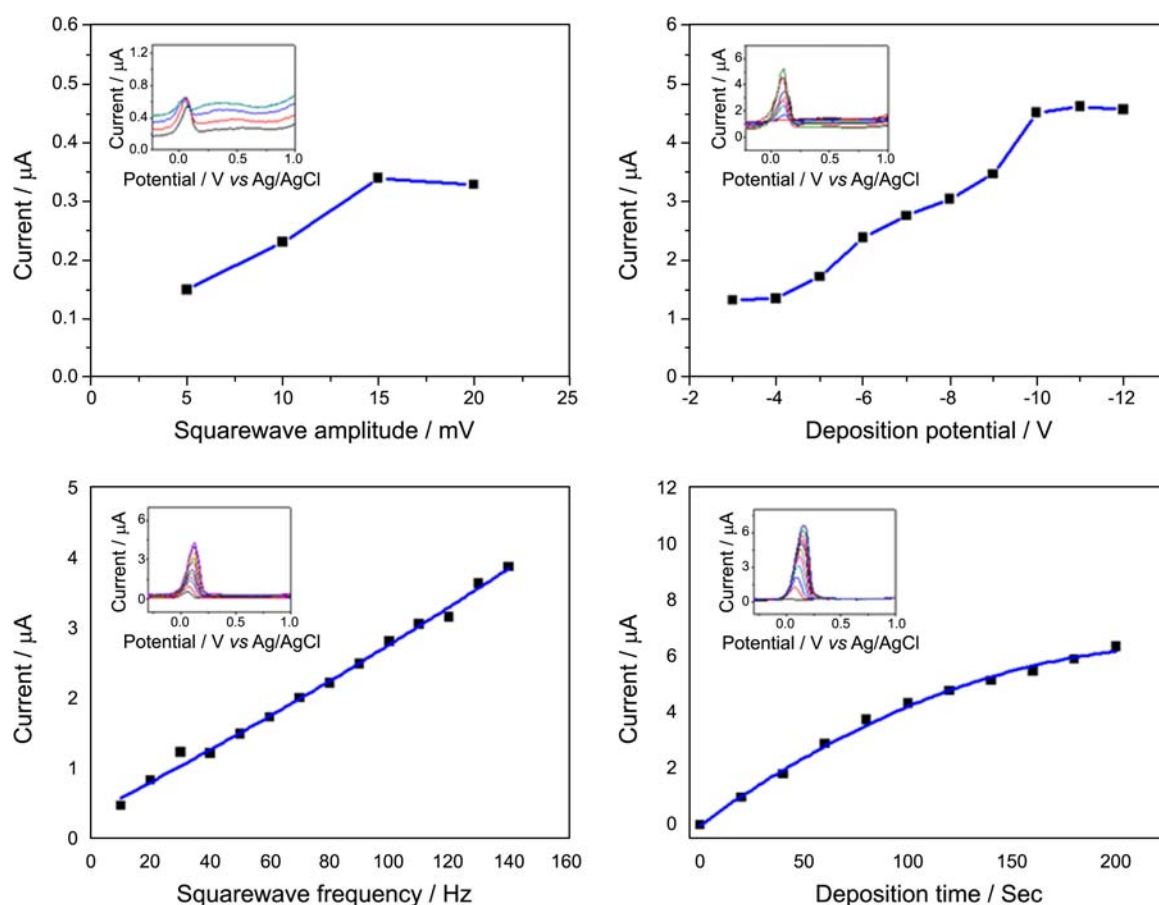
**Figure 1.** Dispersion of CNT and ACNT powders contained in water (polar media)/hexane (non-polar media) mixture, respectively.



