CHAPTER VI

Summary
In chapter III, the adsorption behavior of DMT, AMT and MMT on Au electrode from different solvents was studied. Adsorption of DMT on Au surface from a completely deaerated aqueous solution led to the formation of a multilayer assembly via hydrogen bonding with water molecules, whereas adsorption from acetonitrile, ethanol, dimethyl sulfoxide and chloroform solutions led to the formation of a monolayer. On the other hand, adsorption of AMT and MMT on Au electrode from water and other solvents led to the formation of a monolayer. Since DMT has two S-H groups, it chemisorbed on Au surface through one of its two S-H groups, while the other S-H group is pointing away from the surface. The presence of free S-H groups on the Au surface was confirmed by CV, ATR-FT-IR and XPS. It is presumed that the free S-H groups of DMT on the Au surface form a hydrogen bond with the water molecules. Subsequently, DMT molecules in solution formed a hydrogen bond with the water molecules attached with DMT on Au surface, and this type of hydrogen bonding network goes on increasing when the soaking time of the Au surface in an aqueous solution of DMT increases. The involvement of water molecules in the multilayer formation was confirmed by ATR-FT-IR and XPS techniques.

DMT formed sub-monolayer, monolayer and multilayer on Au electrode depending upon the immersion time. The sub-monolayer of DMT separated the voltammetric signal of UA from AA by 210 mV whereas monolayer and multilayers of DMT failed to separate them. The voltammetric signals of AA and UA were highly stable and reproducible at a sub-monolayer of DMT modified Au
electrode. Fast electron transfer, weak hydrogen bonding interactions with AA and UA and prevention of fouling effect caused by oxidized products of AA can be achieved at the sub-monolayer of DMT. On the other hand, stable voltammetric signals for AA and UA were not observed at AMT and MMT sub-monolayer and monolayer modified Au electrodes. The practical application of the sub-monolayer of DMT was demonstrated by determining the concentration of UA in human urine samples without any pretreatment.

In chapter IV, fabrication of AMT film on electrodes by potentiodynamic polymerization method and its applications to the determination of AA, UA, XN, DA, EP, DOAPC, FA, CY, PA and nitrite ion were studied. AFM images showed that an ultrathin homogeneous film containing spherical structure with a thickness of ~25 nm was formed when the film was deposited by 15 cycles while a non-homogenous film containing cluster like structure with a thickness of ~40 nm was formed for the film deposited by 50 cycles. XPS studies revealed that the polymerization proceeded via S-S, HN-NH and N=N linkages. The possible mechanism for the electropolymerization of AMT was proposed.

The applications of p-AMT film were demonstrated by the determination of AA, UA, XN, DA, EP, DOAPC, FA, CY, PA and nitrite ion. The p-AMT modified electrode oxidized AA and CY at 0.14 and 0.62 V, respectively with a peak separation of 480 mV while bare GC electrode showed only one oxidation
peak at 0.55 V for both AA and CY in a mixture. The determination of CY in the presence of 10-fold excess of AA was achieved using the p-AMT film modified electrode. It also resolved voltammetric signals of AA, DA and UA in 0.2 M PB solution (pH 5.0) whereas bare GC electrode failed to separate them. The amperometric current was linearly increased from 200 nM to 0.80 mM for each AA, DA and UA and the lowest detection limit was found to be 0.92, 0.07 and 0.57 nM, respectively (S/N=3). The practical application of the p-AMT modified electrode was successfully demonstrated by the determination of DA in dopamine hydrochloride injection samples.

The p-AMT film modified electrode was also successfully separated the voltammetric signals of AA, EP, UA and XN in a mixture at pH 5.0 with potential differences of 150 mV between AA and EP, 120 mV between EP and UA and 400 mV between UA and XN whereas bare GC electrode failed to resolve the voltammetric signals of them. The p-AMT film modified electrode exhibited excellent sensitivity and selectivity towards EP, UA and XN in the presence of 40-fold higher concentration of AA. The amperometric current response was increased linearly with increasing EP concentration in the dynamic range of $4.0 \times 10^{-8}$ to $4.0 \times 10^{-5}$ M and the detection limit was found to be $27 \times 10^{-11}$ M (S/N=3). The practical application of the p-AMT film modified electrode was successfully demonstrated by measuring the concentration of EP in epinephrine tartrate injection and XN in human urine samples.
The bare GC electrode failed to resolve the voltammetric signals of AA, DOPAC and UA in a mixture at pH 5.0 whereas p-AMT modified electrode successfully resolved the voltammetric signals of them with potential differences of 140 mV between AA and DOPAC and 130 mV between DOPAC and UA. The modified electrode exhibited an excellent sensitivity and selectivity towards DOPAC even in the presence of 50-fold excess of each AA and UA. The amperometric current response was increased linearly with increasing DOPAC concentration from $4.0 \times 10^{-8}$ to $1.0 \times 10^{-5}$ M and the detection limit was found to be 150 pM ($S/N=3$).

