Stripping voltammetric behavior of nitrogen-doped tetrahedral amorphous carbon thin film electrodes in NaCl solutions

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Conductive nitrogen-doped tetrahedral amorphous carbon (ta-C:N) thin films fabricated with a filtered cathodic vacuum arc technique were investigated for their ability to detect multiple trace heavy metals such as mercury, copper and lead by linear sweep anodic stripping voltammetry in sodium chloride aqueous solutions. The ta-C:N film electrodes exhibited a significant stripping response for determination of individual elements (Pb2+ and Hg2+) and multiple elements (Pb2+ + Hg2+ and Cu2+ + Hg2+), indicating that these electrodes have a great potential for simultaneously tracing multiple heavy metals in aqueous solutions.

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1. Introduction

Contamination, over-use and mismanagement of water resources cause pollution in water including a wide spectrum of chemicals, pathogens, and physical chemistry or sensory changes [1]. The presence of toxic metals such as mercury (Hg), copper (Cu) and lead (Pb) in the aquatic ecosystem directly or indirectly affects biota and human beings. Lead and copper are detrimental to children with chronic exposure to mercury of concentrations as low as mM levels [3–5]. Therefore, tracing and determination of these heavy metals in aqueous solutions are of major importance in electrochemical analysis.

In the past, Hg was the first metal extensively used for electroanalytical purposes in the form of dropping mercury electrode because it can avoid many problems pertaining to electrode poisoning in a complex matrix. However, a drawback of a Hg-based electrode is that only reduction reactions can be investigated due to the self oxidation of Hg. Thus, the detection limit and toxicity with a Hg-based electrode have caused some experimental manipulation difficulties. Therefore, carbon based solid electrode materials such as glassy carbon, graphite, carbon paste and carbon fiber have been developed in order to compensate the limitations of mercury electrodes.

Though glassy carbon is one of the most widely used electrode materials in electroanalytical applications for its qualities such as robust, smooth surface and large electrochemical window, irreproducible background contributions and gradual loss of surface activity frequently affect its electroanalytical performance. Boron doped diamond films prepared by chemical vapor deposition can have remarkable properties such as wide potential window in aqueous and non-aqueous media, low and stable capacitance charging background current, weak adsorption of polar molecules leading to an improved resistance to electrode deactivation and fouling, long-term response stability and superfine structural and morphological stability at high temperatures [6,7]. However, synthesis of diamond films demands a high substrate temperature, which has imposed a severe constraint on fabrication of semiconductors and microelectrode arrays [8].

Nowadays, much interest has been focused on conductive diamond-like carbon (DLC) thin films for electrochemical analysis [9]. DLC films can be fabricated at low temperature and made electrically conductive by doping nitrogen or some metals. It was reported that nitrogen-doped DLC (DLC:N) films prepared by filtered cathodic vacuum arc (FCVA) were also chemically stable and could achieve good mechanical...
properties with a high sp³ content in the films. Moreover, these films may achieve similar chemical characteristics to those of diamond materials, such as excellent chemical inertia, high fouling resistance and large potential window [10]. Khun et al. [11] reported that DLC:N films deposited by FCVA showed high corrosion resistance and long-time stability in corrosive media. Though electrochemical stripping voltammetric measurements are simple, quick and cheap ways of tracing metals, the sensitivities of such measurements change with electrode properties (electrical conductivity, surface roughness, surface cleanliness), operation parameters (scan rate, deposition potential and time, voltammetric method) and environmental parameters (current flow, pH value, metal ion concentration, metal solubility). Liu and Liu reported [12] that DLC:N films could trace single metals such as Hg²⁺, Pb²⁺ and Cu²⁺ and multi-metals (Pb²⁺ + Cu²⁺) simultaneously. Anodic stripping voltammetry has been widely used for detection of heavy metals in various samples because of its remarkably low detection limits [13]. In a linear sweep voltammetric measurement, current response is plotted as a function of voltage, with which well defined and selective peaks can be obtained due to little interference of species that can be adsorbed by working electrode [14].