**Figure 2.** CV curves of CNT and ACNT electrodes measured in “before Cu deposition” and “after Cu deposition”, respectively. For the measurements, the potential was scanned between  $-0.3$  and  $0.3$  V with a potential scan rate of  $100$   $\text{mV s}^{-1}$ . A three electrode system was prepared with CNT and ACNT electrodes as a working electrode, Ag/AgCl (3 M KCl) as a reference electrode and platinum wire as a counter electrode while  $0.1\text{M H}_2\text{SO}_4$  was served as an electrolyte. All the tests were conducted at room temperature.

electrode, while the ACNT electrode demonstrated larger peak current in “after Cu deposition” case. Discrepancies in the CV current peaks between CNT and ACNT electrodes are probably attributed to the exfoliation and the improvement in interfacial adhesion of the ACNTs.<sup>23</sup> Namely, in the ACNT electrode, agglomerated ACNT bundles are disentangled, thereby the number of active site for deposition and stripping of the Cu metal increases. In turn, it promotes better reaction rate, followed by larger background current and Cu stripping peak currents.

**Optimization of Parameters Affecting ASV Measurements.** To enhance detectability of the trace Cu metal, finding out the optimal values of parameters affecting the Cu sensitivity during SWASV measurements is critical. Square-wave amplitude, squarewave frequency, deposition potential and deposition time were considered the parameters.<sup>17</sup> Figure 3 displays how the peak current is influenced by the changes in values of the four parameters during SWASV measurement



**Figure 3.** Optimization processes of four parameters affecting SWASV measurements. As the parameters, squarewave amplitude, squarewave frequency, deposition potential and deposition time were selected. Insets of the figure indicate a relationship between stripping peak current and the corresponding parameter. For these tests, CNT electrode was used and 100 ppb  $\text{Cu}^{2+}$  ions were spiked into 0.1 M  $\text{H}_2\text{SO}_4$  electrolyte. As a result of that, the optimal values of squarewave amplitude, squarewave frequency, deposition potential and deposition time were 15 mV, 60 Hz,  $-1.0$  V vs Ag/AgCl and 200s, respectively.

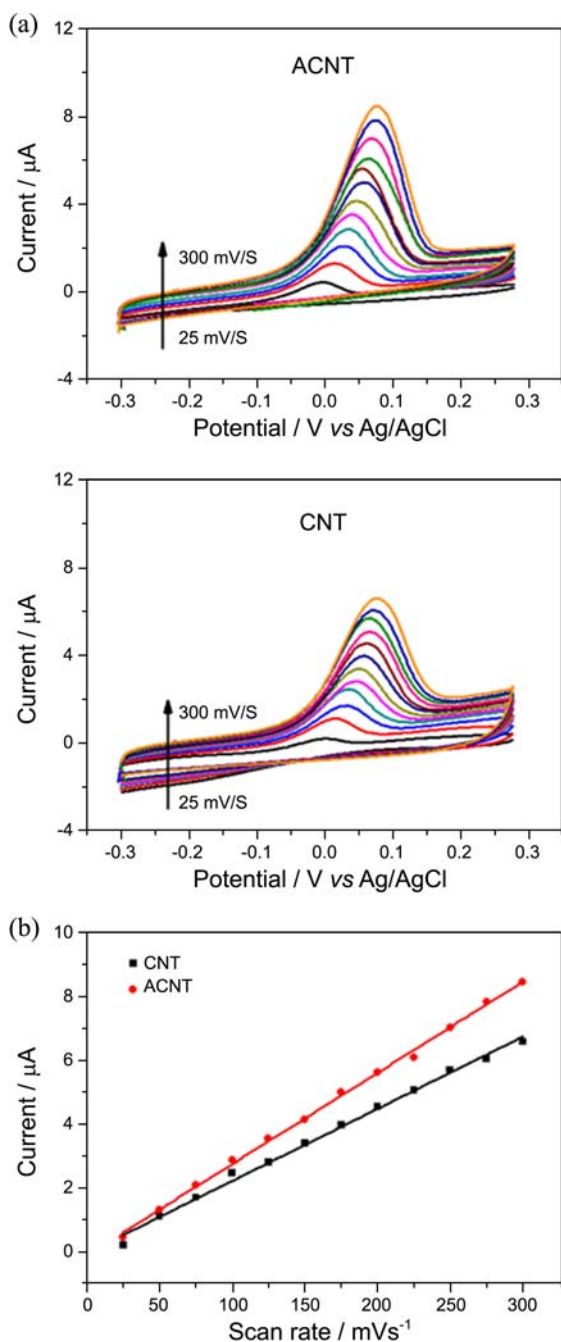
and insets of the figure indicate effects of the parameters on SWASV current.<sup>29</sup> For these tests, CNT and ACNT electrodes were used as a working electrode and 100 ppb  $\text{Cu}^{2+}$  ions were inserted into 0.1 M  $\text{H}_2\text{SO}_4$  electrolyte. According to the experimental data, the optimal values of squarewave amplitude and frequency for SWASV measurement were 15 mV and 60 Hz, respectively, while the values for deposition potential and deposition time were  $-1.0$  V vs Ag/AgCl and 200 s, respectively. Although the results shown in Figure 3 were gained from CNT electrode, the optimal values of the parameters for ACNT electrode were also the same to those for CNT electrode (not shown in the figure).<sup>29</sup>

