氏名（本籍・生年月日）	TRISNA KUMALA SARI（ｲﾝﾄﾞﾈｼｱ・1987年1月11日）
学位の種類	博士（学術）
学位記番号	乙　第　４６　号
学位授与の日付	平成３０年　３月　２０日
学位授与の要件	信州大学学位規程　第５条第１項該当
学位論文題目	Studies on the electrochemical determination of hexavalent chromium in environmental water based on carbon nanocomposite electrodes （ナノカーボン複合電極を用いた環境水中の六価クロムの電気化学分析法に関する研究）
論文審査委員	主査　金　継業　教授　　大木　寛　教授 巽　広輔　准教授　　高橋史樹　助教 鈴木保任　准教授

論 文 内 容 の 要 旨

In environmental water, chromium exists in two thermodynamically stable oxidation states, trivalent chromium Cr(III) and hexavalent chromium Cr(VI). Cr(III) is relatively less toxic and plays an essential role in biological processes, whereas Cr(VI) is a strong oxidizing agent which about 100-1000 times more toxic than Cr(III) due to its carcinogenic and mutagenic properties. In Indonesia, chromium is extensively used in industries such as leather tanning, electroplating, cement, mining, production of paints and pigments, and wood preservation. Therefore, reliable and convenient method for monitoring of Cr(VI) is significantly important in order to provide control of this highly toxic substance for human and environmental concerns. Electrochemical sensors have been proven to be promising analytical tool due to the advantages such as portability, sensitivity, selectivity, and low-cost instrumentation, a number of the electrode materials and detection strategies have been reported for electrochemical quantification of Cr(VI). In order to improve the analytical performance for Cr(VI) detection, this study focus on the development of analytical electrodes based on carbon nanocomposite materials.

First, a graphite/styrene-acrylonitrile (Graphite-SAN) copolymer composite electrode was developed for square wave anodic stripping voltammetry (SWASV) f of trace amounts of Cr(VI) in water without adding any other complexing agents. This method involves a pre-concentration step whereby the trace Cr(VI) is cathodically reduced to Cr(III) on an electrode surface in an acetate buffer (pH 5), followed by anodic stripping technique with a square-wave voltammetric mode. It is shown that the analytical sensitivity is significantly improved at the Graphite-SAN copolymer composite electrode in comparison with conventional glassy carbon electrode, due to the strong interaction between Cr(III) and the nitrile end group of SAN copolymer. Because Cr(VI) exists primarily as an anion ($HCrO_4^-$) in solution, most heavy metal ions, that would interfere with the ASV measurement can be easily removed with an aid of a cationic exchange solid phase extraction (SPE) cartridge. Under the optimal conditions, the stripping peak height linearly increased with the concentration of Cr(VI) in a range from 0 to 150 ng mL^{-1} with a correlation coefficient of 0.997, and the detection limit of 4.2 ng mL^{-1} (S/N≥3) was achieved. The Graphite-SAN composite electrode exhibited some interesting advantages, such as high mechanical rigid, easy surface renewable, higher sensitivity and better peak resolution in comparison with the results at conventional glassy carbon electrodes.

A highly sensitive amperometric sensor using graphene/gold nanoparticles (Graphene/AuNPs) was next proposed for the determination of trace Cr(VI) in river water samples, coupled with solid phase extraction technique. Considering that surfactants-free AuNPs present an improved specific surface activity, due to the absence of surfactants or ligands on the surface, the surfactants-free Graphene/AuNPs nanocomposites are prepared using an alternative sonochemical method by sonication of an Ar saturated aqueous solution containing 200 μM $HAuCl_4$, 1% (v/v) 2-propanol, and graphene (*ca.* 0.09 mg/mL). A novel electrochemical sensor is fabricated by the modification of Graphene/AuNPs onto glassy carbon electrodes by a simple drop casting method. Compared with the gold electrode, the glassy carbon electrode and the AuNPs modified glassy carbon electrode, the Graphene/AuNPs modified glassy carbon electrode exhibited the highest electrocatalytic activity and stability towards the reduction of Cr(VI), based on the results by cyclic voltammetry and electrochemical AC impedance studies. Moreover, the Graphene/AuNPs modified electrode has several advantages such as easy fabrication, excellent reproducibility, and selectivity. This study demonstrated that the Graphene/AuNPs based sensor can detect Cr(VI) with a low detection limit of 10 nM (~0.5 ng mL^{-1}), with a wide dynamic range of 0 to 20 μM (R=0.999).

With the aforementioned two strategies, the analytical advantages, such as inherent stability, high sensitivity, low detection limit, and low cost of analysis are demonstrated in the dissertation. These electrochemical sensors have been applied for the determination of trace level of Cr(VI) in river sample in Indonesia with satisfactory recovery values.