

Quaternary ammonium poly(amidoamine) dendrimer stabilized gold and other metal nanoparticles for biosensor applications

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Abstract

Quaternary ammonium poly(amidoamine) (PAMAM) dendrimer stabilized gold nanoparticles (QPAMAM-AuNPs) were prepared and used for fabrication of new GC-QPAMAM-AuNPs electrode and this in turn was investigated for sensing of trace quantity of H_2O_2 . Further, the QPAMAM-AuNPs were inspected for catalysis of nitrobenzene. Initially, amine-terminated PAMAM dendrimer was neutralised by acetylation followed by quaternization reactions. This quaternized product was used as a template for stabilization of gold nanoparticles by conducting the reactions at room temperature and thus produced quaternized dendrimer stabilised gold nanoparticles labelled as QPAMAM-AuNPs. The synthesized QPAMAM-AuNPs were characterized by UV-Vis, FTIR, 1H NMR, MALDI-TOF and TEM analyses. This QPAMAM-AuNPs was coated on newly produced glassy carbon modified electrode without any binding agent, particularly any enzyme to produce GC-QPAMAM-AuNPs electrode. This newly fabricated electrode in turn were employed for detection and sensing of trace quantity of H_2O_2 and it is observed that the electrode has an ability to detect the H_2O_2 ranging from [100 μM] to [5 mM] in neutral pH. Similarly, it is also proved that QPAMAM-AuNPs has effectively reduced the nitrobenzene and the observed pseudo-first order rate constant was $25.25 \times 10^{-3} s^{-1}$. It is established that the stabilized nanoparticles are water-soluble and stable for three months. Copyright © 2017 VBRI Press.

Keywords: Poly(amidoamine) dendrimer, gold nanoparticle, electrocatalyst, hydrogen peroxide, nitrobenzene, biosensing applications.

Introduction

Hydrogen peroxide (H_2O_2) is a tiny molecule in nature but it has been widely used in chemical and pharmaceutical industries, food manufacturing industries, clinical level, environmental, textile industries because of its strong oxidizing and reducing properties [1]. Specifically, H_2O_2 plays an important role in physiological as oxidative stress marker in aging and disease [2]. Due to its important functions, H_2O_2 can activate several classes of signaling proteins that affect cell proliferation results in neurodegenerative disorders and also disorders like Parkinson's, Alzheimer's, cancer and diabetes [3, 4]. Therefore, the concentration of H_2O_2 in real-world application is so importance and hence it is essential to develop sensor materials/methods to sense the H_2O_2 with simple, fast, low-cost and selective H_2O_2 manner. A variety of methods are already established, namely fluorescence [5], colorimetry [6], chemiluminescence [7] and electrochemistry [8 - 10] so far and used for the analysis of H_2O_2 . In these methods, it is noted that electrochemical technique is proved to be advantages due

to their simple instrumentation, easy miniaturization, high sensitivity and selectivity, as well as rapid response.

In general, the biosensors should be sensitivity, chemical stability, specificity, linearity, reusability and reproducibility on the sensor platform. A variety of linker molecules have been used to bio-functionalize the important substrates like glass, gold, mica etc. The linkers used for the immobilization of capture probes and the immobilization protocol play a vital role in the overall performance of sensors. Amongst the different linkers, scientists have paid more attention on two dimensional architectures, e.g. silanes, polyaniline, alkanethiols and poly-L-lysine etc. But the drawback is, two dimensional linkers have low immobilization efficiencies due to their planar structures [11]. These limitations of the linear linkers are still unresolved and prevent microarray technology from reaching its full potential [12]. Use of three dimensional gels or the membrane-coated surfaces of poly-acrylamide [13] and agarose gel [14] have been suggested to preserve the functionality and affinity of the

biomolecules. The leaching of bio-receptor molecules results in larger variations in signal intensity and thus limiting their use in sensing.