It was reported that nitrogen-doped tetrahedral amorphous carbon (ta-C:N) thin films prepared with DC magnetron sputtering could detect multiple heavy metals (Cd²⁺, Pb²⁺, Cu²⁺) simultaneously. Anodic stripping voltammetry has been widely used for detection of heavy metals in various samples because of its remarkably low detection limits [13]. In a linear sweep voltammetric measurement, current response is plotted as a function of voltage, with which well defined and selective peaks can be obtained due to little interference of species that can be adsorbed by working electrode [14].

1.2 V. deposition potential, t = 200 s on the stripping voltammograms of Pb was investigated in the 1 × 10⁻⁵ M Pb²⁺ + 0.1 M NaCl solutions in terms of pH value of the solutions and potential scan rate, where the deposition potential used is −1.2 V. The ta-C:N film electrodes show the well-defined stripping peaks of Pb even with near zero deposition time, indicating their high sensitivity to the Pb²⁺ ions and the stronger Pb stripping peaks with increasing deposition time for all the pH values and scan rates are observed in Fig. 1a–c. A near linear increase of the Pb anodic stripping peak current with increased deposition time is found in Fig. 1d because the amount of Pb preconcentrated on the ta-C:N film electrode surface is proportional to the deposition time [10]. The shift of the stripping potentials of Pb to lower negative values with increased deposition time (Fig. 1e) can be correlated to the increased amount of stripped Pb²⁺ ions during stripping according to the Nernst equation [16].

\[ E = E^0 - \frac{R}{2nF} \ln \left( \frac{[Pb^{2+}]}{[Pb]_{\text{initial}}} \right) \]

where \( E^0 \), R, T, n, and F are the standard half cell potential of Pb, gas constant, absolute temperature, number of electrons transferred in the half-reaction, and Faraday constant, respectively. It is found that the Pb stripping peaks are more pronounced when measured in a more acidic solution (pH 1) than in a less acidic one (pH 3) under the same scan rate of about 36 mV/s as shown in Fig. 1a and b, which indicates an influence of pH value on the sensitivity of the ta-C:N film electrodes to Pb as depicted in Fig. 1d and is attributed to the restricted transport of the Pb²⁺ ions induced by formation of more insoluble lead hydroxide in the less acidic solution [10]. In addition, unbalanced H⁺ and OH⁻ ions in the solutions also affect the kinetics of the redox reactions of Pb during the stripping analysis, which means that the increased H⁺ ions with decreased pH value of the solution decreases the solution resistivity, leading to an increased mobility of the Pb²⁺ ions during accumulation. The increased stripping peak currents of Pb with the increase of deposition time show a more pronounced trend in the more acidic solution compared to that for the less acidic one, which further reveals a lower restriction in transport of the Pb²⁺ ions in the more acidic solution as shown in Fig. 1d.

The measured standard deviation of stripping peak currents for five stripping cycles of Pb²⁺ (deposition potential = −1.2 V, deposition time = 120 s, pH = 3, scan rate ≈ 36 mV/s) is about 1.5%, that is confirmed by the repeated two hour tests, demonstrating good measurement repeatability and stability of the ta-C:N film electrodes. Dependence of the stripping potentials of Pb on the pH values of the solutions is illustrated in Fig. 1e, where it is clearly indicated that a lower pH value shifts the stripping potential of Pb to more negative values in accordance with the Nernst equation, e.g. from −486 to −429 mV with pH 1 compared to −488 to −415 mV with pH 3, especially at longer deposition durations. This reveals a stronger influence of the amount of H⁺ ions on the stripping potentials of Pb than that of the deposited Pb.
Fig. 1b and c shows an influence of scan rate on the stripping voltammograms of Pb measured in the same solution with the same pH value (pH 1). The stripping peaks measured at the faster scan rate (about 97 mV/s) have larger intensities and widths than the ones measured at the slower scan rate (36 mV/s) as shown in Fig. 1c, which can be explained by taking into account the size of diffusion layer and the time taken to record a scan. A linear sweep anodic stripping voltammetric (LSASV) technique measures an exact form of voltammograms that can be rationalised by voltage and mass transport effect, though the stripping voltammograms of Pb take a longer time to record at the lower scan rate (36 mV/s) at which the diffusion layer grows much thicker than the one measured at the faster scan rate (97 mV/s). Consequently, the flux (electrochemically active species from the bulk solution) to the film electrode surface is considerably smaller at the slower scan rate (36 mV/s) than that at the faster rate (97 mV/s). As a stripping current is proportional to a flux towards the electrode, the stripping peak currents of Pb are thus significantly higher with the scan rate of 97 mV/s than those measured with 36 mV/s as shown in Fig. 1d.