In the prospect of deposition potential, the stripping peak current did not increase at a more negative potential than  $-1.0$  V vs Ag/AgCl, which was ascribed to the complete reduction of  $\text{Cu}^{2+}$  ions included in the electrolyte. When it comes to the optimal deposition time,  $\text{Cu}^{2+}$  ions were accumulated on the electrode linearly with the increase in deposition time, but this increase reached plateau from 200s due to limitation of the active sites on the electrode. Thus,  $-1.0$  V vs Ag/AgCl and 200s were fixed for subsequent measurements.

#### Electrochemistry of Cu Stripped at CNT and ACNT

**Electrodes.** To examine whether stripping of Cu at both CNT and ACNT electrodes is dependent on surface reaction controlled process or mass transfer controlled process, SWASV tests were implemented. After suffering Cu deposition step for 200s, a relationship between stripping current and potential scan rate was measured by SWASV. A potential scan range for the SWASV s was  $-0.3\sim 0.3$  V vs Ag/AgCl and 100 ppb  $\text{Cu}^{2+}$  ions were spiked into 0.1 M  $\text{H}_2\text{SO}_4$  electrolyte. Figure 4(a) shows the SWASV results indicating how stripping current is varied by the potential scan at the two different electrodes, while Figure 4(b) summarizes how stripping peak current are affected by potential scan rate. It was apparent that the stripping peak current increased linearly with potential scan rate on both electrodes ( $I_p \propto v$ ,  $I_p = 0.022v - 0.02$ ,  $R^2 = 0.995$  in CNT electrode and  $I_p = 0.029v - 0.1$ ,  $R^2 = 0.998$  in ACNT electrode. Here, unit of  $v$  is  $\text{mV s}^{-1}$ ). It demonstrates that Cu stripping process is controlled by surface reaction.<sup>29,30</sup>

