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One Pot Synthesis of Coordination Polymer 2,5-Dimercapto-1,3,4-thiadiazole-Gold and its Application in Voltammetric Sensing of Resorcinol

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Abstract

Here in, we report one pot synthesis of coordination polymer using 2,5-Dimercapto-1,3,4-thiadiazole (DMTD) with Gold (Au) and characterization of polymer by FTIR, Raman spectroscopy, UV-visible spectroscopy, XPS, XRD, ^{13}CNMR, HRTEM, Gel Permeation Chromatography and TGA techniques. Results show that Au ions get coordinated by diazole and sulfydryl groups of DMTD throughout the polymeric chain. The polymeric layers stabilize itself through $\pi - \pi$ stacking and hydrophobic interaction. Powder XRD analysis concludes crystalline characteristics of DMTD-Au coordination polymer. The kinetic parameters, such as energy of activation and regression value of the DMTD-Au decomposition have been determined by exploiting thermogravimetric data. HRTEM analysis establishes the nanostucture of polymeric material DMTD-Au. Its voltammetric study reveals that synthesized coordination polymer DMTD-Au exhibit excellent electroactivity towards resorcinol and facilitates fast electron transfer kinetics which is used for electro-sensing purposes. To the best of our knowledge we are the first reporting this coordination polymer DMTD-Au modified carbon paste electrode (DMTD-Au/CPE) for electrochemical detection of resorcinol (RS). DMTD-Au modified carbon paste electrode has been found to be highly sensitive towards resorcinol due to its strong interaction through intermolecular hydrogen bonding. Under the optimized conditions, modified electrode exhibit resorcinol oxidation at low over potential (0.55 V) and the anodic peak current shows a linear response with sensitivity and limit of detection 0.019µA/nM and 29.77nM respectively at S/N (signal-to-noise ratio):3.

Keywords Coordination polymer, 2,5-Dimercapto-1,3,4-thiadiazole, Voltammetric sensing, Resorcinol sensor.

Introduction

In recent years study of coordination polymer (CP) has emerged as a vibrant area of research. Coordination polymers are a family of compounds which are considered as metal-organic frameworks with more than two physical/chemical properties in one (like hybrid materials). CPs are formed by incorporation of metal building blocks in multi-dentate organic or inorganic bridging ligands [1-2]. The design of efficient coordination polymer encapsulated with noble metal ions showed significant interest over the past two decades. Coordination polymers have been widely used for a number of applications including sensing [3], water purification [4], hydrogen fuel storage [5], heterogeneous catalysis or catalyst supporting energy-storage devices such as lithium ion secondary batteries [6-7] and double layer capacitors [8-9]. Therefore, it is becoming more demanding for synthesis of such coordination polymers in commercial purposes through facile routes without catalyst at room temperature [10-12].

In this scenario, 2,5-Dimercapto-1,3,4-thiadiazole (DMTD) may be of great interest for constructing CPs with interesting properties due to its four possible bonding sites (diazole nitrogen atoms and sulfydryl sulfur donors) which provide feasibility for metal ion to be linked with ligand and thus expending chain dimensions. Furthermore, azole rings are superior in terms of hydrogen bonding and **π-π** stacking [13].

We explore the possibility of synthesizing coordination polymer DMTD-Au under optimal conditions without using catalyst or extra control of other experimental condition and pH etc. Simple design reaction is employed, in which the concentration of Au (III), DMTD and reaction conditions are systematically varied with progress of reaction and product, selectivity being monitored by several instrumental techniques. This compound is also compared with the Au(0)-DMTD composite in order to understand the difference in the coordination polymer and composite of the two components [14]. Ultimately, this reaction process leads to an enhanced practical utility of synthesized coordination polymer DMTD-Au, thereby providing a platform for production of such polymers with physical properties competitive with all those of the existing coordination polymers.