Despite of the extensive research according to the reports, researchers are still facing the problems like loading efficiency, limited accessibility of the probes, reduced uniform spacing among the probes and irregular orientation of the probes results in loss of functionality. Three-dimensional gel based matrices have proved to be a better choice, with the disadvantages in leaching of entrapped probe molecules which limited their use in sensor platforms. Taking into consideration, the limitations of two dimensional linkers and three-dimensional gel matrices, supramolecular dendrimer architectures are shown potential in designing and developing the sensor platforms. Dendrimers are well-defined, monodisperse, globular macromolecules with a core unit. The inherent characteristics and tailored making properties of dendritic molecules such as, structural uniformity, globular shape, monodispersity, high functional group density, hydrophilicity, versatility to design their structure, controlled composition, and high density multidentate homogeneous structure for consecutive bioconjugation reactions make them unique and stable for various applications. These macromolecules received extensive applications in various fields such as, drug delivery, gene delivery, biomedical imaging, catalysis, nanocomposite systems, high-capacity chelating agents and biochemical sensors [15]. In various biomedical sciences, dendrimers have been widely used and maximum number of articles related to its application in sensors and biosensors has been observed in the last five years. Number of surface modification techniques has been explored so far for grafting of dendrimers on sensor substrates, mainly gold or silica. They include the Langmuir–Blodgett (LB) technique [16], non-covalent interactions [17], covalent attachments [18] and the spin casting technique. Therefore, designing a sensor with a dendrimer as a linker is a successful approach to obtain a superior sensor with minimum cost.

Nitrobenzene is a significant groundwater contaminant due to its wide usage in explosives, insecticides, herbicides, pharmaceuticals, aniline dyes and also as a solvent in the preparation of products like paints, shoes and floor metal polishes [19]. As a toxic and suspected carcinogenic compound, nitrobenzene is often released to environment from various sources that in turn led to possess a great threat to human health. Hence, any technologies that enable the efficient reduction of nitrobenzene have been received more attention recently [20, 21]. Further, aniline is an important chemical in the manufacture of dyes and vulcanization accelerators and antioxidants. It is usually manufactured by the reduction of nitrobenzene. Taking into consideration of all the factors, it is believed that the quaternized dendrimer stabilized nanoparticle may act as a efficient catalyst for reduction of nitro compounds in biphasic medium. In this article, we have synthesized quaternary ammonium dendrimer by surface modification which in turn used as a

template for stabilization of gold nanoparticles. The obtained quaternary ammonium poly(amidoamine) (QPAMAM-AuNPs) was used for fabrication of new electrode and demonstrated for sensing of trace quantity of H_2O_2 . Apart from electrode fabrication its catalytic potential is also examined by reducing nitrobenzene to aniline as representative reaction.

Experimental

Materials

Methyl acrylate (Sigma Aldrich), Ethylene diamine (SRL), Methyl iodide (Sigma Aldrich), Acetyl chloride (Sd fine), Amberlite anion exchange resin IRA 402 (Sigma Aldrich), Dialysis Membrane (Float-A-Lyzer) (Spectra pore), Membrane filter of pore size $0.45\mu m$ was obtained from Himedia lab. Hydrogen peroxide and Sodium hydrogen phosphate (Na_2HPO_4) and Sodium Dihydrogen Phosphate (NaH_2PO_4) purchased from Merck, Ethanol (Jiangsu Huaxi international trade Co ltd), De-ionized water (Merck), nafion 1 wt% (Sigma-Aldrich) were used without further purification.

The UV-Vis analysis of the freshly prepared nanoparticles was recorded with water/methanol as reference using the Perkin Elmer (Lambda 35) spectrophotometer. FT-IR spectra were recorded using Bruker Tensor-27 FT-IR spectrometer with OPUS software in the range $4000-400\text{ cm}^{-1}$, at ambient temperature in transmittance mode. The pellet for analysis was made by taking equal amounts of QPAMAM-(G3) and KBr (1:1 ratio), the background calibrations have been carried out using pure KBr pellet. The NMR spectra of QPAMAM-(G3) dendrimer in D_2O were acquired using a Bruker 500 MHz spectrometer. MALDI-TOF MS were recorded on a Voyager-DEPRO Bio spectrometry workstation equipped with 337 nm N_2 laser source. All mass spectra were obtained averaging of 100 shots with negative ion mode and in reflection mode. Dithranol was used as a matrix to analyze the QPAMAM-(G3). TEM images were recorded on transmission electron microscope of model JEOL 3010 operated at 300 keV. Samples for the analysis were prepared by placing a micro drop of the prepared nanoparticle solution on a carbon-coated Cu TEM grid. The grid was pre-treated to render the carbon surface by glow discharge with slightly hydrophilic, and then allowing the solvent to evaporate.