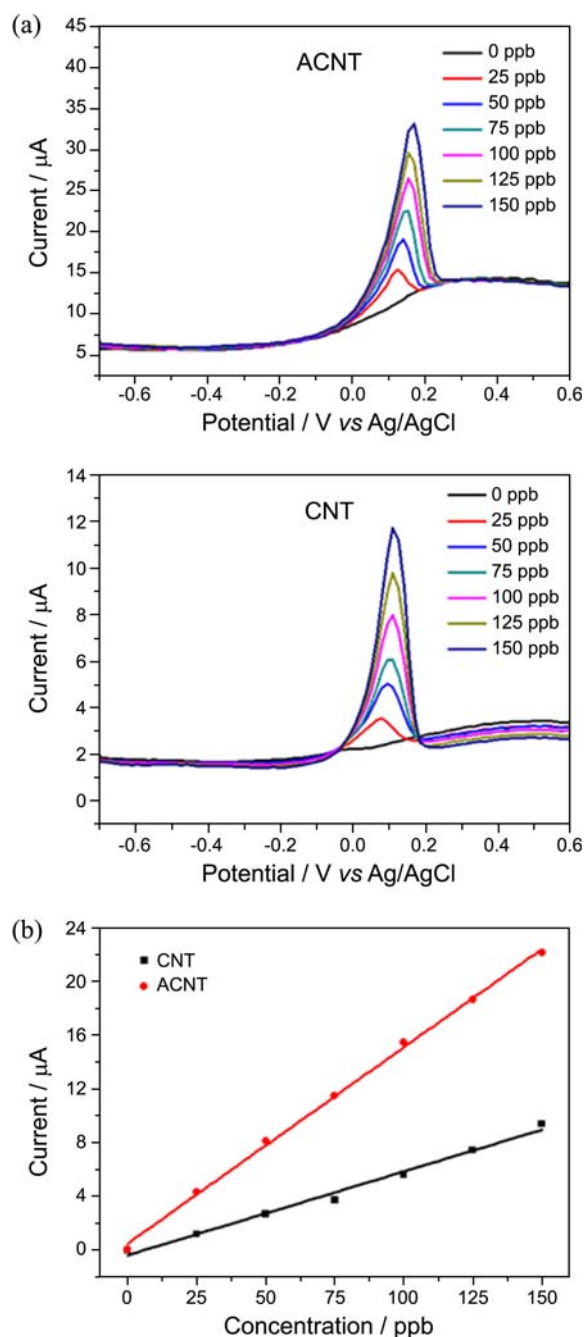
Such a linearity between stripping peak current and potential scan rate is well agreed with the following equation,  $I_p = nFQv/4RT$ , which is permissible when the surface reaction controlled process is the dominant mechanism.<sup>31</sup> Here,  $n$  is the number of electrons transferred,  $F$  is the Faraday con-



**Figure 4.** Effect of potential scan rate on stripping current induced by CNT and ACNT electrodes. SWASV results (a) indicating how stripping current is varied by the potential scan and (b) showing a relationship between stripping peak current and potential scan rate at CNT and ACNT electrodes. For the measurements, 100 ppb  $\text{Cu}^{2+}$  ions were spiked into 0.1 M  $\text{H}_2\text{SO}_4$  electrolyte and the  $\text{Cu}^{2+}$  ions were deposited on the electrodes for 200s. A potential scan range for the SWASVs was  $-0.3\sim 0.3$  V vs Ag/AgCl with a potential scan rate of  $100\text{ mV s}^{-1}$ .

stant,  $Q$  is charge consumed,  $R$  and  $T$  are an ideal gas constant and a room temperature, respectively. Unlike this situation, if the mass transfer is a main mechanism to control Cu stripping, the peak current should have increased linearly with the root of scan rate ( $I_p \propto v^{1/2}$ ).<sup>15</sup>

In the comparison between electrodes, peak current pro-



**Figure 5.** Effect of  $\text{Cu}^{2+}$  ion concentration on stripping current induced by CNT and ACNT electrodes. SWASV results (a) indicating how stripping current is varied by the  $\text{Cu}^{2+}$  ion concentration and (b) showing a relationship between stripping peak current and  $\text{Cu}^{2+}$  ion concentration at CNT and ACNT electrodes. For the measurements,  $\text{Cu}^{2+}$  ions that were in different concentration were initially deposited on the electrodes for 200s and a potential scan range for the SWASVs was  $-0.7\sim 0.6$  V vs Ag/AgCl with a potential scan rate of  $100\text{ mV s}^{-1}$ .

