



Amperometric determination of sodium hypochlorite at poly MnTAPP-nano Au film modified electrode

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ABSTRACT

Poly manganese tetra (o-amino phenyl) porphyrin (MnTAPP)-nano Au film was electrodeposited on glassy carbon electrode (GCE) and indium tin oxide coated glass electrode (ITO) using cyclic voltammetry (CV). Electrodeposited poly MnTAPP-nano Au modified electrodes have been characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques. Poly MnTAPP-nano Au film modified GCE found as electrochemically active and stable. Poly MnTAPP-nano Au modified GCE employed for the amperometric detection of sodium hypochlorite (NaOCl) in the linear range of 24×10^{-6} – 1.07×10^{-2} M. The proposed film holds the capacity to overcome the interference substances and showed the reduction current response for the NaOCl additions. In addition, the poly MnTAPP-nano Au film successfully exhibits the reduction current of NaOCl concentrations in the commercially available bleaching liquids, respectively.

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1. Introduction

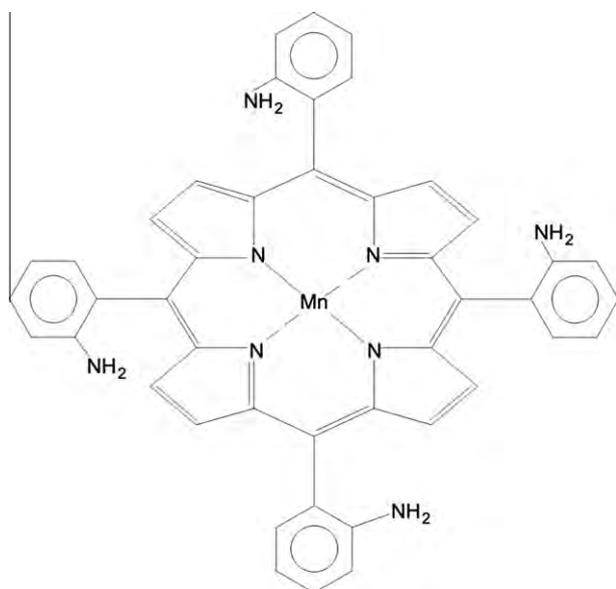
Sodium hypochlorite (NaOCl) solution is a strong oxidizer, commonly known as bleach, frequently used in household purpose as disinfectant or bleaching agent. Generally, household bleaching agents used for laundering cloths contains 3–6% solution of sodium hypochlorite. Here the NaOCl strength varies from one product to another one. NaOCl is widely used in water works for the chlorination of water and as disinfectant for the waste water treatment. Daily sanitizing sprays contain NaOCl as an active ingredient. At the same time, the oxidation reactions of NaOCl were corrosive. Contact with NaOCl solutions may directly affect the skin, irritation in eyes, which results in the damage of human organs. Therefore, analytical detection and determination of NaOCl is important one in our routine life [1,2].

Various analytical methods have been utilized for the determination of NaOCl. Some of the examples were colorimetric [3], iodimetric [4], chemiluminiscent [5], potentiometric [6], and green methods [7]. All these methods are found as suitable for the direct detection of NaOCl in the chemical laboratories. However, detailed studies for the detection and determination of NaOCl using electroanalytical methods will help to fabricate the commercially available proto type electrochemical sensor which will be reliable and easy to use and cost effective one.

Manganese tetra (o-amino phenyl) porphyrin (MnTAPP) contains four branched monomers (Scheme 1) and its polymerization results in the formation of dendrimer [8]. Electropolymerized MnTAPP and MnTAPP adsorbed flavin hybrid films were reported for the various types of electrocatalytic reactions [8,9]. Next, the electrochemical depositions of gold nanoparticles (nano Au) were found as interesting phenomena in the new era. Gold nanoparticles play important role in the fabrication of nanostructured assemblies. Nanostructured Au shows higher electrocatalytic activity than the bulk Au [10,11]. Particularly, the desired shape and size ascertain obvious changes in their catalytic activities [12,13]. Therefore, utilization of gold nanoparticles was found as useful for the development of electrochemical sensors and biosensors. For instance, flower-shaped Au nanoparticles exhibit obvious electrocatalytic properties for the oxidation of methanol, oxygen reduction reactions and the detection of H_2O_2 [14,15]. In particular, fabrication of nanomaterial anchored metalloporphyrins was found as new film materials in the field of electroanalytical chemistry. Hence, in this report we have attempted to fabricate the electropolymerized porphyrins-nano Au film modified electrodes. Cyclic voltammetry (CV) was utilized for the electrochemical fabrication of poly MnTAPP-nano Au film. Poly MnTAPP-nano Au films have been fabricated on glassy carbon and indium tin oxide electrodes (ITO). Electropolymerized MnTAPP, nano Au and poly MnTAPP-nano Au films were characterized using SEM and AFM analysis. Poly MnTAPP-nano Au film modified GCE was employed for the amperometric detection of NaOCl. It showed good response for the detection and determination of NaOCl in lower and higher

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Scheme 1. Structure of MnTAPP.

concentration ranges. Not only limited to lab samples, poly MnTAPP-nano Au film detects NaOCl in commercially available detergents within the linear range limits, respectively.