Material synthesis

Synthesis of quaternary ammonium poly(amidoamine) dendrimer template stabilized gold nanoparticles (QPAMAM-G3-AuNPs)

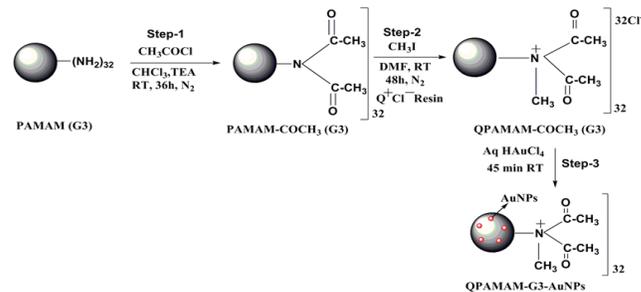
Synthesis was performed in three steps by following the reported methods of Murugan *et al.* [22] (Scheme 1). In the first step, surface amine groups of the commercial PAMAM (G3) dendrimer was neutralized and in the second step the internal tertiary amines were methylated and thus generated quaternary ammonium ions. That is,

PAMAM (G3) dendrimers (0.1g, 0.2mmol) was taken in a round bottomed flask. To this, 2 ml of triethylamine and 10 ml of chloroform were added. The temperature of the RB was reduced to 0°C. To this (2 ml, 0.5mmol) acetyl chloride was added and the temperature was brought back to room temperature. This was kept stirring for 36 h maintaining N₂ atmosphere. After the reaction was over, the acetic acid and triethylamine in the solution were removed with the help of extensive dialysis for a day with the frequent replacement of outer aqueous medium and the solution was lyophilized to get a semi solid product. In the second step, the obtained semi solid product (0.1g, 0.025mmol.) was dissolved in 5ml DMF using 100 ml Round bottom flask. To this, excess methyl iodide diluted in 5ml DMF was added slowly and stirred for 48h in N₂ atmosphere at room temperature. The resulting clear solution was precipitated in diethyl ether and the residues were dried in vacuum oven. The dried residue was dissolved in water and passed through amberlite anion resin to exchange I⁻ into Cl⁻ ions. The eluted solution from the resin was lyophilized and thus produced surface modified quaternary ammonium poly(amidoamine) dendrimer template viz., QPAMAM-(G3) with COCH₃ as surface group. The resulting QPAMAM (G3)-COCH₃ were characterized by FTIR, ¹HNMR and MALDI TOF Spectral techniques.

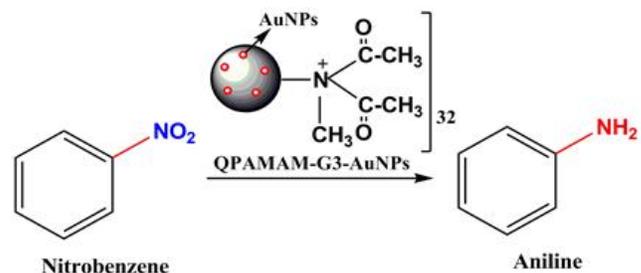
In the third step, quaternized dendrimer stabilized gold nanoparticle (QPAMAM-G3-AuNPs) catalysts were prepared by varying the [HAuCl₄] load. Initially, gold-dendrimer complex was prepared by taking 1.89 × 10⁻⁵ M (50 mg) of QPAMAM-G3 dendrimer and dissolving the same in 2 mL of double distilled water and to that 2.53 × 10⁻⁶ M (1 mg) of HAuCl₄ dissolved in 1 mL of double distilled water was added and the mixture was stirred vigorously for 45 min. The colour changes to a deep red indicating the spontaneous formation of AuNPs and thus obtained homogeneous nanoparticle catalyst which in turn labelled as QPAMAM-G2-AuNPs and was characterized by UV-vis and TEM analyses.

Catalytic reduction of nitrobenzene

The catalytic performance of the QPAMAM-G3AuNPs catalyst was examined by conducting the aqueous phase reduction of nitrobenzene keeping under identical reaction conditions as a model reaction. The reaction procedure for the reduction of nitrobenzene was, a standard quartz cuvette having a 1-cm path length was taken in which 2.5 mL of water, 0.25 mL of aqueous NaBH₄, 0.25 mL of nitrobenzene and 100 μL of the respective QPAMAM-G3-AuNPs catalyst solution was added. The kinetics of the reaction catalyzed by catalyst was quantitatively measured by recording the UV-vis absorbance of characteristic peak at 273 nm (-NO disappearance) at regular time intervals. The control experiment was also carried out using the above procedure in the absence of QPAMAM-G3-AuNPs catalyst. Using the rate equation $k_{obs} = \ln [(A_{\infty}-A_0)/(A_{\infty}-A_t)]/t$, the pseudo-first order rate constant was calculated. Where, A₀ -initial absorbance, A_t -absorbance at time 't', A_∞-absorbance at infinity time.



Scheme 1. Synthesis of quaternary ammonium poly(amidoamine) dendrimer template stabilized gold nanoparticles (QPAMAM-G3-AuNPs).