It is found that the stripping potentials of Pb also change with the scan rate. A faster scan rate (97 mV/s) shifts the stripping potentials of Pb to less negative values (−474 to −385 mV) than those (−488 to −415 mV) obtained at a lower scan rate (36 mV/s) as shown in Fig. 1b and c, which can be explained by the kinetic limitation of electrode reactions that causes an oxidation of Pb at less negative potentials [17]. If the kinetic of the reactions is lower corresponding to 97 mV/s than that corresponding to 36 mV/s, it means that the stripping current of Pb takes more time to respond to the applied voltage at a faster scan rate, resulting in the stripping potentials of Pb shifted to less negative values.

The stripping voltammograms of Pb obtained from the ta-C:N film electrodes in the same solutions as used from Fig. 1 as a function of deposition potential are shown in Fig. 2a and b, where more negative deposition potentials from −1.0 to −1.6 V give rise to apparently stronger stripping peaks of Pb with both pH values. More negative deposition potentials result in an increase of ion mobility from the bulk solution to the film electrode surface, leading to a proportional increase in the amount of Pb deposited on the electrode surface. Furthermore, when the pH of the solution is reduced to unity, the stripping peaks of Pb become more pronounced (Fig. 2b) as well as the sensitivity of the ta-C:N film electrodes to the Pb²⁺ ions is significantly enhanced (Fig. 2c). However, a falling stripping peak current of Pb (Fig. 2c) is found in the more acidic solution (pH 1) when the deposition potential is more negative than −1.4 V, which is probably due to a concomitant hydrogen evolution occurring earlier in the more acidic solution during accumulation [12,18].

In Fig. 2d, the stripping potentials of Pb shift to less negative values (−0.446 to −0.441 V for pH 1 and −0.436 to −0.434 V for pH 3) with
more negative deposition potentials from $-1$ to $-1.2$ V, which has shown a quasi-reversible reaction of the Pb$^{2+}$ ions on the ta-C:N film electrode surface. It is known that the concentration of redox species involved in the electrode reactions is established at the film electrode surface, indicating a much slower transport of the metal ions [17].

Therefore, the observed quasi-reversible reaction of Pb indicates that the concentration of Pb$^{2+}$ ions (0.1 mM) used in this study is high enough so that the kinetics of the electrode reactions is not much faster than the transport of the Pb$^{2+}$ ions caused by a large concentration gradient between the interface region and the bulk solution. When the deposition potential is further shifted to more negative values up to $-1.6$ V, it is found that the stripping potential of Pb is shifted to more negative values from $-0.441$ to $-0.445$ V for pH 1 and from $-0.434$ to $-0.437$ V for pH 3, revealing that greater negative deposition potentials result in the reversible reactions of the Pb$^{2+}$ ions on the ta-C:N film electrode surface. It is known that the larger the negative value of a deposition potential, the closer the hydrogen evolution is. Therefore, when the deposition potential is more negative than $-1.2$ V, the developed hydrogen evolution near the film electrode surface disturbs the flux to the surface so that the kinetics of the electrode reaction on the film electrode surface becomes faster than the transport of the Pb$^{2+}$ ions causing downward shifts of the stripping potentials of Pb as shown in Fig. 2. In terms of pH value, it is found that the stripping potentials of Pb as a function of deposition potential are more negative in the more acidic solution (pH 1) than those measured in the less acidic one (pH 3), which can be correlated to the increased concentration of H$^+$ ions with decreased pH by applying the Nernst equation.