This is for the first time to use gold salt for synthesis of coordination polymer, establish its structural features and its application in voltammetric sensing of resorcinol (RS) up to nanomolar level. Phenolic compounds which are extensively used in tanning, cosmetic, dye, pesticides, flavoring agents, medicines, antioxidants and photography, are highly toxic and low degradable in ecological environment therefore they have listed as environmental pollutants by the US Environmental Protection Agency (EPA) and European Union (EU) [15-18]. Resorcinol is one of the phenolic compounds having high toxicity, it can be easily absorbed through the gastric tract and human skin, which can cause dermatitis, catarrh, convulsion, cyanopathy [19-20]. In recent years, a lot of methods have been applied for determination of RS such as spectrophotometry, high-performance liquid chromatography, quartz crystal microbalance, surface Plasmon resonance and fluorescence spectroscopy [21-23]. However these methods require expensive and sophisticated instrumentation or complicated sample preparation with a moderate limit of detection. Further electrochemical technique has always offered simple instrumentation, low cost and its portability. In this process, the concept of modified electrode is one of the exciting fields of electro analytical chemistry [24-26]. Several existing electrochemical methods for RS sensing are based on immobilization of enzyme on modified electrode however we have demonstrated a simple non-enzymatic, highly accurate and rapid voltammetric method with DMDT-Au modified carbon paste electrode for ultra trace level sensing of RS within a wide range of concentration.

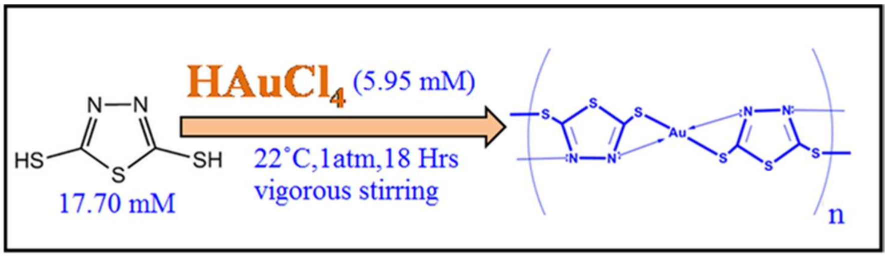
2. Experimental

2.1. Materials

2,5-Dimercapto-1,3,4-thiadiazole (DMTD) and $HAuCl_4$ were purchased from Sigma Aldrich (India). Ethanol, Resorcinol, Sodium Dihydrogen phosphate and Disodium hydrogen phosphate (SRL, India) were used as received unless otherwise mentioned. The glassware used in the synthesis of polymer were cleaned with freshly prepared aqua regia (3:1, HCl/HNO_3) and rinsed comprehensively with ultrapure water (Merck India).

2.2. Synthesis of coordination polymer (DMTD-Au)

In a typical synthesis of coordination polymer (DMTD-Au), ethanolic solution of $HAuCl_4$ (5.95 mM) was added to 2,5-Dimercapto-1,3,4-thiadiazole (17.7 mM, prepared in ethanol solution) under vigorous stirred condition for 18 hrs at 22 °C under a thin stream of nitrogen gas (shown in reaction scheme) to avoid other partial oxidation of precursor molecule. Initially monomeric solution was clear and transparent which changed into turbid brown during the course of reaction and finally pale yellow precipitate was obtained. The pale yellow precipitate was purified by washing several times with water ethanol mixture (30:70 v/v) to remove un-reacted DMTD and gold salt thereafter dried in vacuum at 28 °C for 15 hrs. Yield obtained was 64% and stored below 25 °C for further use .



Scheme: Reaction scheme for synthesis of Co-ordination Polymer DMDT-Au.

2.3. Instrumentation

Infrared spectra in KBr pellets were recorded with a Fourier transform infrared (FTIR) spectrometer (Nicolet-6700, USA) scanning from 2500 to 400 cm^{-1}. Raman spectra were measured with a Micro Raman Spectrometer at 180° scattering geometry (Renishaw, Germany) with a 514.5 nm line of an Ar^+ laser at 50 mW at room temperature. TEM measurements were performed with Jeol Jem 2010 electron microscope operating at 200 kV on a carbon-coated copper grid modified with 5 µL of polymer solution in ethanol. ^{13}C NMR spectra of resulting polymer was recorded on a JEOL Al300 NMR (300 MHz) in DMSO-d_6 solvent and reported in parts per million (δ) from residual solvent peak. Thermogravimetric analysis (TGA) was performed on a NETZSCH, STA 409 PC analyzer with a heating rate of 20 °C min^{-1} under a flow of nitrogen gas. X-ray diffraction pattern for powder samples of coordination polymer DMTD-Au and DMTD were carried out with 18 kW rotating anode powder X-ray diffractometer from 10° to 80°, Rigaku, Japan with Cu-Kα radiation operating in Bragg-Brentano geometry and fitted with a graphite monochromator in diffracted beam with 3° min^{-1} scan rate. UV-vis absorption spectra was recorded in Perkin Elmer Lambda-25 spectrophotometer by using a quartz cuvette having optical path length of 1 cm. Elemental analysis was recorded with X-ray photoelectron, Kratos Analytical Instrument, Shimadzu group company, Amicus XPS UK. The number-average molecular weight (Mn) and poly dispersity index (Mw/Mn) were determined by Youglin ACME 9000 gel permeation chromatography in DMF at 40 °C with flow rate 0.5 $mLmin^{-1}$ on two polystyrene gel columns [PL gel 5 µm 10E 4 Å columns (300 7.5 mm)] connected in series to Gradient Pump and a RI detector. The columns were calibrated against seven poly(methyl methacrylate) (PMMA) standard samples (Polymer Lab, PMMA Calibration Kit, M-M-10). Electrochemical workstation (model-CHI7041C), CH-Instrument Inc., USA was used for electrochemical measurement using three electrodes assembly (as shown in figure 1) consisting DMTD-Au carbon paste modified electrode as a working electrode, Pt foil as counter electrode and Ag/AgCl as reference electrode for all electrochemical measurements.