Scheme 1a. Reduction of nitrobenzene to aniline.

Electrochemical measurements

Electrochemical experiments were performed using a CHI 1130A electrochemical work station (USA). A conventional three-electrode cell consisting of a glassy carbon working electrode modified with electro-catalyst sample, a platinum wire counter electrode and a saturated Ag/AgCl reference electrode were used for voltammetric experiments. The current was normalized to the apparent surface area of the glassy carbon electrode (0.0314 cm²). The surface of the GCE was cleaned first mechanically by polishing with 0.05 and 1.0 μm alumina powder on a polishing cloth (Buehler) followed by sonication in DD water for 10 min. The electrode was then sonicated with absolute ethanol and double-distilled water for about 5 min, respectively. It was rinsed thoroughly with double-distilled water and then dried under ambient temperature. The solution containing electro catalyst samples *i.e.* 1.0 mg/ml in distilled water was prepared by agitating the mixture with ultrasonic for 30 min and used as a stock solution. After the GC electrode surface was air dried, 5.0 μL of stock solution was drop casted onto the surface of the pre-treated GC electrode with a micropipette and then it was dried in air.

Fabrication of QPAMAM-(G3)-AuNPS modified glassy carbon electrode for electro-catalytic reduction of H₂O₂

The glassy carbon electrode (GCE) was modified by coating with QPAMAM-AuNPs and thus produced GC-QPAMAM-AuNPs electrode. In order to inspect the electro-catalytic activity of GC-QPAMAM-AuNPs electrode, its electrochemical reduction of hydrogen peroxide was used as representative reaction and the study was performed using cyclic voltammetry (CV). Prior to the fabrication, GCE was polished with finer grade

alumina powders having the pore size of 0.05 and 0.3 individually and then electrode was purified by successive washing with ethanol and distilled water via sonication and the fresh electrode was dried at room temperature. Then 0.5mg of the QPAMAM-AuNPs was dispersed in 500 μL water and was used as a stock solution. Prior to the surface coating, the stock was sonicated for 5 min and 5 μL of the suspension was drop-coated on the pre-treated GCE and allowed it to dry in ambient temperature and thus produced GC-QPAMAM-AuNPs electrode.

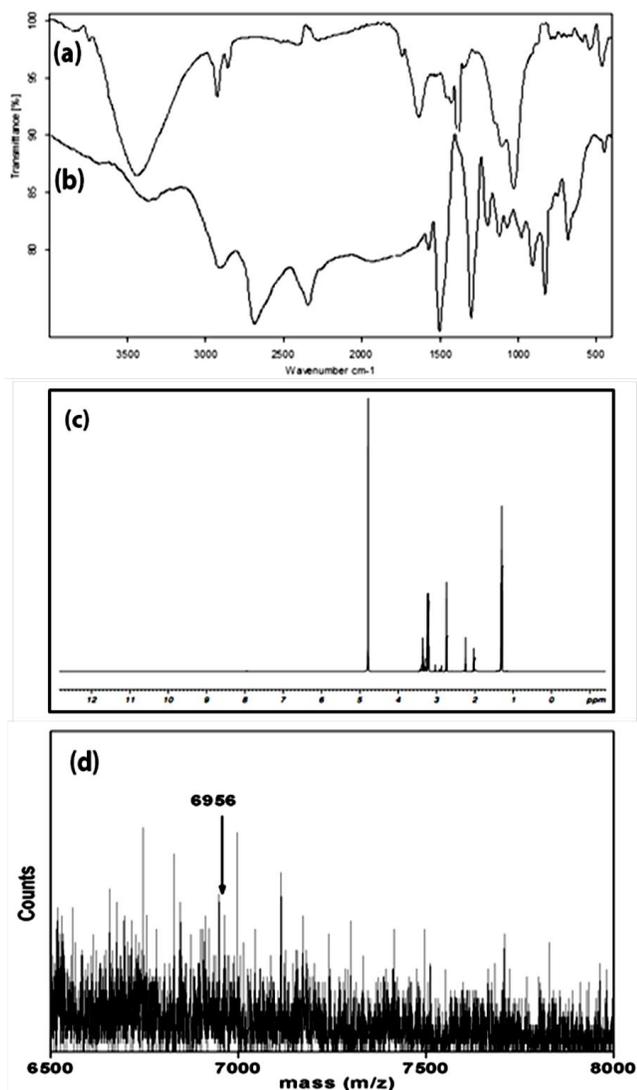


Fig. 1. FT-IR spectra of (a) PAMAM (G3) (control) and (b) QPAMAM (G3), (c) ¹H NMR spectrum of QPAMAM (G3) dendrimer template, and (d) MALDI-TOF MS spectrum of QPAMAM (G3) dendrimer template.