The stripping voltammograms of Hg obtained from the ta-C:N film electrodes in the solutions containing $1 \times 10^{-5}$ M Hg$^{2+}$ and different NaCl concentrations as a function of deposition time are shown in Fig. 3a and b, where the pH values of the solutions are not compensated by HCl in order to make the solutions near neutral (pH 7). The deposition potential and scan rate are $-1.2$ V and 36 mV/s, respectively. It is clearly seen that the stripping peaks of Hg measured in the 0.2 M NaCl solution are apparently pronounced compared to those measured in the 0.15 M NaCl solution. However, all the stripping peaks measured in both solutions are still affected by the restricted mobility of the Hg$^{2+}$ ions due to a low ionic conductivity of the neutral solutions. In addition, the reactions of the Hg$^{2+}$ ions with the OH$^-$ ions existing in the solution adjusted to the neutrality should be taken into account because of a high probability to form insoluble mercury (II) hydroxide that in turn affects the stripping voltammograms of Hg. That increasing concentration of NaCl in the solution from 0.15 to 0.2 M gives rise to stronger and sharper stripping peaks of Hg (Fig. 3a) due to a promoted ionic conductivity of the 0.2 M solution, which makes the mobility of the Hg$^{2+}$ ions faster.

The concentration of electrochemically active species (EAS) in the solutions such as H$^+$ and Cl$^-$ ions mainly influence the stripping currents of Hg during the stripping because the number of electrons released by dissolving the deposited Hg atoms is proportional to the concentration of the EAS [17]. When the solution has a limited supply of EAS at a large pH value and a low NaCl concentration, the transport of the EAS can restrict the access of EAS to the ta-C:N film electrode surface due to their low concentration gradient between the interfacial region and the bulk solution, resulting in diffusion controlled stripping peaks of Hg that are shown in Fig. 3a and b as the fluctuating stripping peaks [19]. Therefore, the replotted stripping peak currents of Hg vs. deposition time are consistently higher in the higher NaCl concentrated solution than those measured in the lower NaCl one (Fig. 3c).

Though a shift of stripping potential of Hg to more positive values (98 to 128 mV) with increased deposition time according to the Nernst equation is observed in the 0.2 M NaCl solution (Fig. 3a and d), a correlation between the stripping potential and deposition time is not...
found in the 0.15 M NaCl solution up to 120 s (Fig. 3b) as a deposition time less than 120 s may not be enough for a more dilute solution to follow the Nernst equation. Therefore, it is suggested that a longer deposition time is required to correlate the stripping potential of Hg with the deposition time for the solution with a lower NaCl concentration.

Fig. 4a and b displays the stripping voltammograms of Hg at the concentrations of $1 \times 10^{-4}$ M and $1.1 \times 10^{-7}$ M in the 0.1 M NaCl solutions as a function of deposition time at a scan rate of 36 mV/s and a deposition potential of $-1.2$ V. It is found that a higher concentration of Hg$^{2+}$ ions ($1 \times 10^{-4}$ M) gives rise to much better-defined stripping voltammograms of Hg as shown in Fig. 4a. A possible reason is that an increased concentration gradient of Hg$^{2+}$ ions can facilitate the transport of the Hg$^{2+}$ ions. However, a much lower concentration of Hg$^{2+}$ ions ($1.1 \times 10^{-7}$ M) can also generate the smooth stripping peaks of Hg in the 0.1 M NaCl solution (Fig. 4b) compared to the stripping peaks of Hg obtained from the solutions having $1 \times 10^{-5}$ M Hg$^{2+}$.
and higher (0.2 and 0.15 M) NaCl concentrations as shown in Fig. 3a and b. It may be supposed that the concentration of the EAS existing in the 0.1 M NaCl solution is sufficient for stripping the Hg deposit resulted from the very low concentration of $1.1 \times 10^{-7}$ M Hg$^{2+}$. A proportional increase of the stripping peak current of Hg with deposition time for both concentrations is found in Fig. 4a-c. Such experimental results point out that the ta-C:N film electrodes can have a very low detection limit of Hg$^{2+}$ ions in near neutral solutions compared to the stripping performance of similar ta-C:N film electrodes as reported in Ref. [12].

The Hg stripping potentials continuously shift to more positive values with longer deposition durations as shown in Fig. 4d, except the deposition time of 200 s for $1.1 \times 10^{-7}$ M Hg$^{2+}$. The lower concentration of Hg$^{2+}$ ions ($1.1 \times 10^{-7}$ M) results in the stripping potentials of Hg at lower values (77 to 100 mV) compared to those (154 to 246 mV) that resulted from the higher concentration of Hg$^{2+}$ ions ($1 \times 10^{-4}$ M). As mentioned above, herein an increased amount of Hg deposit with increased deposition time causes a shift of the stripping potentials of Hg to more positive values according to the Nernst equation.

