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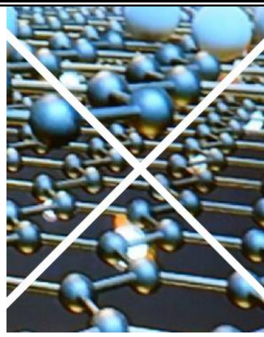

DEVELOPMENT AND VALIDATION OF MOLECULAR IMPRINTED SENSORS AND APPLICATIONS TO REAL SAMPLES

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Abstract

In this review, novel imprinted sensors approach based on nanomaterials including graphene/graphene oxide/graphene quantum dots, carbon nanotubes, carbon nitride nanotubes and two-dimensional (2D) hexagonal boron nitride (2D-hBN) nanosheets were presented for important agent's detection in real samples. Firstly, the chemical and physical properties of novel nanomaterials in development of nanosensors were investigated. After that, various techniques such as x-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods were explained for the characterization of the molecular imprinted sensors. The molecular imprinting sensors have been used for many applications such as chemistry, pharmacy, energy. Finally, the development and procedure of the imprinted electrodes on nanomaterials were investigated.

Keyword: Nanosensors, Nanomaterials, Characterization, Molecular Imprinting, Application

1. Introduction

In the last two decades, quantitative analysis of important chemicals and agents such as pharmaceuticals, pesticides, heavy metals is essential. Until recent years, several analytical methods were developed for significant agent detection. These procedures, however, entail several

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extraction processes and complex equipment. Owing to these situations, cheap and sensitive techniques based on nanomaterials are needed. Moreover, new electrochemical methods based on nanomaterials have significant functions such as sample preparation, selective signals and detection in biological matrices [1]. The nanostructured materials are significant modifiers because of efficient electron mediators and surface areas [2-5]. The nanocomposites are frequently utilized for nanosensor development [6-11]. The crucial developments were carried out in the production of nanosensors with suitable cost, selectivity and sensitivity [12].

Nonetheless, there are still problems like as weak results and the use of unnecessary chemicals in development. In order to overcome these problems, novel nanomaterials having high conductivity, surface area and eco-friendly are needed. Nanomaterial-modified sensor methods show a chief driver towards the target molecule since novel nanomaterials and their composites have functional tunability, high electrical, optical and catalytic properties. These materials with nano diameter are tunable catalysts, owing to their plasmonic structure. These nanomaterials are used in analysis methods based on catalysis. Nanomaterials such as carbon nanotube and graphene/graphene oxide show efficient electron transfer kinetics because of the conductivity towards analyte molecule. The synthesis of these nanomaterials in the 1 – 100 nm size range is very significant owing to functional tenability and the ability of self-assembly [13, 14]. New materials which are created by combining at least two distinct materials at the macro level are called composite materials. This chapter is focused on the novel class of nanomaterials. We take attention on how novel nanomaterials and their composites can affect the electron transfer in the detection of key agents and how nanomaterials with molecular imprinted polymers gain sensitivity and selectivity.

2. Types of Carbon-based Nanomaterials

2.1. Graphene/Graphene Oxide

Graphene/graphene oxide is "a rising star" in the class of carbon materials owing to its mechanical strength [15, 16], low density and efficient conductance [17, 18]. It has two-dimensional sheet and its honeycomb structure is based on the other significant allotropes. π-conjugation in graphene/graphene oxide shows magnificent thermal and mechanical properties. Firstly, Geim and co-workers produced single-layer graphene [19]. The first isolation of graphene inspired great interest in researchers. First reports explained graphene's field effect [19], the quantum Hall effect [20] and high carrier mobility [21]. These excellent properties occurred effective interest in the possible applications of graphene such as nanosensors and modified electrodes for ultra-sensitive detections and fuel cells. The one of the most efficient techniques is the production of atomically thin specimen to isolate graphene. The absorbance of graphene was measured at 2.3%, indicating direct visual observation [22]. The scientific group in England utilized an interference effect at 300 nm thickness of SiO_2 to observe single flakes under white-light illumination [23]. Graphene quantum dots have a large surface area and high conductivity for electronic or optoelectronic sensors [24]. They also are surface grafting material. Therefore, the investigations on graphene quantum dots are important studies on especially chemistry and interdisciplinary science [25].