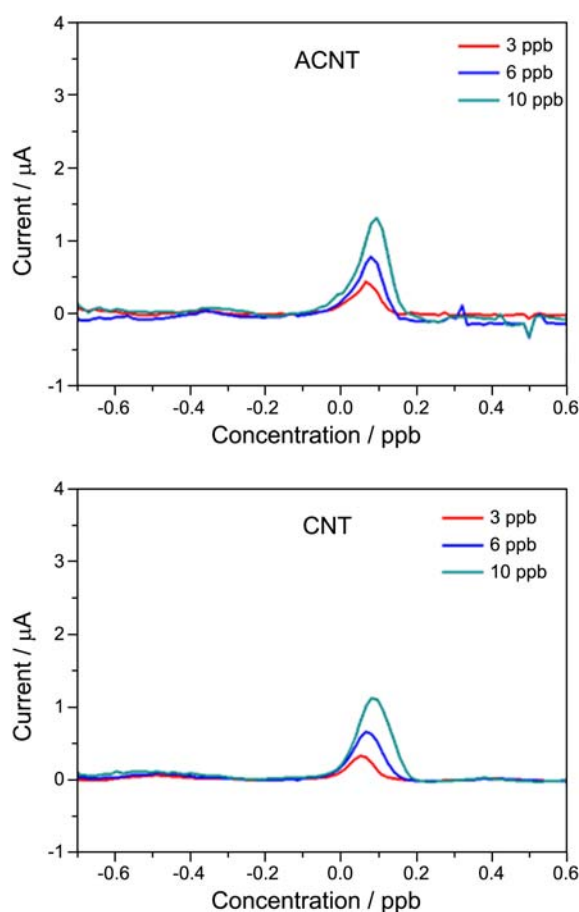
duced at ACNT electrode is larger than that produced at CNT electrode, indicating that stripping capability of Cu at ACNT electrode is better than that of Cu at CNT electrode. It is probably attributed to the exfoliation and strong adhesion of ACNT electrode and this result is compatible with CV of Figure 2.

**Sensitivity Measurement of Cu at CNT and ACNT Electrodes.** To evaluate the sensitivity of Cu detected by CNT and ACNT electrodes, measurements by SWASV were carried out. For the measurements, Cu was deposited on the electrode for 200s and 0.1 M H<sub>2</sub>SO<sub>4</sub> that was diluted by three different solutes - DI water, tap water and river water - was considered electrolyte. Figure 5(a) indicates SWASV showing how current is displayed by Cu<sup>2+</sup> ion concentration in the two electrodes and Figure 5(b) summarizes an association between stripping peak current and Cu<sup>2+</sup> ion concentration. The concentration of Cu<sup>2+</sup> ions used for SWASV measurements was from 25 ppb to 150 ppb with the increment of 25 ppb.

In the test, stripping peak current increased with Cu<sup>2+</sup> ion concentration in both electrodes ( $I_p = 0.062C - 0.04$ ,  $R^2 = 0.988$  in CNT electrode and  $I_p = 0.146C + 0.485$ ,  $R^2 = 0.998$  in ACNT electrode. Here, unit of  $I_p$  is  $\mu\text{A}$  and that of  $C$  is  $\mu\text{M}$ ). From the linear relationship, the sensitivity of Cu and its calculated LOD (when S/N ratio is 3) were determined. In CNT electrode, the sensitivity of Cu was  $3.99 \mu\text{A} \mu\text{M}^{-1}$  and its calculated LOD was 16.8 ppb, while the sensitivity was  $9.36 \mu\text{A} \mu\text{M}^{-1}$  and its calculated LOD was 7.1 ppb in ACNT electrode. The sensitivities in both electrodes are higher than those published previously. For instance, the sensitivities of Cu using Au electrode ( $0.0075 \mu\text{A} \mu\text{M}^{-1}$ )<sup>4</sup> and 4-carboxy phenyl diazonium tetrafluoroborate (DCOOH) electrode ( $1.06 \times 10^{-9} \mu\text{A} \mu\text{M}^{-1}$ )<sup>32</sup> were far lower than our results.