2. Materials and methods

2.1. Reagents

$\text{KAuCl}_4 \cdot 3\text{H}_2\text{O}$ was obtained from Strem chemicals (USA). The Mn(o-TAPP) was purchased from Porphyrin Products (Logan, Utah, USA). NaOCl (5% chlorine) was purchased from Wako Chemicals Ltd. (Japan). Other chemicals were of analytical grade. Double

distilled deionized water was used throughout the experiments. All the experimental results were obtained at room temperature. Commercially available bleaching liquid (containing NaOCl) has been obtained from local departmental store. NaOH buffer solution (pH 10.4) was utilized for the electrocatalytic reactions. Pure nitrogen was passed through all the experimental solutions.

2.2. Apparatus

Electrochemical measurements like cyclic voltammetry (CV) and amperometric experiments were performed using CHI 627a and CHI 750 Potentiostats (CH Instruments, Austin, TX). A conventional three-electrode system was used throughout the experiments. Glassy carbon electrodes ($\phi = 0.3$ cm in diameter) (BASi, USA) were in the form of disks sealed in a Teflon jacket having an exposed geometric surface area of 0.07 cm². The working electrode was bare or poly MnTAPP-nano film Au modified GCE. The auxiliary electrode was platinum wire and Ag/AgCl electrode was used as a reference. All the potentials mentioned in this paper were referred to this reference electrode. The morphological characterizations of the film were studied by using SEM (Hitachi S-3000H) and AFM (Being Nano-Instruments CSPM-4000). UV-vis spectra were obtained using Hitachi U-3300 spectrophotometer (Japan). Here, indium tin oxide (ITO) thin film coated glass electrodes were used for AFM and UV analysis.

2.3. Fabrication of poly MnTAPP-nano Au film modified GCE

The bare GCE was polished with the help of a BAS polishing kit using aqueous slurries of alumina powder (0.05 μm), rinsed and ultrasonicated in double distilled deionized water. 1 mM KAuCl_4 and 0.1 mM MnTAPP were prepared in pH 1.0 H_2SO_4 solution. Later the stock solution was prepared by mixing 3 ml of 1 mM KAuCl_4 with 1 ml of 0.1 mM MnTAPP. Poly MnTAPP-nano Au film has been electrochemically fabricated on GCE by applying repetitive potential scan between 1 and 0 V at the scan rate of 0.1 V/s for 15 cycles

