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Nano silver imprinted polyvinyl alcohol nanocomposite thin films for Hg^{2+} sensor

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ABSTRACT

Silver nanoparticle (Ag NP) imprinted sodium alginate (SA)/polyvinyl alcohol (PVA) nanocomposite thin films are fabricated using "one pot" synthetic protocol. Herein, sodium alginate is behaved as both, reducing and stabilizing agent during preparation of Ag NPs. The formation of Ag NPs is optimized through the variation of reaction temperature and confirmed by UV–vis spectroscopy. Transmission electron microscope (TEM) and Fourier transform infrared (FTIR) studies of nanocomposite thin films are performed to establish the microstructure and surface functionalities. Structural analysis of SA-Ag/PVA nanocomposite thin films is investigated carried out through by X-ray diffraction (XRD) study. As-prepared SA-Ag/PVA thin films are found to capable of detecting a very low concentration of Hg^{2+} in aqueous solution. The lower limit of detection (LOD) and limit of quantification (LOQ) of the SA-Ag/PVA nanocomposites thin film are found to be 0.9 ppb and 3.04 ppb respectively. This nanocomposite thin film shows a linear response for Hg^{2+} (aq) from 0.9 ppb to 1200 ppb. The decrease in intensity and blue shift in the surface plasmon resonance (SPR) band of imprinted Ag NPs is observed even at 2 min in the presence of mercury. Different analytical parameters, such as contact time, temperature and pH of the analyte medium are varied to investigate practicability of the sensor film. The SA-Ag/PVA nanocomposite thin film shows a good response to Hg^{2+} (aq) in pH 2.0–10. The interference of the other metal ions towards the detection of Hg2 + (aq) is found poor and therefore SA-Ag/PVA nanocomposites thin films can be assigned for the sensitive and selective detection of Hg^{2+} in aqueous phase.

1. Introduction

The daily consumption of toxic mercury (Hg^{2+}, Hg^{+}, Hg) and its slow accumulation in living organisms from soils or water bodies cause various disorders like brain damage, kidney failure, lung problems [1–3] and other severe diseases like acrodynia, Hunter-Russell, minamata [4,5]. The higher concentration of mercury (II) in blood vessels and brain has also been accused for the development of Alzheimer's disease [5]. Therefore, the maximum permissible range of mercury has been restricted to ~2 ppb in drinking water by the U.S. Environmental Protection Agency and ~1 ppb by the China government [6]. Hence, the maximum research interest has been devoted to design efficient sensor materials for mercury detection. Metal ion based fluorophore systems, polymeric materials and proteins have been successfully designed for the detection of mercury. The operational behaviour of these sensors is carried out in vapour state whereas; the most essential issue remain left, like aqueous phase detection of mercury for drinking water safety. An effective and good sensor is characterized with its selectivity, ultra-high sensitivity; reliability and environmental friendly nature. Various techniques like inductively coupled plasma mass spectrometry (ICPMS) [7], atomic absorption/emission spectrometry (AAS/AES) [8], atomic fluorescence spectrometry (AFS) [9], high-performance liquid chromatography (HPLC) [10] and flame photometry [11] are used for the determination of Hg^{2+}. Instead of their excellent performance, the uses of these methods are limited due to the expenses of expensive instrumentation and time-consuming sample preparation and preconcentration procedures [12]. Colorimetric sensors provide the instance optical feed, but this technique is carried out only *in situ* method. Whereas, the use of nanocomposite thin film for the detection of Hg^{2+} (aq) by UV–vis absorption spectroscopy are blessed with several benefits, like simplicity, high sensitivity, faster response and ease of measurement. Moreover, the nanocomposite thin film can be used as *ex situ* as well. To develop better Hg^{2+} sensing performance into the fabricated polymeric films, different technologies are introduced recently [13]. "Molecular imprinting"

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is one of them [14,15]. It introduces the recognition properties into synthetic polymers. It would give the polymer "memory" function which is similar to natural biological recognition system. The process of molecular imprinting involves the polymerization of functional monomer and cross-linkers around a molecular template [16,17]. This is categorized into five main division and these are non-covalent, electrostatic/ionic, covalent, semi-covalent and metal centre co-ordination [18]. Instead of designing different molecular imprinting polymer (MIP) probes for selective detection of mercury, researchers are also motivated to incorporate different nanomaterials to the functional polymer to enhance the sensing performance by the synergetic effect of nanomaterials and functional groups of polymeric component.

Recently, research efforts are also dedicated to the formulation of different metal nanoparticles, particularly gold and silver nanoparticles[]. It is because of their size, shape, surface functionality and local dielectric environment dependent optical properties. These unique optical properties of noble metal nanoparticles open up novel applications in biological and chemical sensors for mercury detection. Synthesis of noble metal nanoparticles using inorganic reducing agents has now been abridged [19,20] and the researchers are running behind the green synthesis of metal nanoparticles using bio-reducing agents.