There are several noticeable things to report on sensitivity results of the trace Cu metal in both CNT and ACNT electrodes. First, stripping peak current is linearly proportional to Cu<sup>2+</sup> ion concentration without plateau region within the given concentration range of Cu<sup>2+</sup> ion. Such a result proves that the electrode surface possesses enough active sites to enable continuous Cu stripping reaction irrespective of the Cu<sup>2+</sup> ion concentration. Conversely, if the number of active site within the electrode surface is smaller than that of Cu<sup>2+</sup> ion provided, the stripping reaction will be saturated and although Cu<sup>2+</sup> ion concentration increases, current will not increase. Second, a higher sensitivity in ACNT electrode than in CNT electrode indicates that active surface area of ACNT electrode is larger than that of CNT electrode, which is well agreed with results of Figure 2. Namely, according to the CVs of Figure 2, area occupied by ACNT is larger than that occupied by CNT in both "Before Cu deposition" and "After Cu deposition" cases. It implies that charging current of ACNT is larger than that of CNT. Because the capacitive charging current is proportional to electrochemical double layer and it is known that the size of double layer depends on the catalytic surface area, essentially, the CV area can reflect active surface area of the corresponding electrode.<sup>33,34</sup>

The LOD of Cu was also experimentally measured in both electrodes using background subtraction stripping voltammogram.<sup>35</sup> Figure 6 displays the results. According to the Figure 6, in both electrodes, Cu<sup>2+</sup> ions were apparently detected from around 3 ppb level. It is significantly accurate result and meets the WHO regulation ( $\sim 1$  ppm level) for accept-