2.2. Carbon Nanotubes

Carbon nanotubes are graphite sheets. The structure of carbon nanotubes is not similar to diamond whose 3-D structure is cubic crystal type having four neighbors with tetrahedron. However, 2-D sheet of carbon atoms into nanotubes is formed as arranged in a hexagonal array [26]. The properties of nanotubes are related to atomic arrangement and the length of the tubes. Nanotubes have two types: (1) single-walled (SWCNTs), (2) multi-walled carbon nanotubes (MWCNTs) structures. Figure 1 demonstrates TEM image of MWCNTs, showing that several layers of graphitic carbon.

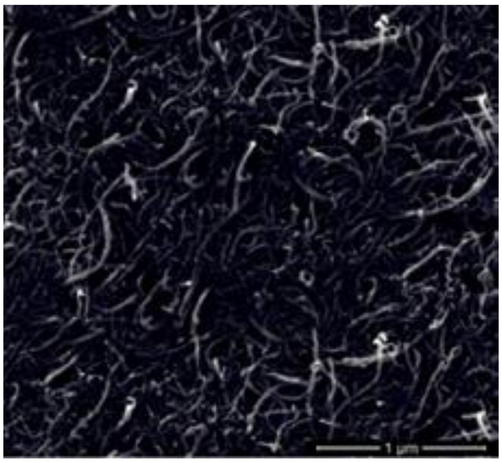

Figure 1. TEM micrograph of MWCNTs [27]

They are concentric single walled tubes with different chirality. These nanotubes are in interaction with secondary and van der Waals bonding. In addition, MWCNTs and SWCNTs can enable composite material formation by functionalization of structures.

3. Types of Nanomaterials Including Hetero Atoms

3. 1. Graphitic Carbon Nitride (g-C_3N_4)

g-C_3N_4, as a photocatalyst, is a good stability nanomaterial. Among carbon-based nanomaterials, g-C3N4 is a carbon allotrope. It is useful in energy applications such as fuel cells. Van der Waals interactions dominate its structure. It is used in nanosensors and catalytic processes. Pure g-C_3N_4 has electron-hole pairs in recombination on activity. Owing to its electronic structure, it is good material for functional materials on the sensor signal [28]. g-C_3N_4 involving van der Waals forces is converted into the ultra-thin g-C_3N_4 (utg-C_3N_4) for sensor applications [29, 30]. The bulk structure of g-C_3N_4 is on Figure 2A. The g-C_3N_4 is converted into utg-C_3N_4 nanosheets after ultrasonic treatment (Figure 2B). The structure of nanotube is on the SEM image of C_3N_4 NTs (Figure 2C). During the hydrothermal treatment, the tubular structure is formed by curling utg- C_3N_4 [31].