A simultaneous tracing of multiple elements is carried out in the $1 \times 10^{-4}$ M Pb$^{2+} + 9 \times 10^{-5}$ M Hg$^{2+} + 0.1$ M NaCl solution (pH 1) as a function of deposition time with the resulted stripping voltammograms of Pb and Hg shown in Fig. 5a in which the Hg stripping peaks are pronounced than the Pb ones. The deposition potential and scan rate used are $-1.2$ V and 36 mV/s, respectively. A near linear relationship between the stripping peak current and deposition time for both Pb and Hg is observed in Fig. 5b. Though the concentration of Pb$^{2+}$ ions is larger than that of Hg$^{2+}$ ions, the stripping peak currents of Hg vs. deposition time are consistently higher than those of Pb (Fig. 5b), which implies that the ta-C:N film electrode used has a higher sensitivity to Hg$^{2+}$ than to Pb$^{2+}$ in the NaCl solution because Pb has a smaller deposition overpotential compared to that of mercury at the same deposition potential of $-1.2$ V [20]. Mercury’s tendency towards oxidization would have contributed to the sensitivity of the ta-C:N film electrode to Hg$^{2+}$ during the multi-element tracing. Because different elements have different redox potentials, their stripping potentials are also expected to be different, e.g., the stripping potentials of Pb and Hg are found from $-454$ to $-411$ mV and from $133$ to $175$ mV, respectively, depending on the deposition time as shown in Fig. 5c. A simultaneous detection of Pb and Hg also shows the same phenomenon mentioned above that increased deposition time shifts the stripping potentials of both metals to more positive values.

Fig. 6 shows the well-defined stripping voltammograms obtained from a simultaneous detection of Cu and Hg in the $1 \times 10^{-4}$ M Cu$^{2+} + 9.3 \times 10^{-5}$ M Hg$^{2+} + 0.1$ M NaCl solution (pH 1) as a function of deposition time, where the deposition potential and scan rate used are $-1.2$ V and 36 mV/s, respectively. Although a higher concentration of Cu$^{2+}$ ions than that of Hg$^{2+}$ ions is used during accumulation, the
sensitivity of the ta-C:N film electrode to the Cu$^{2+}$ ions is much lower than that to the Hg$^{2+}$ ions due to stabilization of Cu(I) by forming CuCl$_2^-$ through the following electrochemical mechanism [21]:

$$\text{Cu}_0 \leftrightarrow \text{Cu}^{2+} + 2e^- \quad [22]$$

$$\text{Cu}^{2+} + 2\text{Cl}^- \leftrightarrow \text{CuCl}_2^- \quad [23].$$

In addition, a larger deposition overpotential and self oxidation of Hg are the main reasons contributing to the higher sensitivity of the ta-C:N film electrode to the Hg$^{2+}$ ions.

The different redox potentials of Cu and Hg result in the stripping potentials of Cu at more negative values (−0.114 V to −0.072 V) compared to those of Hg (0.147 to 0.179 V) (Fig. 6). The stripping voltammograms recorded from the simultaneous analysis of multi-elements (Cu and Hg) show the third peaks that are the shoulders of the Hg peaks and might have resulted from the formation of the amalgamated Cu–Hg [24].

4. Conclusions

The experimental results showed that the ta-C:N film electrodes were suitable for the determination of single elements such as Pb$^{2+}$ and Hg$^{2+}$ and simultaneous multi-elements such as Pb$^{2+}$ + Hg$^{2+}$ and Cu$^{2+}$ + Hg$^{2+}$. It was observed that the sensitivities of the ta-C:N film electrodes to these elements were apparently influenced by deposition time, deposition potential, concentrations of both trace metal ions and electrolytes in solutions, pH value of solutions, and scan rate. The simultaneous tracing of Pb$^{2+}$ + Hg$^{2+}$ and Cu$^{2+}$ + Hg$^{2+}$ using linear sweep anodic stripping voltammetry produced well-defined stripping peaks with good peak separations. Some other trace heavy metals such as Cd, Fe, Ni, As, Ag, and Au in aqueous solutions will be investigated with the ta-C:N film electrodes developed in this study in future works.

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