The p-AMT film modified electrode successfully resolved the voltammetric signals of AA, FA and UA in a mixture at physiological pH whereas bare GC electrode failed to resolve them. The oxidation current of FA was enhanced at p-AMT film modified electrode when compared to bare GC electrode due to the hydrophobic interaction between the modified electrode and FA molecules. It exhibited an excellent sensitivity and selectivity towards FA even in the presence of 200-fold AA and 100-fold UA. The amperometric current response was increased linearly with increasing FA concentration in the linear range of $1.0 \times 10^{-7}$ to $8.0 \times 10^{-4}$ M and the detection limit was found to be $0.23 \times 10^{-9}$ M ($S/N=3$). The practical application of p-AMT modified electrode was successfully demonstrated by measuring the concentration of FA in human blood serum samples.
A detection of 100 nM nitrite ion in the presence of 1000-fold higher concentrations of common interferents such as Na\(^+\), F\(^-\), Ca\(^{2+}\), Cl\(^-\), Mg\(^{2+}\), SO\(_4\)^{2-}, NH\(_4\)^{+}, K\(^+\), CO\(_3\)^{2-} and NO\(_3\)\(^-\) and common physiological interferents such as glucose, urea and oxalate was achieved at p-AMT modified electrode by amperometry method. Further, the amperometric current was linearly increased from \(5.0 \times 10^{-8}\) to \(1.6 \times 10^{-5}\) M and a detection limit was found to be 340 pM \((S/N=3)\). The practical application of the p-AMT film modified electrode was successfully demonstrated by the determination of nitrite ion in water samples.

The bare GC electrode failed to resolve the voltammetric signals of AA and PA whereas p-AMT modified electrode successfully resolved the voltammetric signals of them with a potential difference of 240 mV. The modified electrode exhibited an excellent sensitivity and selectivity towards PA even in the presence of 500-fold excess of AA. The amperometric current response was increased linearly with increasing PA concentration from \(5.0 \times 10^{-8}\) to \(5.0 \times 10^{-5}\) M and the detection limit was found to be 0.34 nM \((S/N=3)\). The p-AMT modified electrode was successfully applied to the determination of PA in commercial drugs. Since p-AMT film contains positively charged backbone and also heteroatoms, it is expected that anionic forms of AA, UA, DOPAC and XN were electrostatically interacted with the positively charged backbone of the p-AMT film whereas positively charged EP and DA electrostatically interacted with the heteroatoms of the p-AMT film. Therefore, both positively charged and negatively charged
analytes oxidations current were dramatically enhanced at p-AMT film modified electrode when compared to bare GC electrode.

In chapter V, an ultrathin ATD polymer film was prepared on GC and ITO electrodes in 0.10 M H₂SO₄ by potentiodynamic polymerization method. The absence of a binding energy at 284.0 eV due to C-C or C=N clearly indicated that the electropolymerization of ATD proceeded via C=N and C-N linkages. The surface coverage calculated for the p-ATD film deposited by 15 cycles was found to be 2.12 × 10⁻¹⁰ mol cm⁻². This indicated that nanostructured ATD film was formed on electrode surface. The AFM image showed that the deposited p-ATD film has a homogeneous spherical structure with a thickness of ~ 25 nm.

The ultrathin film of p-ATD was successfully used for the determination of AA, UA, XN, DA, NEP and HCY. A detection limit of 51 pM (S/N=3) HCY was achieved at physiological pH. The bare GC electrode failed to separate the voltammetric signals of AA, NEP and UA in a mixture whereas p-ATD modified electrode successfully resolved the voltammetric signals of AA, NEP and UA with enhanced peak currents. The amperometric current was linearly increased from 40 nM to 25 µM for NEP and the lowest detection limit was found to be 0.17 nM, respectively (S/N=3). The practical application of the p-ATD film was successfully demonstrated by the determination of NEP in norepinephrine hydrochloride injection samples.

The p-ATD modified electrode separated the voltammetric signals of AA, DA, UA and XN with potential differences of 110, 152 and 392 mV between AA-
DA, DA-UA and UA-XN, respectively in 0.20 M PB solution (pH 5.0) whereas bare GC electrode failed to distinguish the voltammetric signals of them. The oxidation currents were increased from 30 to 300 μM for AA, 5 to 50 μM for DA and 10 to 100 μM for each UA and XN, and the lowest detection limit was found to be 2.01, 0.33, 0.19 and 0.59 μM for AA, DA, UA and XN, respectively (S/N=3). The practical application of the p-ATD film modified electrode was successfully applied for the determination of AA, UA and XN in human urine samples.

Similar to p-ATD film, p-ATD film also contains positively charged backbone and heteroatoms, hence it is expected that anionic forms of the AA, UA and XN were attracted by the positively charged p-ATD back bone and positively charged DA and NEP were attracted by heteroatoms of the p-ATD film. Thus, remarkable enhancement in the oxidation peaks current of both positively and negatively charged analytes with less positive potential shift were observed at p-ATD modified electrode when compared to bare GC electrode.