Results and discussion

Synthesis and characterization of quaternary ammonium poly(amidoamine) dendrimer template stabilized gold nanoparticles (QPAMAM-G3-AuNPs)

PAMAM-G3 dendrimer with $-\text{NH}_2$ surface group was acetylated using acetyl chloride and thus produced PAMAM-G3-COCH₃. The acetylated product was

quaternized using CH₃I and yielded QPAMAM-G3 template. The occurrence of acetylation and quaternization on PAMAM-G3 was confirmed through FTIR (**Fig. 1(a & b)**), ¹H NMR (**Fig. 1(c)**) and MALDI-TOF (**Fig. 1(d)**) spectral techniques. In the FTIR spectrum of QPAMAM-G3 (**Fig. 1(b)**), it is noticed that strong $-\text{C}-\text{H}$ stretching peak at 2975 cm⁻¹ and 2766 cm⁻¹ along with peak at 1415 cm⁻¹ assigned to $-\text{C}-\text{H}$ bending, $-\text{C}=\text{O}_{\text{str}}$ at 1721 & 1656 cm⁻¹ and $\text{C}-\text{N}_{\text{str}}$ at 1296 were appeared. The ¹H NMR spectrum (**Fig. 1(c)**) gives an intense singlet signal at δ 2.673 due to $-\text{COCH}_3$ (acetyl protons) and a sharp singlet at δ 3.241 due to $(\text{N}-\text{CH}_3)$ methyl protons were observed and the m/z value obtained from MALDI-TOF gave peak at 6956 confirms the formation of QPAMAM-G3.

The synthesized QPAMAM-G3 dendrimer template was used for stabilization of AuNPs and thus produced QPAMAM-G3-AuNPs catalyst. The resulting QPAMAM-G2-AuNPs are characterized with UV-Vis and TEM analyses. In the catalyst preparation using QPAMAM-G3 dendrimer template (**Scheme 1**), the stabilization of AuNPs catalysts were obtained by spontaneous reduction of Au³⁺ in QPAMAM-G3 template without using any external reducing agent like NaBH₄.

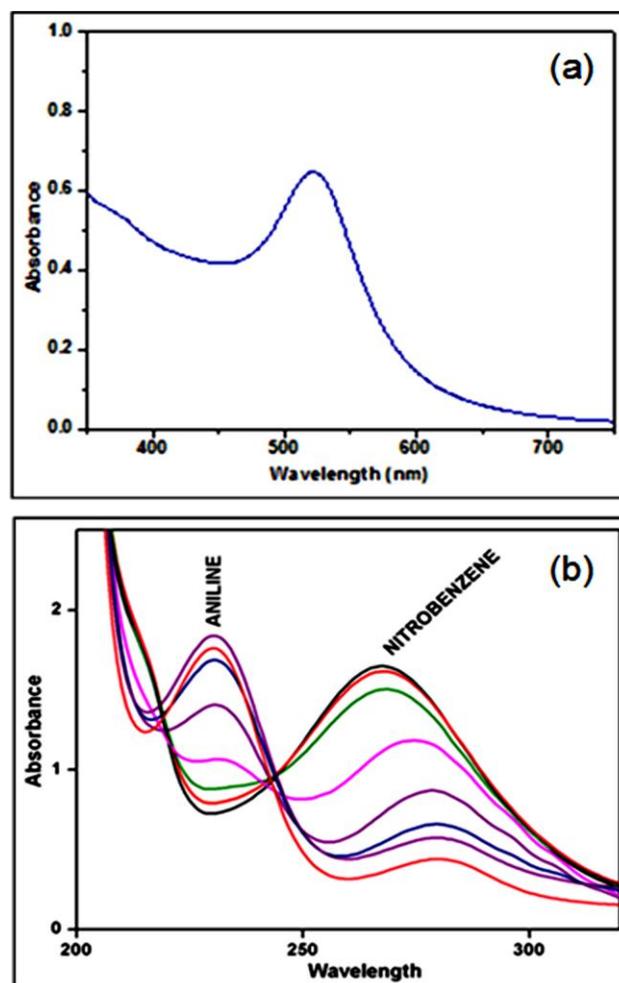


Fig. 2. UV-vis spectra of (a) QPAMAM-G3-AuNPs (b) UV-vis spectra of reduction of nitrobenzene using QPAMAM-G3-AuNPs.