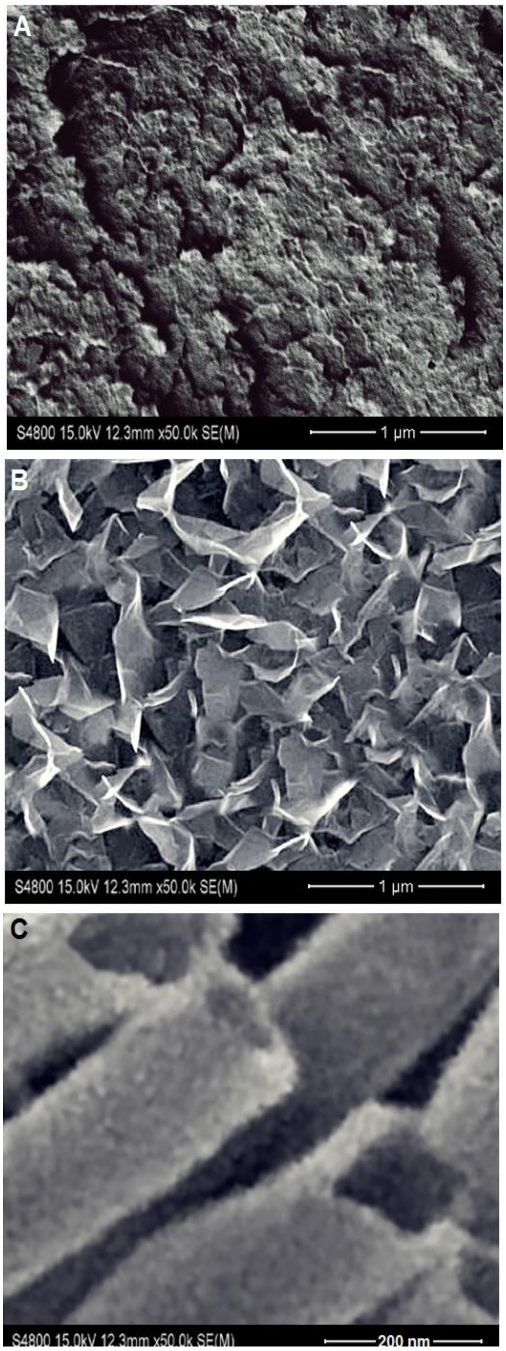

Figure 2. SEM images of (A) bulk g-C_3N_4; (B) utg-C_3N_4 nanosheets; (C) C_3N_4 NTs [31]

3. 2. Hexagonal Boron Nitride

2D-hBN nanosheets are a class of 2D materials. They have significant sensor and catalysis applications [5, 32]. Due to stable dispersions, they have high temperature stability, large surface area and transparent property in IR region [33]. Figure 3A reveals XRD pattern of bulk boron nitride (curve a) and 2D-hBN nanosheets (curve b). The diffraction peaks corresponding to (100), (101), (102) planes are shown. Nonetheless, (002) plane remains intact [34]. SEM image (Figure 3B) of boron nitride verifies the structure of bulk. The irregular morphology is obtained. After its ultrasonication, 2D-hBN nanosheets are obtained. Their particle thickness decreases in comparison with the bulk structure (Figure 3C).

4. Molecular Imprinting Polymers

Molecular imprinting polymers (MIPs) are the copolymerization of functional and cross-linking monomers in target molecule. In addition, the active tips on analyte is the presence of crosslinked polymeric networks. Subsequent removal of the imprint molecule reveals binding sites. Hence, the cavities are formed to specific template (Figure 4). MIPs are artificial recognition media and the techniques based on molecular imprinting are used for drug delivery, catalysis and sensor technology [35].

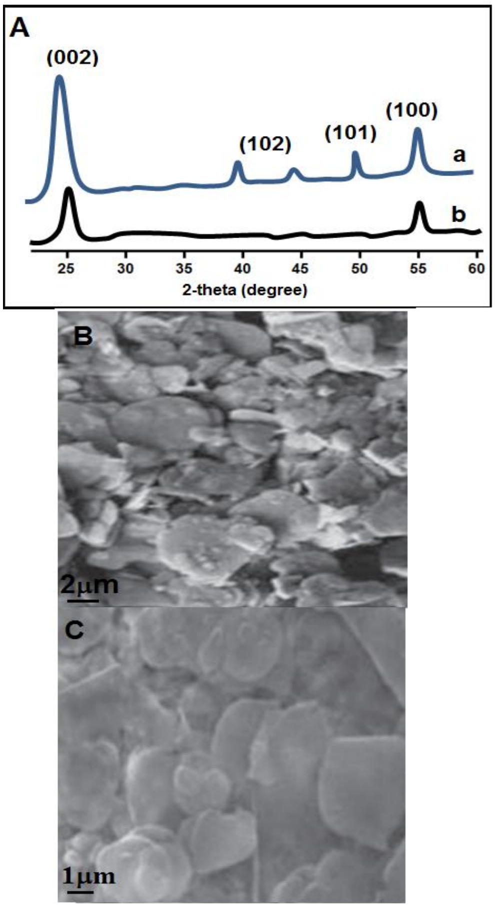

Figure 3. XRD pattern (A) of bulk boron nitride (curve a) and 2D-hBN nanosheets (curve b); SEM images of (B) bulk boron nitride; (C) 2D-hBN nanosheets [34]