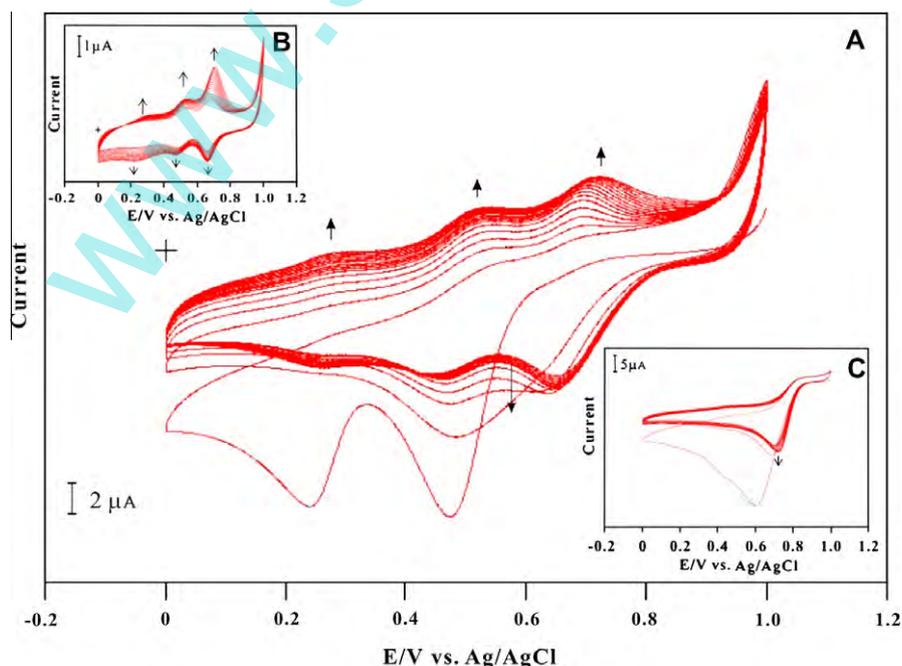


Fig. 1. (A) Electrochemical deposition of poly MnTAPP-nano Au film on GCE from pH 1.0 H_2SO_4 containing 0.1 mM MnTAPP and 1 mM KAuCl_4 at the scan rate of 0.1 V/s for 15 cycles. (Potential scan range: 1 – 0 V). Insets (B and C) represent the electrochemical deposition of only poly MnTAPP film and electrochemical deposition of Au at the GCE, respectively.

[15]. Poly MnTAPP-nano Au film modified GCE washed with deionized water and employed for the detailed electrochemical analysis.

3. Results and discussion

3.1. Characterization of poly MnTAPP-nano Au film modified GCE

Fig. 1A shows CVs of the electrochemical fabrication of poly MnTAPP-nano Au in aqueous H_2SO_4 solution (pH 1) containing 0.1 mM MnTAPP and 1 mM KAuCl_4 . At the initial scan, the peak around 0.5 V depicts the reduction of Au^{3+} and another one reduction peak shows the electrodeposition of poly MnTAPP. For the continuous cycles, this reduction peak shifts to positive potential (at 0.66 V). Also, this reduction peak overlay with the third reduction peak of poly MnTAPP. For the continuous cycles, the growth of the CV showed two redox couples with the formal potentials of $E^0 = 0.69$ and 0.48 (vs. Ag/AgCl) indicates the Mn(II)/Mn(III) redox couple and the porphyrin ring of MnTAPP [8,9].

Here the third redox couple ($E^0 = 0.69$ V) was not obvious because the co-deposition of nano Au [15]. The sharp oxidation peak around 1 V resembles the oxidation process of both Au and poly MnTAPP. This result has been verified by the individual electrodeposition of poly MnTAPP (Fig. 1 Inset (B)) and Au (Fig. 1 Inset (C)) modified GCEs, respectively. Comparing the Fig. 1A with the Fig. 1B and C, it can be clearly seen that the electrochemical deposition of Au and poly MnTAPP occurs together, respectively.

Here in Fig. 1C, at the initial stage, the electrodeposition of Au particles occurs with the higher reduction currents. Also in Fig. 1A at the initial scan range the reduction current appears higher than the only poly MnTAPP electrodeposition (Fig. 1B). Therefore, the higher reduction current is due to the initiation of Au electrodeposition process which exhibits at the initial scan, respectively [15]. As a result, in the hybrid film (poly MnTAPP and nano Au) the redox peaks of poly MnTAPP not that much as visible as like only poly MnTAPP. Here the redox couple with the formal potential of $E^0 = 0.25$ V indicates the formation of polymer bridged

