

Spontaneous Growth of Nanoparticles for Utilization in Sensing Platforms

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Opinion

Synthesis of nanoparticles to functionalize electrode surfaces in order to avail the sensing ability towards a particular analyte is highly desirable nowadays [1]. However, we have experienced a problem over the years during the fabrication of sensors using nanoparticles that is the assembly of nanoparticles is totally distinct in each separate modification process. Such random assembly of nanoparticles renders it difficult in reproducing the sensors and hence ineffective for developing real-life sensing devices. Herein, electrode surface charge dependent spontaneous growth of nanoparticles would be the most attractive solution. In such a case, the electrode might possess an inherent charge on its surface, an intrinsic crystalline facet, or the surface might be electrochemically charged to assemble nanoparticles on its surface. We were able to grow nanoparticles of various elements that exhibited high sensing performance. For instance, a simple Glassy Carbon Electrode (GCE) where all the carbons are sp^2 hybridized becomes negatively charged when kept in a basic solution. Later, the charged surface can attract diverse metal ions when immersed in a metallic salt solution, for example, $CuSO_4$ or $AgNO_3$. The metal ion is then reduced at the electrode surface and nucleates to produce a definite structure. For instance, we were able to grow Ag nanoparticles having dendrite structure on GCE surface with high reproducibility [2]. The as-prepared nanostructure was successfully employed as an ascorbic acid sensor. Such a method could come handy for easy preparation of diverse nanostructure without the need for any nucleating agent or high temperature and pressure. This method works fine in basic solutions only. However, another technique can be applied for growing nanoparticles on GCE in an acidic solution. Anodic scanning of a GCE using a potentiostat can develop carbonyl (C=O) group on the surface. Afterward, a cathodic scanning towards a negative potential can impart negative charges to the C=O groups. The developed negative charges can drive the spontaneous growth of nanoparticles by reducing the metal ions from a metal salt solution. Using such a method, we were able to grow flower-shaped gold nanoparticles on a GCE surface [3]. The flower-shaped gold nanostructure was homogeneously dispersed on all over the GCE surface. This method is expected to help easily grow other metal nanoparticles on the electrode surface for sensor application.

Sometimes the innate crystalline facets on an electrode surface can help induce monolayer nanoparticle growth. For instance, a polycrystalline gold surface is known to have three key facets i.e., Au (100), Au (110), and Au (111). These crystalline facets can help spontaneous growth of diverse anions other than metal atoms, for example, thiocyanate, thiol, chloride, bromide, fluoride etc. A pure polycrystalline gold electrode is often unfavorable for carrying out many electrochemical reactions due to rapid surface fouling. Herein, we found that a surface coating using self-assembled monolayer molecules can remove surface fouling issue. Furthermore, monolayer of different molecules can be employed for sensing different analyte. Particularly, we have found that an iodine adlayer forms on polycrystalline gold electrode when the electrode is immersed in potassium iodide salt solution. The iodine layer was pretty stable on the electrode and was employed to quantitatively sense and measure paracetamol drug from solution [4]. We also achieved spontaneous immobilization of sulfur atom nanoparticles monolayer on the same polycrystalline gold electrode. When the electrode is immersed in sodium sulfide solution, sulfur atoms self-assemble on the electrode surface via chemisorption mechanism [5]. Here, sulfur atoms receive charge from gold surface owing to their high polarizable character and induces positive charge on the gold electrode. When some sulfur atoms are removed in the electrochemical process, the charged and activated gold electrode gets exposed. The unblocked area of the electrode renders the sensing of different analyte possible. The sulfur adlayer modified polycrystalline gold electrode was employed for sensing hydrogen peroxide. Sulfur-based species are perhaps favorable for sensing of hydrogen peroxide. Cysteine is a thiol (-SH) group containing non-essential amino acid. We tried forming a self-assembled monolayer of thiol group containing cysteine on polycrystalline gold electrode. We were successful in obtaining the monolayer which was later employed for electrochemical sensing of hydrogen peroxide. The thiol group modified sensor was able to detect hydrogen peroxide with high efficiency showing no interference effect [6]. The thiol group activated the gold electrode in a similar fashion with that of sulfur monolayer. We then made an attempt to create monolayer of another sulfur-based species i.e., thiocyanate (SCN⁻). Thiocyanate was chemisorbed on the gold electrode almost instantaneously and strongly. Oxidation of uric acid is viable on a polycrystalline gold electrode. However, rapid surface fouling occurs by reaction products of uric acid oxidation. When the electrode was immersed in a potassium thiocyanate solution for several minutes, a thiocyanate monolayer immobilizes on the electrode surface spontaneously. Such a simple technique was able to dodge fouling issue of the polycrystalline gold electrode surface facilitating efficient sensing of uric acid via electrooxidation reaction [7].

Despite the advancements discussed so far, there is still much to be explored in terms of the potential for in-situ spontaneous immobilization of nanoparticles of different molecules in the formation of a mono adlayer. The ability to immobilize nanoparticles in a controlled manner so easily would revolutionize the development of sensing devices. More research is yet needed to identify the most appropriate electrode materials and nanoparticle types for developing high-performance electrochemical sensors. The development of new sensing devices that can detect analytes with high precision and accuracy could have far-reaching implications in fields such as point of care medical devices, on-site environmental and food safety monitoring etc. Therefore, continued investment in research aimed at advancing the field of spontaneous nanoparticle immobilization is essential for unlocking the full potential of electrochemical sensing and leveraging their application in real life.



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