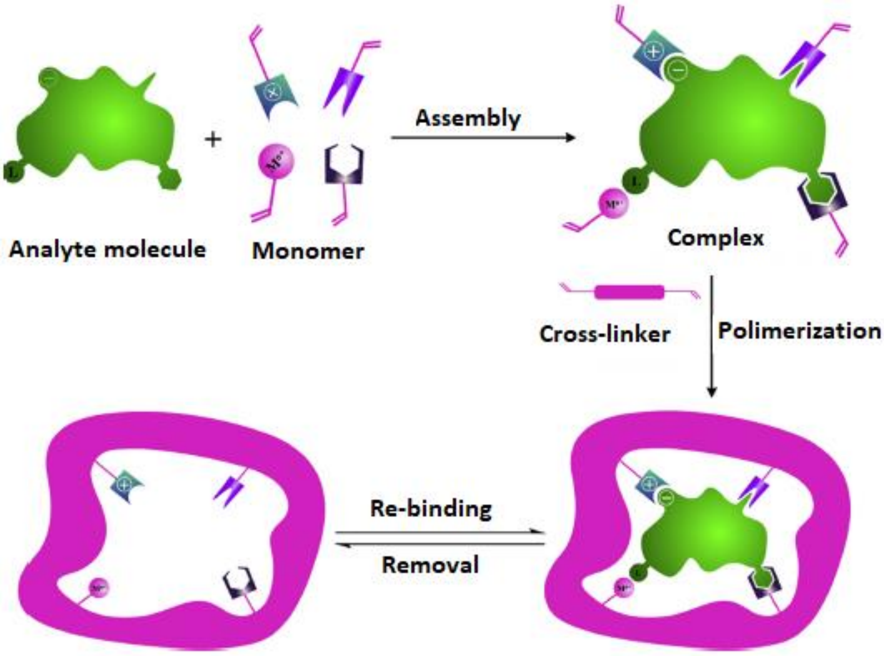

Figure 4. The preparation of molecular imprinted polymers [36]

5. Important Applications of Molecular Imprinted Sensors

Many studies were reported about molecular imprinted applications based on novel nanomaterials and nanocomposites for sensor developments. Atar et al. reported citrinin (CIT)-imprinted electrochemical sensor based on glassy carbon electrode (GCE) modified with platinum nanoparticle (PtNPs)/polyoxometalate (POM) functionalized reduced graphene oxide (rGO) (Figure 5). The created sensor was utilized to measure CIT, a mutagenic and carcinogenic metabolite [37]. Firstly, the nanomaterials in suspension were dropped onto the GCE surface. After the solution was removed by an infrared (IR) lamp, PtNPs/POM/rGO nanomaterial modified GCE was obtained. In this case, it is useful to say that the modified electrode has higher surface area than un-modified surfaces and the better conductivity and sensor response were obtained. According to EIS results (Figure 6A), the highest conductivity was seen on PtNPs/POM/rGO/GCE in comparison rGO/GCE and POM/rGO/GCE. In addition, the performances of different electrodes were compared by differential pulse voltammetry (DPV) (Figure 6B). The sensor performance of MIP/PtNPs/POM/rGO/GCE (curve d of Figure 6B) is better than other imprinted electrodes. After that, the imprinted sensor was carried out via electropolymerization of pyrrole containing CIT.