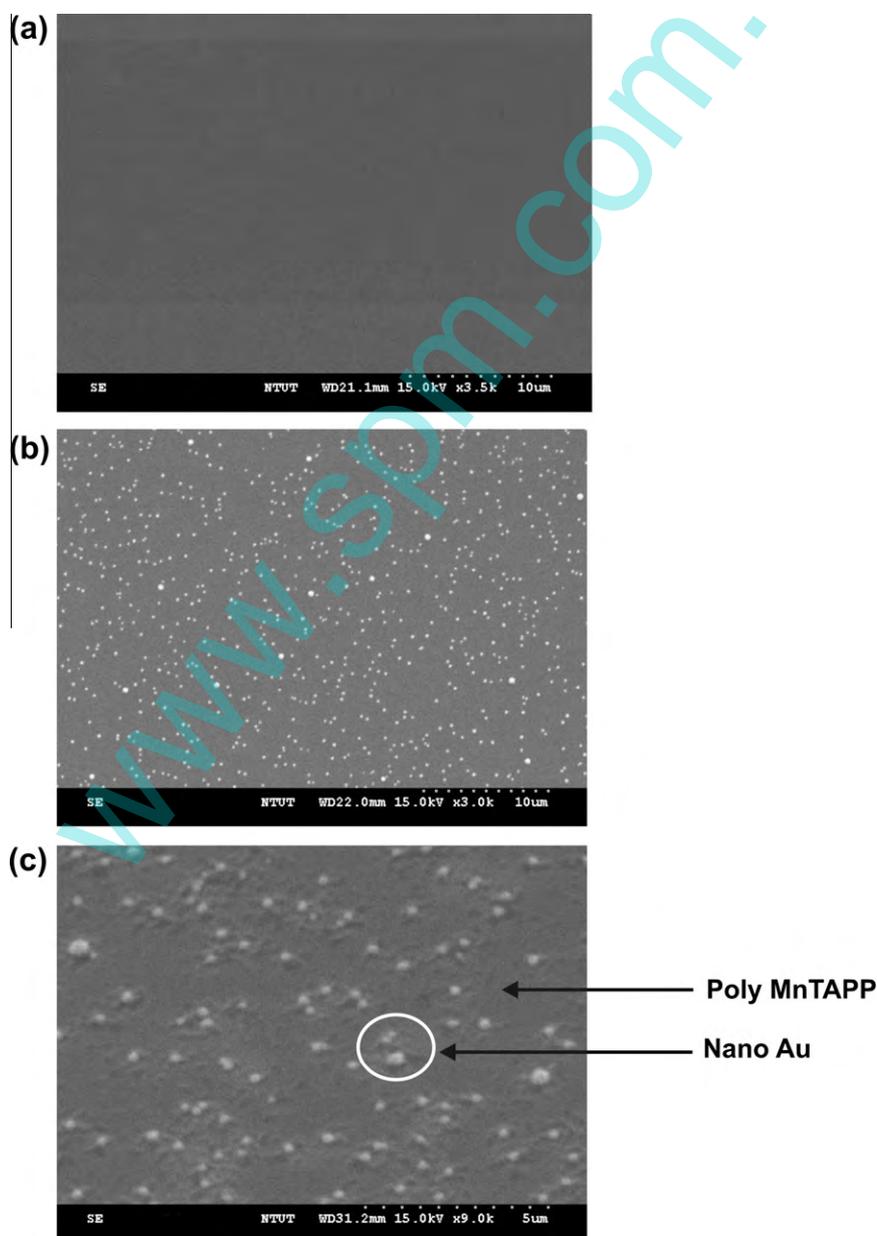


Fig. 2. The typical SEM image obtained for the electrodeposited (a) poly MnTAPP, (b) electrodeposited poly MnTAPP-nano Au (view angle: 90°), (c) poly MnTAPP-nano Au (view angle: 60°).

functional groups of MnTAPP [9,10]. The poly MnTAPP-nano Au film modified GCE was washed with deionized water and examined for the electrochemical studies. Based on the previous literature reports, pH 10.4 buffer solution was found as suitable for the detection of NaOCl [7]. Therefore, we have selected this buffer solution for the detailed electroanalysis of NaOCl.

3.2. SEM, AFM and UV-vis analysis

Fig. 2a SEM image shows the electrodeposited poly MnTAPP. From the SEM image (Fig. 2a), we can reveal that the poly MnTAPP has been deposited as a thin layer on the electrode surface. Fig. 2b and c shows the 90° and 60° view of the electrodeposited poly MnTAPP-nano Au modified GCE. This figure clearly depicts the presence of poly MnTAPP as a thin layer and nano Au as particles on the electrode surface. Here the electrodeposited nano Au particles formed as a group on the electrode surface. Further the group of nano Au particles size varies in the range of 170–350 nm. All these SEM results show the surface nature of the electrodeposited poly MnTAPP and nano Au particles.

Next the poly MnTAPP, poly MnTAPP-nano Au film modified ITOs have been examined using tapping mode in AFM. Fig. 3a and b shows a typical AFM 2D image of the electrodeposited poly MnTAPP and poly MnTAPP-nano Au film. From Fig. 3a it can be seen that the electrodeposited poly MnTAPP film has been found as distorted thin layer on the electrode surface. At the same time, poly MnTAPP film modified with nano Au displays the group of nano Au particles very clearly on the ITO surface. This result validates the deposition of both poly MnTAPP and nano Au on the ITO. Further the AFM analysis similarly resembles and corroborate with the SEM results. A detailed surface morphological study has been done for the above mentioned films and various surface parameters have been analyzed using AFM.

Table 1 shows the several AFM image analysis ($n = 5$) results of the bare, poly MnTAPP and poly MnTAPP-nano Au modified ITO. The average roughness's (AR) of these ITOs have been examined several times and the average values have been given in the Table 1. From this Table 1 result we can see the increase in the average roughness (AR) value from bare to poly MnTAPP and poly MnTAPP-nano Au modified ITO. These results validate the presence of both poly MnTAPP and poly MnTAPP-nano Au on the ITO surface. Here the poly MnTAPP-nano Au film possesses the higher roughness average value comparing with the only poly MnTAPP film. This is because the presence of group of nano Au particles. Also, the only poly MnTAPP film modified ITO's average roughness is higher than the bare ITO. This confirms the electrodeposition of poly MnTAPP on the ITO, respectively. Based on the SEM and AFM analysis, the maximum diameter of the group of nano Au particles are found in the size range of 170–350 nm. Here the average diameter of the group of nanoparticles was found as 235 nm. The average height of the electrodeposited nano Au particles was found as 70 nm.