In the reaction mixture during agitation, the yellow color of the reaction mixture slowly changed into wine red, indicating the reduction of Au^{3+} to Au^0 . The metal nanoparticles prepared by using any external reducing agents, which in turn create severe pollution. But in our case, it is to highlight here that QPAMAM-G3 template itself is acting as a reducing agent for reduction of gold and the spontaneous formation of AuNPs was confirmed by the appearance of SPR band at 530 nm through UV-Vis spectrophotometer (**Fig. 2(a)**). In the UV-Vis spectrum (**Fig. 2(b)**), the SPR band intensity observed at 530 nm was gradually increased with time and after 20 minutes the observed SPR peak broadened along with a red shift. After 45 minutes, the intensity of SPR band and their broadening further maximized and the SPR peak showed a split confirming the formation of different sizes of AuNPs stabilized by QPAMAM-G3 template. Similar observation was also observed for the photochemical synthesis of AuNPs using TX-100 as a stabilizer and reported that the peak broadening and splitting were due to the formation of different size and shape of the AuNPs. Also, a shoulder peak was appeared in the spectrum which is due to aggregation effect of the particles and such a conclusion agreed well with our results.

The (i) stabilization and monodispersibility of AuNPs in QPAMAM-G3 and (ii) reduction of Au^{3+} to Au^0 using QPAMAM-G3 dendrimer were performed without adding any external reducing agent. The stabilization of AuNPs with QPAMAM-G3 template has been explained as follows. In the first step the Au^{3+} metal ions are extracted from the solution to tertiary amines through electrostatic interaction, forming a complex and the lone-pair electrons present on each nitrogen atom has donated electrons for the reduction of Au^{3+} to Au^0 . The same observation was also observed in our previous studies [23]. Similar observations are also reported by Xiangyang et al for the spontaneous formation of Au DSNPs using glycidol hydroxyl-terminated PAMAM-G5 dendrimers [24]. Dong et al also reported the synthesis of AuNPs using PPI-G3 at 80 °C with the size in the range of 4–33 nm [25]. In contrast, high temperature is not required in our case in the presence of QPAMAM-G3, and the reaction was performed at room temperature only. The terminal groups present on the periphery of the dendrimer were tailored to control the solubility of nanocomposite. Further, it is important to mention here that the prepared AuNPs catalysts are stable for three months without any aggregation which proves that QPAMAM-G3 worked as an effective stabilizing agent for the formation of AuNPs. The morphology of the formed QPAMAM-G2-AuNPs was evaluated by TEM analysis. **Fig. 3** shows the TEM image which revealed that the sizes of the AuNPs were in the range of 7 to 10 nm. Most of the particles were spherical in shape. In general, the dendrimer stabilized AuNPs involve a nanostructure where one dendrimer molecule entraps one or more AuNPs. Therefore, compare to literature reports and TEM results, it is concluded that, the AuNPs can be effectively stabilized by one or more QPAMAM-G2 dendrimer with the average size of 10 nm.

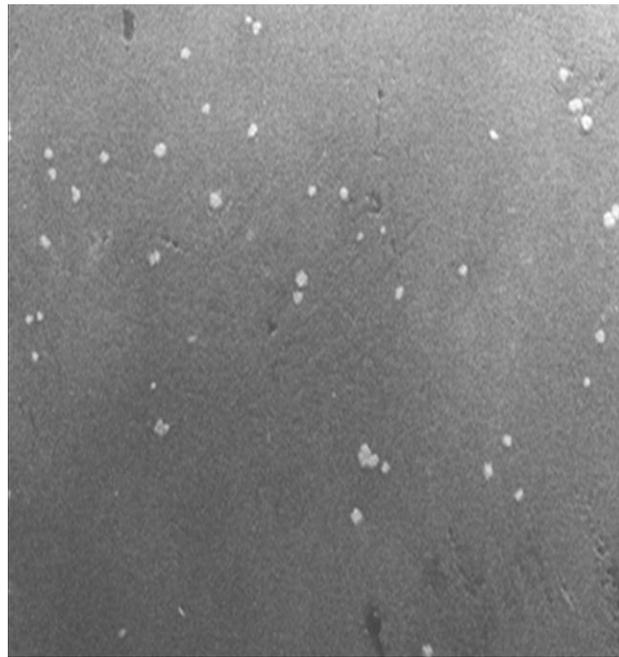


Fig. 3. TEM images of QPAMAM-G3-AuNPs.