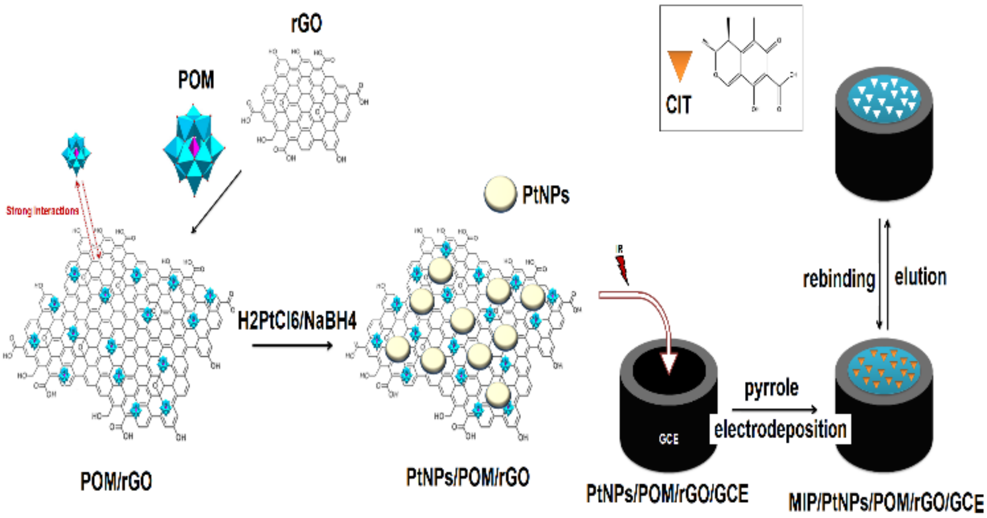

Figure 5. The development of CIT- imprinted sensor [37]

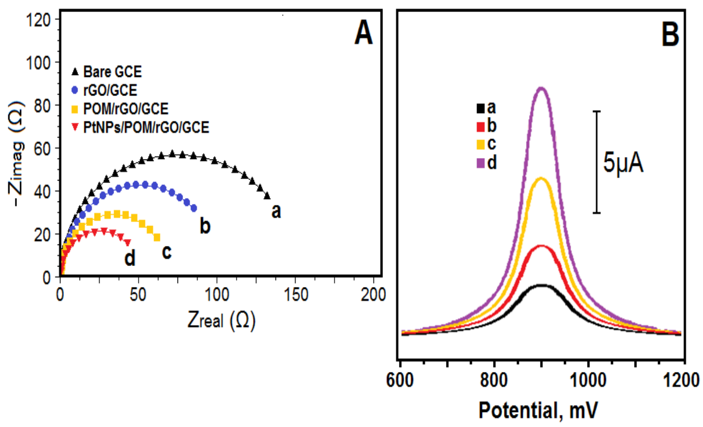

Figure 6. (A) Fitting of impedance spectrums and (B) DPV curves of electrodes (curve d: MIP/PtNPs/POM/rGO/GCE) [37]

The imprinted voltammetric sensor with gold nanoparticles (AuNPs) decorated graphene oxide (GO) for tyrosine detection was developed [38]. The imprinted electrode was prepared by CV in the presence of phenol and tyrosine (Figure 7A). The imprinted sensor was found as linear (1.0×10^{-9}-2.0×10^{-8} M) and sensitive. Stability and reproducibility were also investigated. After the modification of electrodes with nanomaterials, EIS results were obtained (Figure 7B) and AuNPs/GO modified electrode showed characteristic of a diffusional step. In addition, DPV curves show that the currents increased linearly with tyrosine amounts (Figure 7C). The detection limit (LOD) was calculated 1.5×10^{-10} M. In another work, silver nanoparticles (AgNPs) were used in POM functionalized rGO modified GCE to test for ochrattoxin A, a mycotoxin [39]. After characterization studies, the developed sensor was utilized for the recovery experiments. Hence, the high selectivity was founded in grape and wine samples. In the presence of the other mycotoxins, the imprinted sensor demonstrated high stability and selectivity.