In the next step, UV-vis spectroscopy has been employed for the analysis of poly MnTAPP-nano Au modified ITO. Fig. 4 shows the UV-vis absorption spectra of the poly MnTAPP-nano Au electrodeposited ITO (Inset of Fig. 4 shows the poly MnTAPP electrodeposited ITO). For the poly MnTAPP-nano Au modified ITO, UV-vis absorption peaks appear at 475, 520, 575 and 805 nm. At the same time, for poly MnTAPP modified ITO the absorption peaks appears at 435, 475, 565 and 637 nm (Inset of Fig. 4). Here the absorption peaks differ in the hybrid film because the presence of both poly MnTAPP and nano Au on the ITO surface. Finally, the SEM, AFM and UV-vis spectroscopy results clearly show the surface morphological properties and the presence of the electrodeposited poly MnTAPP-nano Au film.

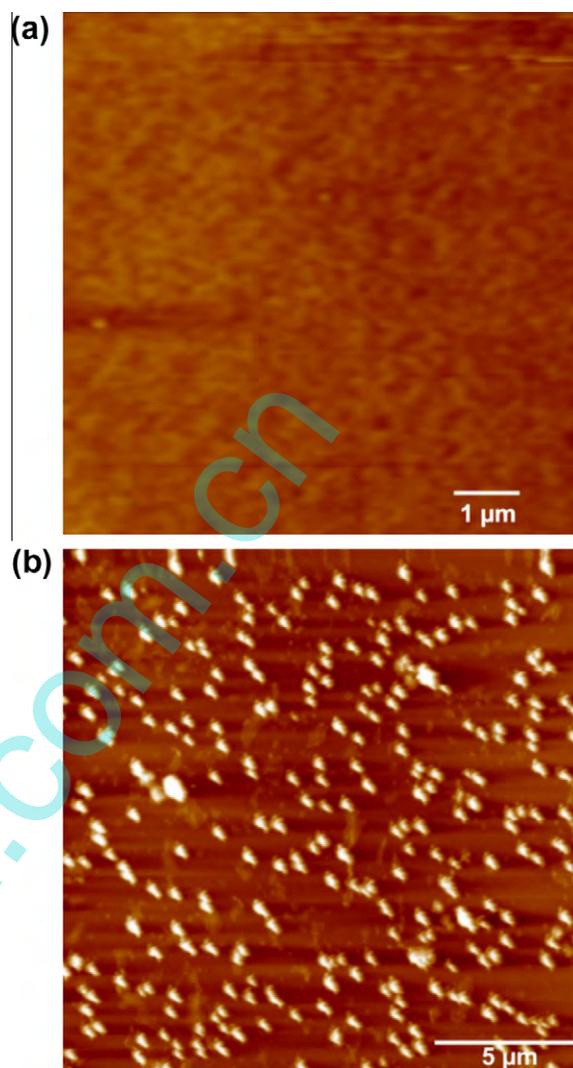


Fig. 3. (a) Tapping mode AFM image of poly MnTAPP film, (b) poly MnTAPP-nano Au film on ITO.

Table 1
AFM analysis.

AFM parameters	Bare ITO ^a	Poly MnTAPP modified ITO ^a	PolyMnTAPP-nano Au modified ITO ^a
Average roughness (AR) (nm)	2.19 (s.d = 0.737)	3.82 (s.d = 1.58)	26.9 (s.d = 4.68)

Standard deviation (s.d).

^a ($n = 5$).

3.3. Amperometric detection of NaOCl

Electrocatalytic response of poly MnTAPP-nano Au film (NaOCl detection) has been compared with bare and poly MnTAPP modified GCE (Fig. 5A). Fig. 5A curve (c) shows the CV response of poly MnTAPP-nano Au film modified GCE in pH 10.4 NaOH (absence of NaOCl). For the 0.01 M concentration range, in pH 10.4 NaOH, poly MnTAPP-nano Au film modified GCE exhibits NaOCl electrochemical signal at around -0.15 V (Fig. 5A, curve a). At the same time, the poly MnTAPP film modified GCE (Fig. 5A, curve b) and the bare GCE (Fig. 5A, curve a') does not show any enhanced current response for the detection of NaOCl. Only, the poly MnTAPP-nano Au film shows the enhanced reduction current response at -0.15 V. Based on this, it proves that poly MnTAPP-nano Au film