The up-growing demand of silver nanoparticles in different sectors of the advanced research, such as catalysis, sensing, optics, anti-bacterial activity and data storage is due to their chemical stability, good thermal, electrical conductivity, catalytic properties and antibacterial properties towards Gram-positive and Gram-negative bacteria [21–24]. Therefore, nano silver containing composite films are widely used in various industries including electrical, medical, pharmaceutical, food and food packaging industries [25,26]. Sodium alginate (Na-Alg) is a poly-anionic copolymers, comprised of 1,4 linked β-D mannuronic (M) and α-L guluronic acid (G) [27]. The increasing interest in sodium alginate as supporting matrix for metal nanoparticles is due to its unique properties like biocompatibility, low toxicity and relatively low cost [28]. The film forming ability of PVA is widely used in packaging industry to form strong polymeric films. It is because of their high mechanical strength, environmental stability and easy processability [29,30]. On the other hand, PVA is non-toxic, semicrystalline, hydrophilic, biocompatible and easily soluble in water [31,32]. The higher value of standard reduction potential of Hg^{2+}/Hg (0.85 V) system as compared to Ag^{+}/Ag (0.80 V) system is accounted the formation of silver/mercury amalgam [33,34] and thereby recently, nano silver imprinted polymeric films are widely used for the detection and removal of mercury from drinking water [35]. Although, Au NPs can be used as sensors but these are relatively high cost with lower value of molar extinction coefficients as compared to AgNPs which are able to detect mercury in all oxidation states [36,37]. Yang et al. [36] has successfully designed the colorimetric biosensor, through the functionalization of water soluble silver nanoparticles with functional DNA probe (mercury-specific oligonucleotide) for easy detection of mercury ion (Hg^{2+}). For effective detection of Hg (II), use of FAM-labeled single standard DNA (ss-DNA) functionalized silver nanoparticles is recently reported [38]. Unlike the present investigation, reported processes are costly in nature due to use of expensive biomolecules like ssDNA. In another work, silver nano-cubes have been generated within the sodium alginate network through the reduction of $AgNO_3$ solution using sodium borohydride ($NaBH_4$) for the detection of Hg^{2+} in presence of rhodamin-6G (Rh6G) [39]. But the synthesis technique is accompanied with the addition of inorganic reducing agent.

Herein, low cost green technique is adopted to fabricate nano silver imprinted sodium alginate/polyvinyl alcohol (SA-Ag/PVA) nanocomposite thin films in "one pot" reaction scheme. As compared to the earlier report of Ag NP embedded PVA thin film [35] where, silver nanoparticles are generated using hazardous inorganic reducing agent, sodium borohydride ($NaBH_4$) and embedded in poly vinyl alcohol (PVA) thin film to detect the Hg^{2+}(aq) through SPR technique. But in our present investigation, spherically shaped colloidal silver nanoparticles with an average diameter of 25 nm is generated within sodium alginate network through bio-reduction. Hence the process of Ag NPs generation is more biocompatible and eco-friendly in nature. The as-prepared silver nanoparticles are designed onto the polyvinyl alcohol (PVA) surfaces by means of mechanical stirring of silver nano fluid and PVA slurry. The swollen capacity of PVA in SA-Ag/PVA nanocomposite thin films helps the aqueous phase detection of Hg^{2+}. The detection capability of the nanocomposite thin film is investigated using UV–vis spectrophotometer in various concentration of Hg^{2+}. Due to the efficient capping by various functional groups of sodium alginate, no leaching of Ag NPs from the fabricated SA-Ag/PVA nanocomposite thin film to the aqueous phase is observed (Fig. S-1). Moreover, the biogenic Ag NPs within the SA/PVA network shows greater affinity to Hg^{2+}(aq) and thereby shows lower value of LOD (4.6 nM) as compared to the earlier literature [35].

2. Experimental

2.1. Materials

Polyvinyl alcohol (Mw = 30,000–70,000), silver nitrate ($AgNO_3$, 99.8% purity) and Mercury Nitrate, used in this work were purchased from Sigma-Aldrich (Chemical Co. U.S.A.). Sodium alginate from brown algae was purchased from Sigma-Aldrich (viscosity ≥ cps for 2% solution at 25°C, average Mw = 100,000–350,000; G: M blocks = 66:34). All reagents were of analytical grade and used as such without further purification.

2.2. Synthesis of SA-Ag/PVA nanocomposite thin films

Na-alginate reduced silver nanoparticle imprinted poly vinyl alcohol (SA-Ag/PVA) nanocomposite thin films were fabricated using "one pot" synthetic protocol. In a typical procedure, 0.5% w/v of sodium alginate was dissolved in double distilled water with stirring for 30 min. The presence of numerous free carboxyl (—COOH) and hydroxyl (—OH) groups made it soluble in water [40]. After that, calculated amount of $AgNO_3$ solution was added to the reaction vessel. The whole mixture solution was then stirred for 30 min at 90 °C (optimized temperature) till the colour of the solution turned in to reddish yellow. The formation of silver nanoparticles was confirmed by the UV–vis spectroscopy. In next step, the prepared PVA slurry (0.05% w/v) was poured into the SA-Ag solution and stirred well for 30 min. Then the whole solution was casted on plastic petridishes and dried in hot air oven at 50 °C for 1 day.

In this approach, instead of using any functional monomer and cross-linking agent, we used biopolymer, sodium alginate for imprinting process. Being blessed with several functional groups, such as —COOH,—OH and —NH_2, it introduced its functionality to co-coordinate with Ag^{+}(aq). After thermal activation, the —OH functionality acts as a bio-reducing agent and converts Ag^{+}(aq) to $Ag^{(0)}$ and the *in situ* formed Ag NPs are stabilized within the sodium alginate network by different functional groups. Hence, Ag NPs imprinted sodium alginate network was formed, which was then transformed into a nanocomposite thin film by the use of poly vinyl alcohol (PVA). The whole imprinting process is schematized in Scheme 1.