Yola et al. proposed an electrochemical sensor for chlorpyrifos detection based on carbon nitride nanotubes (C3N4NTs) coated with graphene quantum dots (GQDs) [40]. The obtained nanocomposites were characterized. The bulk structure of g-C_3N_4 was observed in Figure 8A. The g-C_3N_4 is formed into utg-C_3N_4 nanosheets after crashing (Figure 8B). The nanotube structure is shown in Figure 8C). The transparent GQDs was shown in Figure 8D. Figure 8E indicates nanojunction and nanopore structure (C_3N_4NTs@GQDs) with cross-linking together. After the formation of chlorpyrifos imprinted polymer on modified electrode, the layer of polymer was seen on the C_3N_4NTs@GQDs modified surface (Figure 8F). Finally, the experiments of linearity and LOD were calculated.

A novel molecular imprinted sensor technique based on decorated 2D-hBN nanosheets with core-shell nanoparticles. (Figure 9) was shown for the detection of cypermethrin (CYP) in wastewater samples. Imprinted sensor was generated in presence of phenol and CYP as analyte by CV. In wastewater sample analysis of deltamethrin (DEL), tetrametrin (TET), and permethrin (PER), linearity and LOD were determined to be 1.010^{-13} - 1.010^{-8} M and 3.010^{-14} M, respectively.

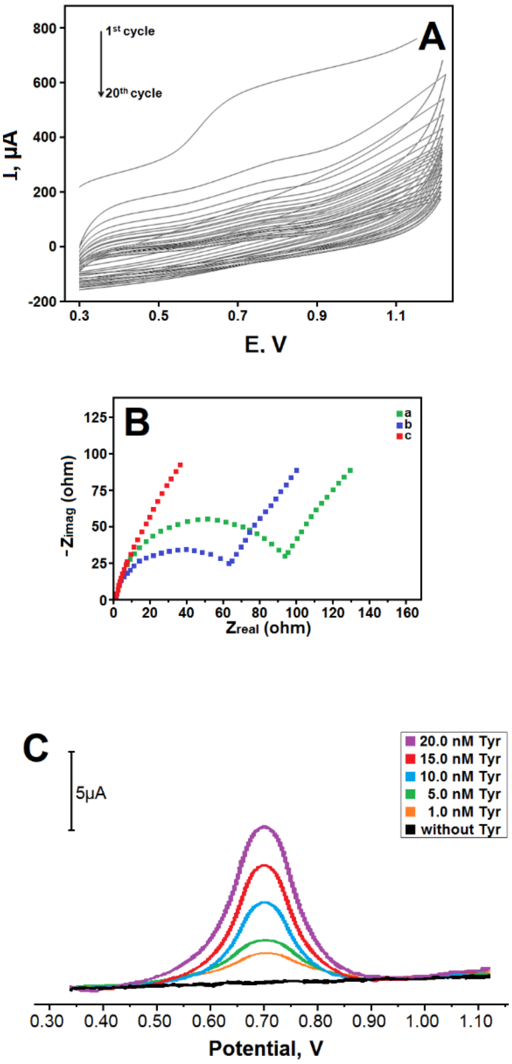

Figure 7. (A) Electropolymerization on AuNPs/GO modified electrode by CV, (B) EIS spectrums of modified electrodes (curve a: bare electrode, curve b: GO modified electrode, curve c: AuNPs/GO modified electrode), (C) DPVs of the MIP/AuNPs/GO modified electrode on different tyrosine amounts [38]