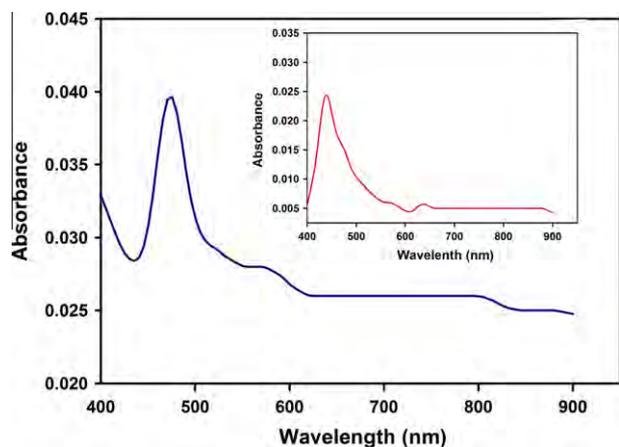


Fig. 4. UV-vis absorption spectra of poly MnTAPP-nano Au modified ITO (Inset shows the UV-vis absorption spectra of poly MnTAPP modified ITO).

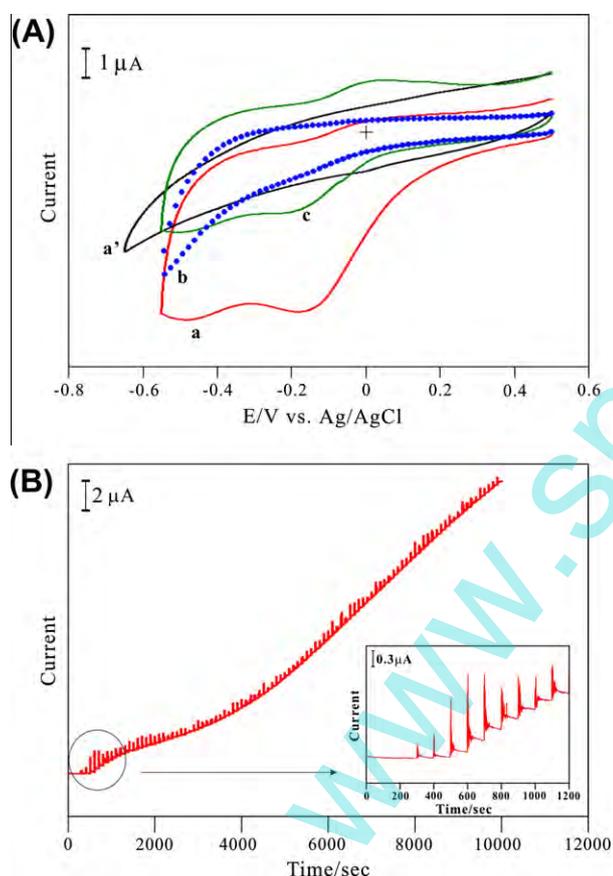
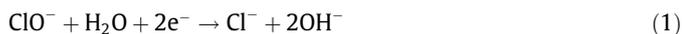


Fig. 5. (A) CV response for NaOCl detection (0.01 M) at (a') bare, (a) poly MnTAPP-nano Au, (b) poly MnTAPP modified GCE and (c) CV response of poly MnTAPP-nano Au film modified GCE in pH 10.4 NaOH (absence of NaOCl). (B) Amperometric i-t response of the poly MnTAPP-nano Au film modified GCE in pH 10.4 NaOH for the sequential additions of NaOCl (2.47×10^{-5} – 1.07×10^{-2} M, potential: -0.1 V). The inset shows the magnified view of the NaOCl detection.

modified GCE is suitable for the electrocatalytic reduction of NaOCl comparing with the other electrodes (bare and poly MnTAPP modified GCE).

Therefore, increase in the reduction peak current and decrease in the over potential at poly MnTAPP-nano Au show that the proposed film modified GCE successfully detects the NaOCl.



It is more complicated to predict the exact reaction mechanism for the NaOCl reduction and the electrode reaction mechanism for the proposed film. Also, here this film has been focused and developed for the NaOCl electro reduction process. Therefore, based on the previous literature reports [16,17] here we propose a general electrocatalytic reduction mechanism for the NaOCl reduction. This mechanism is purely based on the previously literature reports which says that the chlorine may present in two forms in water. They are HOCl and ClO^- . At the same time in higher pH conditions (>8.5) ClO^- will be the dominant in water. Here we use pH 10.4 NaOH as buffer solution. Therefore, the above provided mechanism will be the expected general mechanism for the electrocatalytic reduction of NaOCl, respectively.

To study the detailed electrocatalytic activity of NaOCl reduction, amperometric i-t method has been employed for the lab and real sample analysis. Fig. 5B shows the amperometric response of poly MnTAPP-nano Au film modified GCE in pH 10.4 NaOH for the different concentrations of NaOCl. Here for each 1.5 min the NaOCl has been added in the buffer solution (pH 10.4 NaOH, -0.1 V) and the current response has been noted.