Catalytic activity of QPAMAM-G3-AuNPs for the reduction of nitrobenzene

The catalytic activity of QPAMAM-G3 stabilized AuNPs catalysts were examined by studying the aqueous phase reduction of nitrobenzene as a model reaction under identical pseudo-first order experimental conditions. The prepared QPAMAM-G3 template is possible to accommodate maximum load of AuNPs which further influenced the stabilization of AuNPs and showed enhanced catalytic activity. The control experiment for the reduction of NB in the absence of QPAMAM-G3-AuNPs catalyst was also performed, and the UV-vis spectrum showed no product peak (or) decrease in characteristic peak intensity ($-\text{NO}_2$) at 273 nm. In contrast, the plot shown in **Fig. 2(b)** (absorbance against time) indicates the reduction of NB using QPAMAM-G3-AuNPs catalyst under fixed concentration of substrate takes place effectively. Also, it was noted that, a constant decrease in the absorbance of the substrate and within 40 min the added substrate was completely reduced to aniline. The results were similar to the reported studies [26 – 32]. The enhanced catalytic activity ($25.25 \times 10^{-3} \text{ s}^{-1}$) observed in our QPAMAM-G3-AuNPs is credited to the hydrophilic/hydrophobic environment created by the dendrimer backbone which stabilizes the aryl nitro substrates to the catalytic sites which in turn facilitates the reduction of nitro groups [33].

Electrochemical investigation of GC-QPAMAM-G3-AuNPs electrode for sensing the hydrogen peroxide

The electro-catalytic behavior of the newly fabricated viz. GC-QPAMAM-AuNPs electrode was evaluated in sensing/reduction of H_2O_2 and the study was performed through cyclic voltammetry and their corresponding CVs

are shown in **Fig. 4**. To inspect the sensing ability of this electrode with H_2O_2 substrate, initially CV study was conducted for blank medium containing 20 mL of 0.1 M PBS keeping the potential range at -1 to 1 V vs Ag/AgCl with a scan rate of 50 mV/s. Subsequently, 100 μM of hydrogen peroxide was added into the same medium and the CVs were recorded and shown in **Fig. 4**. From the **Fig. 4**, redox peaks around 0.72 V and 0.6 V were observed, which corresponds to the redox behavior of gold that is oxidative peak observed in the forward scan was due to oxidation of Au^0 to Au^{3+} whereas reductive peak in the reverse scan was due to the reduction Au^{3+} to Au^0 respectively. And also, another redox peak at 0.017 V and 0.12 V appeared in the same figure is attributed to H_2O_2 in PBS. Whereas peaks were observed in the reverse scan suggesting that the reduction process is a quasi-reversible one. The electron transfer occurs in this case is mainly by self-exchange of electron between Au atoms.

Further, the experiments were carried out to evaluate the electro catalytic activity of the GC-QPAMAM-AuNPs electrode at various concentration of H_2O_2 and observed results were shown in **Fig. 4**. On increasing the $[\text{H}_2\text{O}_2]$ from 100 μM to 1200 μM , the intensity of reduction peak current is also increased proportionately. To understand the electron transfer mechanism of H_2O_2 reduction reaction, CVs were recorded at different scan rates from 10 to 100 mV/sec. The obtained cyclic voltammogram are shown in **Fig. 5(a)**, in which the systematic increase in cathodic peak current (i_{pc}) against increase in the scan rate was observed for GC-QPAMAM-AuNPs electrode. Plot of i_{pc} vs square root of scan rate ($v^{1/2}$), resulting linear line (**Fig. 5(b)**) suggesting that, the electron-transfer reaction was diffusion controlled [34]. Therefore, based on the results and explanations it is observed that the GC-QPAMAM-AuNPs electrodes are efficient in sensing and reduction of H_2O_2 especially at low potential.

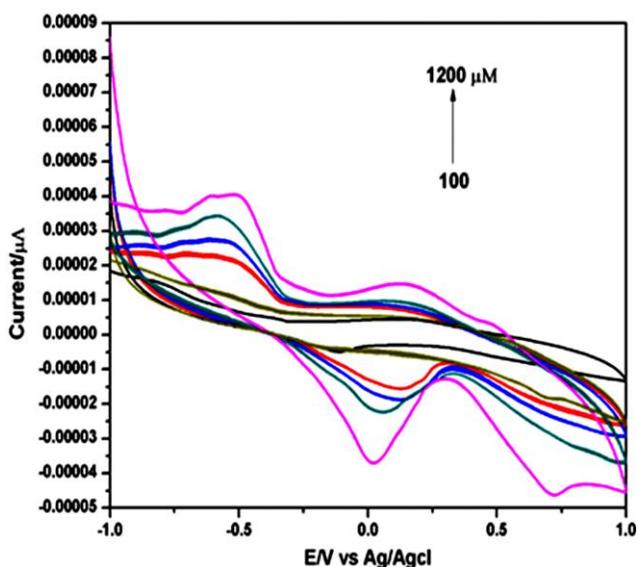


Fig. 4. Cyclic voltammogram of QPAMAM (G2)-AuNPs modified GCE in 0.1 M PBS at 50 mVs⁻¹ scan rate from the concentration range of 100 μM to 1200 μM H_2O_2 .