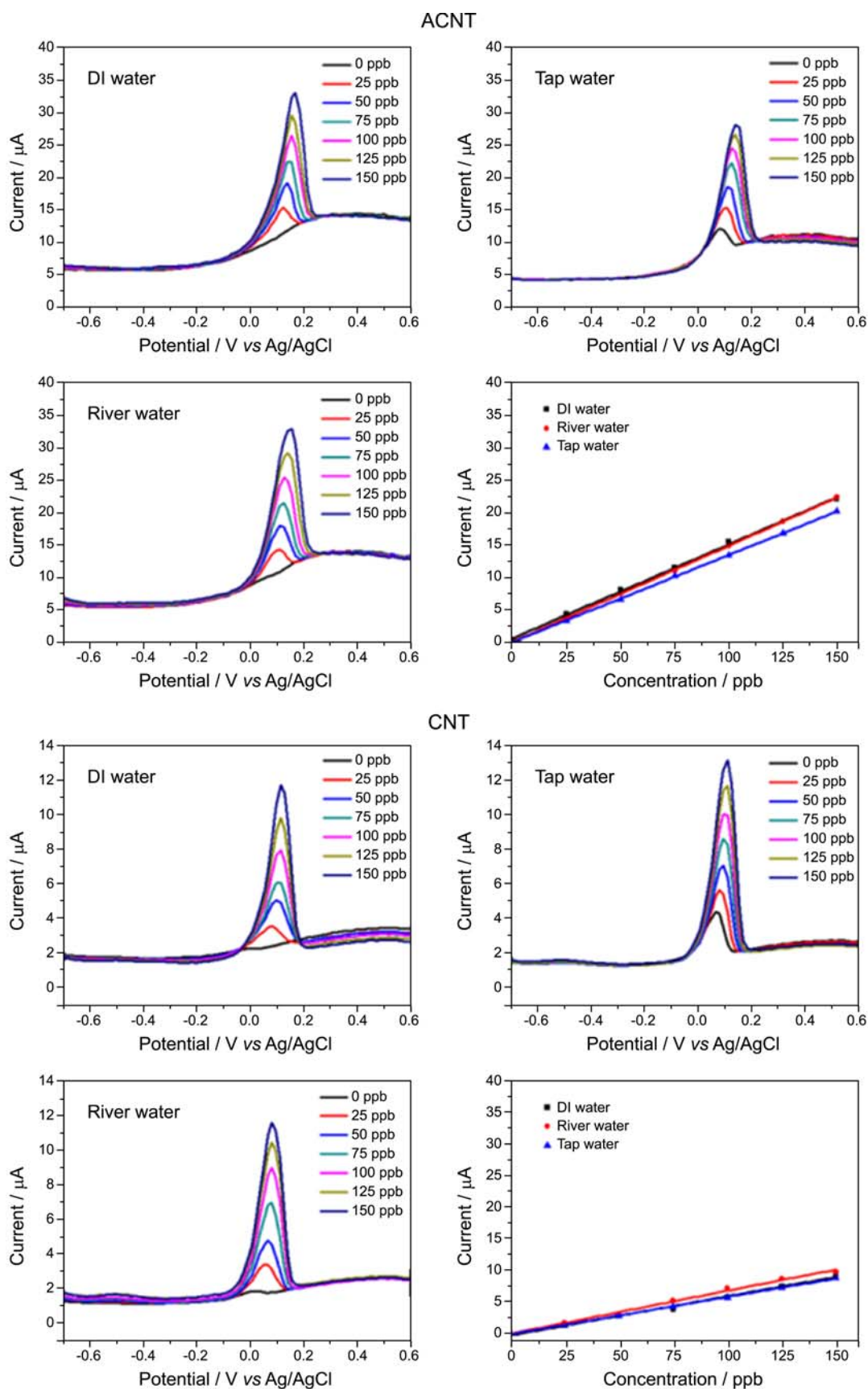


**Figure 6.** The LODs of Cu that were experimentally measured in CNT and ACNT electrodes using background subtraction stripping voltammogram. For the measurements, a potential scan range used was  $-0.7$ – $0.6$  V vs Ag/AgCl and the corresponding Cu<sup>2+</sup> ions were spiked into 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte.

able Cu concentration by a wide margin. Such an excellent precision reflects that the reduction (stripping) reaction by SWASV causes effective stripping of the Cu from both CNT and ACNT electrodes. It is enough evidence that both CNT and ACNT are useful sensor electrode materials for Cu detection in various water systems.

For further inspecting whether (1) concentration of Cu<sup>2+</sup> ions included in tap water filtered from river water satisfies the WHO regulation and (2) CNT and ACNT electrodes meet the safety provision for on-site monitoring of the Cu, we measured the sensitivity of Cu in 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte diluted by not only DI water, but also actual waters (tap water and river water).

Figure 7 displays the SWASVs exhibiting (1) how stripping current is displayed by Cu<sup>2+</sup> ion concentration and (2) how stripping peak current is linked to Cu<sup>2+</sup> ion concentration in the two electrodes and three different water systems. Table 1 summarizes quantitative values of the main data obtained in Figure 7. As a result of that, when the tap water based electrolyte and river water based electrolyte were used, their stripping peak currents still increased linearly with Cu<sup>2+</sup> concentration in both electrodes (tap water:  $I_p = 0.059C - 0.15$ ,  $R^2 = 0.999$  and river water:  $I_p = 0.068C -$



**Figure 7.** The SWASVs showing effect of  $\text{Cu}^{2+}$  ion concentration on stripping current in two electrodes (CNT and ACNT electrodes) and three different water systems (DI water, tap water and river water). For the measurements,  $\text{Cu}^{2+}$  ion concentration that were supplied to 0.1 M  $\text{H}_2\text{SO}_4$  electrolyte was from 25 to 150 ppb and the  $\text{Cu}^{2+}$  ions were deposited on the electrodes for 200s. A potential scan range for the SWASVs was  $-0.7$ – $0.6$  V vs Ag/AgCl with a potential scan rate of  $100 \text{ mV s}^{-1}$ .