For the every additions, the reduction current was increasing with respect to the increasing concentrations of NaOCl and examined up to the value of 1.07×10^{-2} M. The amperometric current response for NaOCl reduction reached within 5 s following with the additions of NaOCl and this current response were directly proportional to the NaOCl concentrations, respectively. Based on the i-t current response we partially assume that the initial concentration of NaOCl (2.47×10^{-5} M) will be the detection limit of this film. From this result, the electrocatalytic activity of poly MnTAPP-nano Au film modified GCE for NaOCl detection has been validated. Table 2 shows the comparison study of the NaOCl detection with previous studies. Here the proposed film shows the sufficient range of detection of NaOCl comparing with other reports, respectively.

3.4. Amperometric detection of NaOCl in real samples and interference studies

In the next attempt, poly MnTAPP-nano Au film modified GCE directly employed for the detection of NaOCl in real samples (Fig. 6A). Commercially available bleaching agent (containing 5% Cl) has been examined. For every 1.5 min the NaOCl has been added in the NaOH buffer solution (pH 10.4 NaOH, at: -0.1 V) and the current response has been noted. The poly MnTAPP-nano Au film successfully shows the amperometric response for the detection of NaOCl in higher concentrations ranges. As expected, the poly MnTAPP-nano Au film modified GCE shows the amperometric current response for the NaOCl detection within 5 s for the additions of bleaching solution in pH 10.4 NaOH.

Table 2
Comparison table for sodium hypochlorite detection.

Type	Buffer	pH	Potential (V)	Range	Ref.
Green method	NaOH	10.4	–	0.07–0.42 g Cl_2 l^{-1}	[7]
FIA system	NaCl (10 mM)	5.5	0.2	5 $\mu\text{g}/\text{ml}$	[17]
Oxidized GCE	NaCl (0.1 M)	–	–0.2	–	[18]
Dendrimer-Au GCE	–	–	–	–	–
Pt indicator electrode	Acetate buffer (0.1 M)	4.7	–	3.7–60 μM	[19]
Poly MnTAPP-nano Au GCE	NaOH	10.4	-0.1	2.47×10^{-5} – 1.07×10^{-2} M	This work