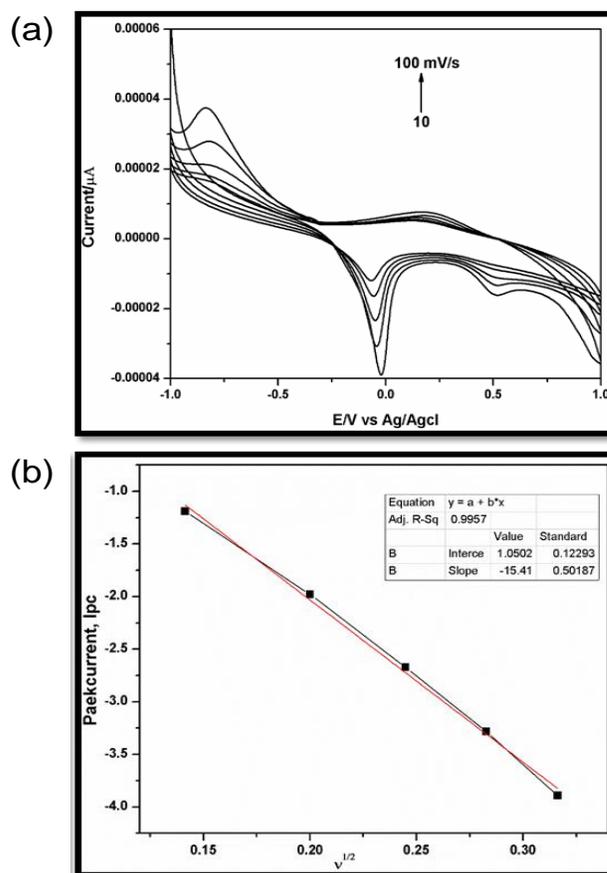


Fig. 5. (a) Effect of scan rate for QPAMAM (G2)-AuNPs modified GCE at 0.1mM H_2O_2 and 0.1 M PBS (pH 7) and (b) peak current vs square root of scan rate ($v^{1/2}$).

Conclusion

New quaternary ammonium poly(amidoamine) dendrimer template (QPAMAM-(G3)) was developed by surface modification of PAMAM (G3). The surface functionalization of COCH_3 group onto the terminal amines of PAMAM (G3) was confirmed with FT-IR, ^1H NMR and MALDI-TOF techniques. The developed QPAMAM (G3) was used as a template for stabilization of AuNPs which produced homogeneous QPAMAM-(G3)-AuNPs catalyst. The catalyst was characterized with UV-vis spectrometer and TEM micrographs. TEM images reveal that the developed QPAMAM (G3) template has yielded the smaller AuNPs with size in the range from 7 to 10 nm. These overall observations confirms that the newly developed QPAMAM (G3) and QPAMAM (G3)-AuNPs were showed effective encapsulation of AuNPs and effective dual function as sensing/detection of H_2O_2 by newly fabricated GC-QPAMAM (G3)-AuNPs electrode and catalysis for reduction of nitrobenzene to aniline. The newly fabricated GC-QPAMAM (G3)-AuNPs electrode is proved to be sensitive enough to sense/detect the H_2O_2 to the tune of 100 μM to 5 mM. Similarly, the catalytic studies performed on reduction of nitrobenzene to aniline proves that the catalytic rate constant was found to be higher activity ($25.25 \times 10^{-3} \text{ s}^{-1}$) than the earlier reported catalysts. In addition to the

reduction of Au³⁺ to Au⁰ it can also act as a stabilizing agent for AuNPs. Further, it helps to enhance the miscibility of nitrobenzene in water. Based on the performance of QPAMAM –G3 it was observed that, other types of dendrimers and metal nanoparticles which having similar properties could also be exploited for the same application. Therefore, the present study confirms that the newly developed QPAMAM (G3)-AuNPs is a promising catalyst for the application in the field of sensing and catalysis.

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