NICKEL BASED NANOMATERIALS FOR ELECTROCHEMICAL SENSORS

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By

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ABSTRACT

Nanotechnology has the potential to revolutionize various fields, offering solutions to challenges in medicine, electronics, energy, materials science, and more. In recent years, the topic of nanotechnology has significantly expanded opportunities for researchers, producers, and consumers across various sectors. Among the different types of nanoparticles, nickel nanoparticles (NPs) have garnered considerable interest. This is primarily due to their distinct magnetic, chemical, physical and electrochemical properties. Nickel nanoparticles can be nickel hydroxides, layered double hydroxides, metal oxides, metal clusters, metal organic frameworks, etc. The electrochemical property of the nickel nanoparticles opened a way to use it was electrochemical sensor.

We have synthesized a range of nanomaterials based on nickel via a simple and facile method at room temperature. A thorough analysis of the morphology and electrochemical properties of these substances has been conducted, showcasing their utility as electrochemical sensors for identifying biological, environmental, and industrially significant analyte molecules. The studies conducted using various nanomaterials given in this Thesis are briefed below.

Dopamine (DA), uric acid (UA) and α-lipoic acid (ALA) are biologically important molecules for human metabolism. The imbalance in DA, UA and ALA levels can cause several neurological problems, hyperuricemia and cardiovascular diseases respectively. We have opted for electrochemical sensing since the method is simple and fast with high sensitivity, low LOD and excellent selectivity. Electrochemical characterizations were carried out using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and differential pulse voltammetry (DPV). $Ni(OH)_2$ nanosheets synthesized was able to sense DA, UA and ALA individually and simultaneously in PBS solution. The detailed mechanism behind the sensing of DA, UA and ALA using $Ni(OH)_2$ nanosheets are studied and it was observed that the interaction of the analyte with -OH groups on nanosheets is the key step in the detection process. The LOD for electrochemical sensing were 1.32 μM and 1.701 μM and 2.66 μM for DA, UA and ALA, respectively. The method of electrochemical sensing of DA, UA and ALA are pH-dependent, and the number of electrons involved in the oxidation mechanism is 2.

To improve the properties of $Ni(OH)_2$ nanosheets a composite of $Ni(OH)_2$ with MoS_2 has been synthesized and the morphological and electrochemical properties have been investigated. The composite synthesised has better electrochemical properties including active surface area and charge transfer resistance. The composite was able to detect DA and ALA in PBS solution and the calculated LOD values were 56 nM for DA and 51 nM for ALA. The mechanism of interaction between composite and analyte was studied in detail and it was found to interaction of the analyte with -OH groups on nanosheets and the synergistic effect

of electronic interaction between $Ni(OH)_2$ and MoS_2. The stability and selectivity of the synthesized composite as electrochemical sensor has also been investigated.

Apart from $Ni(OH)_2$ nanosheets, ligand protected nickel clusters were also synthesized. The synthesis of nickel clusters is difficult since the magnetic properties can result in faster aggregation and nickel clusters have the tendency to get oxidized. Therefore, it is necessary to protect Ni NCs with capping ligands like thiols, phosphines, polymers, dendrimers, etc. These ligands can react with nickel precursor through the reduction of nickel metal precursor using a reducing agent or laser treatment or microemulsion and they can control the size of the nickel core and stabilize the clusters. Also, the nanoclusters synthesized here are used as such without adding other electrochemically active materials like CNT, graphene etc. The clusters have good electrochemical properties making them a potential candidate for electrochemical sensing. Two types of nickel clusters have been synthesized: dodecanethiol protected clusters and α-lipoic acid protected clusters. The dodecanethiol capped nickel clusters were able to detect Hg^{2+} and Cd^{2+} ions in PBS solution individually and simultaneously. The LOD values for Hg^{2+} and Cd^{2+} were found to be 13 nM and 22 nM, respectively. The clusters were also able to simultaneously detect both metal ion in the same PBS solution with the LOD values of 18 nM for Hg^{2+} and 44 nM for Cd^{2+}. The investigations were carried out to understand the interactions occurring between clusters and Hg and Cd ions and it was observed that the electrochemical sensing was based on the hard acid soft base (HSAB) principle, where soft metal ions interact with soft functional groups containing sulfur and undergo electron transfer.

α-lipoic acid protected Ni nanoclusters (NCs) were synthesized using $NaBH_4$ as a reducing agent. The material characterization of clusters was carried out using microscopic and spectroscopic methods. The electrochemical characterization of the clusters was carried out to understand the electrochemically active surface area and charge transfer resistance by using CV and EIS. The clusters were used as electrochemical sensor to detect riboflavin (Rb, vitamin B2) in 0.1 M PBS solution at a pH of 7.4. The LOD value was found to be 15 nM with a linear range of 45-90 nM. The sensing mechanism is based on the electroredox reaction happening between riboflavin and α-lipoic acid resulting in reduced form of riboflavin and β-lipoic acid. The stability, repeatability and selectivity of the sensor was studied in detail.

We presented simple approaches to produce electrochemically active nickel-based nanomaterials and explored their application in detecting valuable molecules. A comprehensive grasp of the materials, the sensing mechanism, and the stability of the material would contribute to expanding the application of these materials in electrochemical sensor technologies.