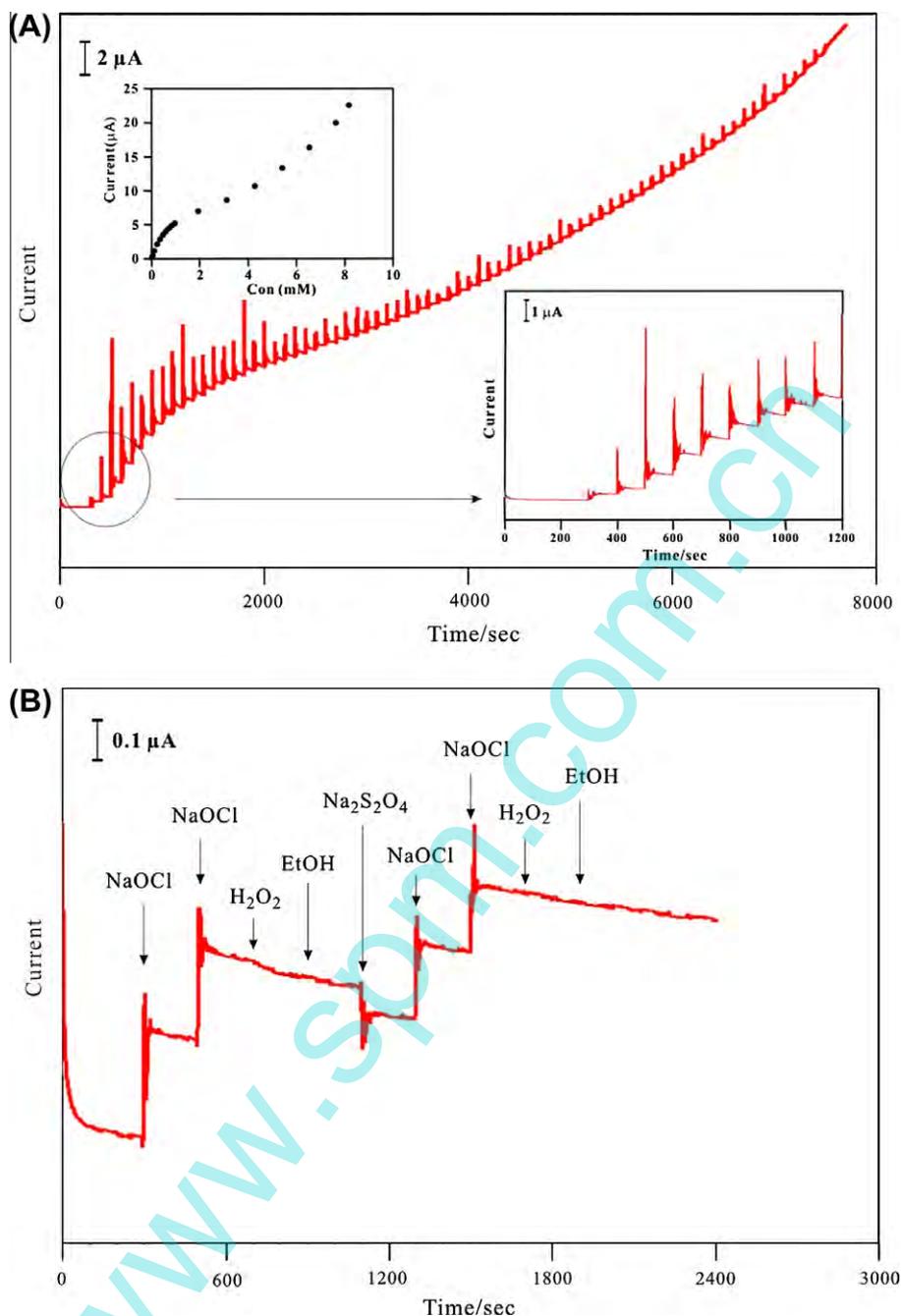


Fig. 6. (A) Amperometric *i-t* response of poly MnTAPP-nano Au film modified GCE in pH 10.4 NaOH for the sequential additions of NaOCl (2.47×10^{-5} – 1.07×10^{-2} M, potential: -0.1 V). The inset shows the magnified view of the NaOCl detection. (B) Amperometric current response of the poly MnTAPP-nano Au film for the each sequential additions ($100 \mu\text{L}$ of each concentration 1.2×10^{-3} M) of NaOCl, H_2O_2 , $\text{C}_2\text{H}_5\text{OH}$, $\text{Na}_2\text{S}_2\text{O}_4$, H_2O_2 and $\text{C}_2\text{H}_5\text{OH}$ in pH 10.4 NaOH.

In the next step, the interference studies have been examined with five different species: NaOCl, H_2O_2 , $\text{C}_2\text{H}_5\text{OH}$, $\text{Na}_2\text{S}_2\text{O}_4$, H_2O_2 and $\text{C}_2\text{H}_5\text{OH}$ ($100 \mu\text{L}$ of each concentration 1.2×10^{-3} M) (Fig. 6B). Here the poly MnTAPP-nano Au film exhibits the current increase for the sequential additions of NaOCl. At the same time, for the additions of H_2O_2 and ethanol, poly MnTAPP-nano Au film does not show the interference current response. However, for $\text{Na}_2\text{S}_2\text{O}_4$ addition, it showed a small decrease in the current value. Further for the continuous additions of NaOCl, the current response were increasing and for the continuous additions of H_2O_2 there was no interference current at the poly MnTAPP-nano Au film modified GCE. This shows that poly MnTAPP-nano Au film successfully overcomes the interference signals and show only

the NaOCl detection signals, respectively. The repeatability and reproducibility nature of the modified GCE has been examined for the fixed concentration of NaOCl and in the five other GCEs and the relative standard deviation (% RSD) for these measurements were found as 4.43% and 3.52%. Further the stability of the film has been examined by keeping the modified GCE exposed in open air condition at the room temperature. After 1 day the background study have been done and there is 2% decrease from its initial value. This shows that the proposed film holds the enough stability. Based on this stability examination, we assume that the shelf-life of this film modified GCE will be 3 days which is based on the decrease in the background current response in pH 1.0 H_2SO_4 solution.

4. Conclusion

Here we propose a simple one step electrochemical deposition method for the fabrication of poly MnTAPP-nano Au film on GCE and ITO surface. The poly MnTAPP, poly MnTAPP-nano Au films have been characterized using SEM, AFM and UV analysis. Poly MnTAPP-nano Au film was found as electrochemically active and stable. The proposed film modified GCE successfully employed for the detection of NaOCl. Not only limited to lab sample, poly MnTAPP-nano Au film modified GCE successfully detects the NaOCl in commercially available real samples in the wide concentration ranges. Also, this film successfully overcomes the interferences and shows only the electrochemical signal of NaOCl, which indicates the special nature of this film. In conclusion, the poly MnTAPP-nano Au film could be employed as prototype sensor for the detection of NaOCl.

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