**Table 1.** The sensitivities and LODs of the trace Cu metal in two electrodes (CNT and ACNT electrodes) and three different water systems (DI water, tap water and river water)

Electrolyte	Electrode					
	ACNT			CNT		
	Sensitivity ( $\mu\text{A } \mu\text{M}^{-1}$ )	R <sup>2</sup>	LOD (ppb)	Sensitivity ( $\mu\text{A } \mu\text{M}^{-1}$ )	R <sup>2</sup>	LOD (ppb)
DI water	9.36	0.998	7.1	3.99	0.988	16.8
River water	9.54	0.999	2.0	4.36	0.992	4.5
Tap water	8.65	0.999	2.6	3.78	0.999	6.0

0.09, R<sup>2</sup> = 0.992 in CNT electrode while tap water: I<sub>p</sub> = 0.135C – 0.06, R<sup>2</sup> = 0.999 and river water: I<sub>p</sub> = 0.149C – 0.03, R<sup>2</sup> = 0.999 in ACNT electrode. Here, unit of I<sub>p</sub> is  $\mu\text{A}$  and that of C is  $\mu\text{M}$ .

There are three important observations to be mentioned. First, in both electrodes, the sensitivity of Cu was hardly degraded even in the situation of tap water and river water. In CNT electrode, difference in sensitivity between the highest and the lowest was 13%, while the difference was 7% in ACNT electrode. It can be explained that there are little interrupting electroactive compounds in these waters to affect the stripping of Cu, indicating that (1) Cu is very selective and easy to detect with the uses of CNT based electrodes and (2) all the applied waters do not have easily reducible materials, which can compete with Cu deposited on the electrode.<sup>33</sup> Second, in comparison between CNT and ACNT electrodes, the ACNT electrode demonstrated a higher sensitivity than CNT electrode irrespective of water types. On average, sensitivity in ACNT was 2.3 times higher than that in CNT. This result is well agreed with other experimental results (see, Figures 2-4). Third, experimental LODs of Cu that were measured using background subtraction stripping voltammogram are lower than its calculated LODs that were gained from a linear relationship between stripping peak current and Cu<sup>2+</sup> ion concentration (see Table 1 and Figure 6). According to our experimental results, experimentally measured LOD like data of Figure 6 was about 3 ppb irrespective of water systems. Such a disparity between experimentally obtained LODs and LODs calculated by a formula in low Cu<sup>2+</sup> ion concentration region is probably due to the ambiguity of calculated LODs, which are the approximate values induced by formula.

In brief, it was apparent that CNT and ACNT were very effective electrodes for obtaining excellent sensitivity and LOD for the detection of trace Cu metal that was included in three different types of waters. In addition, the SWASV that was used to measure the detectability of Cu by CNT and ACNT electrodes worked well even in the low Cu concentrations.

### Conclusions

New electrode materials - CNT and ACNT - for detecting trace Cu metal included in the several water systems were

suggested. In a bid to determine sensitivity and LOD of the Cu, SWASV was used. Initially, the impacts of potential scan rate and Cu<sup>2+</sup> ion concentration on stripping current induced by the two electrodes were investigated. As a wake of that, it was found that ACNT electrode was more affordable as sensor electrode for Cu detection than CNT electrode and Cu stripping reaction was governed by surface reaction on both electrodes. According to the detailed sensitivity and LOD measurements of Cu, the Cu was detected even in the 3 ppb that was much lower value than that regulated by WHO (~1 ppm) and its maximum sensitivity ( $9.54 \mu\text{A } \mu\text{M}^{-1}$ ) was far better than other results. Also, there were no large differences in sensitivity and LOD of Cu irrespective of water systems. Based on the abovementioned results, it is obvious that the use of these CNT based electrodes with measurement by SWASV can be accommodated for sensor applications like on-site monitoring apparatus of trace Cu metal.

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