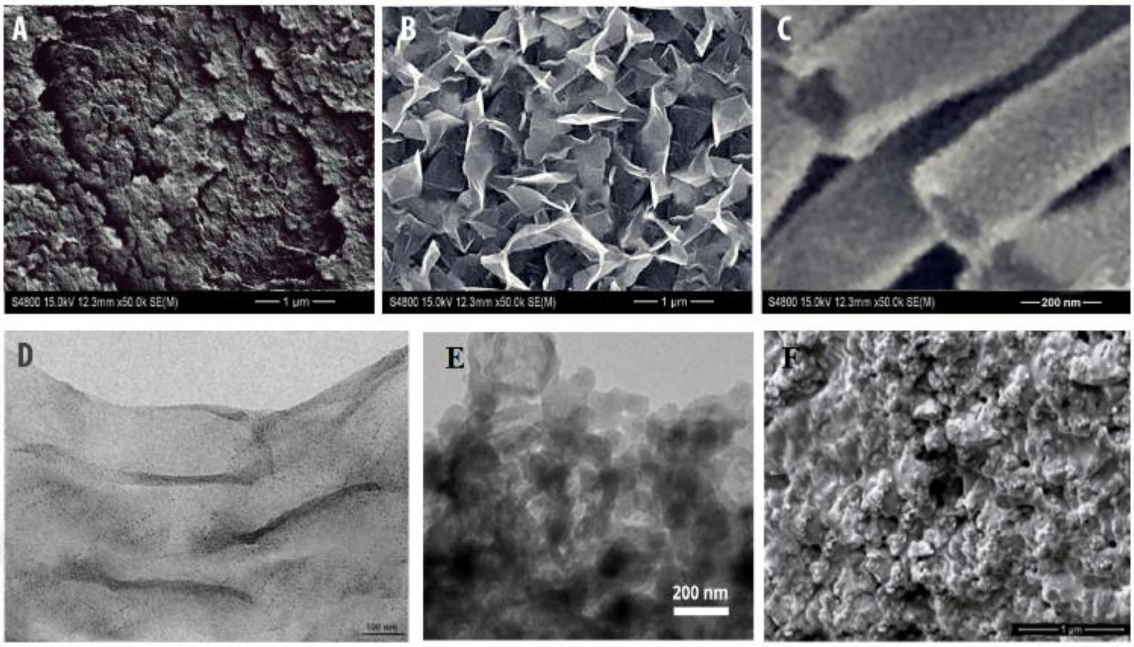

Figure 8. SEM images of (A) bulk g-C_3N_4; (B) utg-C_3N_4 nanosheets; (C) C_3N_4 NTs; TEM image of (D) GQDs; (E) C_3N_4NTs@GQDs nanohybrid; (F) SEM image of MIP/C_3N_4NTs@GQDs modified surface [40]

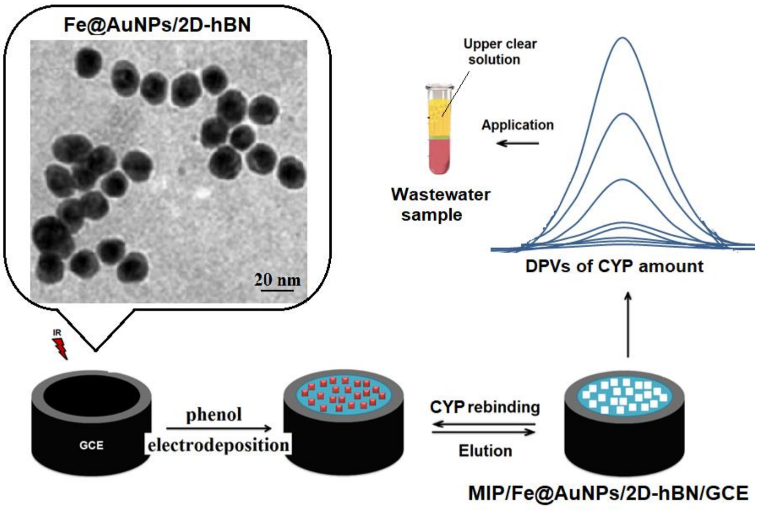

Figure 9. The procedure of MIP/Fe@AuNPs/2D-hBN/GCE [41]

6. Conclusions

This review proposes the molecular imprinted nanosensors based on novel nanocomposites with graphene/graphene oxide, carbon nanotubes, carbon nitride and hexagonal boron nitride. The molecularly imprinting electrochemical sensors based on nanomaterials, in particular, have recently received a significant attention. These nanosensors based on polymer and nanomaterials have high selectivity, sensitivity and good stability for real samples analysis. In this chapter, the critical applications in sensors and the significance of graphene/graphene oxide, carbon nanotubes, carbon nitride and hexagonal boron nitride have been discussed. More sensor applications based on new nanocomposites will be demonstrated in the near future.

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Conflicts of Interest
The authors confirm that this article content has no conflict of interest.

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