Neutral Phosphate buffer (pH 7.0) was used as a supporting electrolyte and scan rate was kept 50mV/s for each measurement.

2.4. Modified carbon paste electrode preparation for RS sensing

The active carbon paste was made by mixing known amount of DMTD-Au (2.5 %w/w) with graphite powder (67.5%w/w) in a mortar pestle followed by addition of Nujol oil (30%w/w). The absence and presence of DMTD-Au in active paste resulted into the formation of unmodified CPE and modified CPE/DMTD-Au systems. The mixture was thoroughly homogenized and filled manually in the cavity (1mm diameter) of electrode body. Electrode surface was smoothed on clean butter paper applying pressure to get better electrical contact.

3. Results and discussion

3.1. Structural, Morphological and Molecular weight studies of synthesized coordination polymer DMDT-Au

FTIR spectra of DMTD-Au and DMTD have been recorded in region 400-2500 cm^{-1} as shown in figure 1. In case of DMTD, region from 2450-2350 cm^{-1} contains several weak bands that derived from C-H stretching overtones and Fermi resonances. Peaks appearing in the region 1300-1205 cm^{-1} are assigned to ring modes coupled to (exocyclic) C-C stretch and a ring stretching mode. The most prominent of these are the asymmetric stretches (ν_{as}) at 1500 cm^{-1} and symmetric stretch (ν_s) at 1407 cm^{-1} of C=N respectively, ν_{as} and ν_s modes of C-S-C stretches have been assigned to peaks at 718 and 658 cm^{-1} respectively. Further a strong IR-absorbing band at 1075 cm^{-1} is assigned due to an out of phase combination of N-N and symmetric C-S-C stretches which get reduced to 1049 cm^{-1} in DMDT-Au. DMTD-Au shows C=N band at 1384 cm^{-1}. Diminution in intensity of C=N bond and reduction in stretching frequency of C=N in DMDT-Au indicates interaction of nitrogen atom with gold which is also confirmed by Raman Spectroscopy.

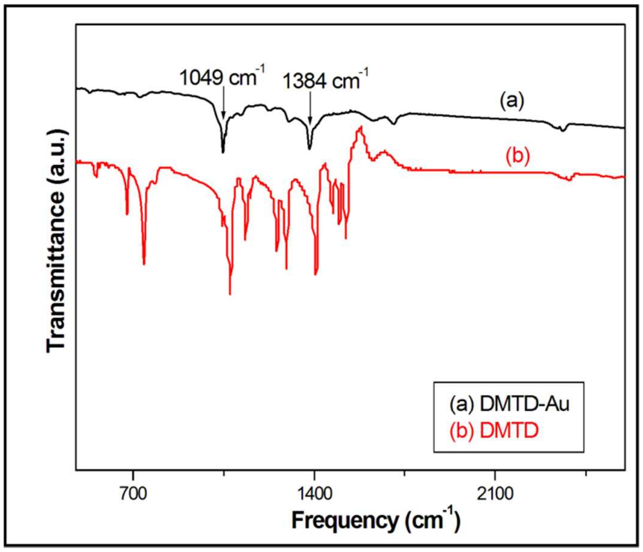


Fig. 1 FT-IR spectra of DMTD-Au (a) and DMTD (b).

Raman spectrum of DMTD-Au as shown in figure 2 exhibit band at 380 and 546 cm^{-1} which arises due to Au-S and Au-N linkage respectively ensuring the metal-sulphur and metal-nitrogen linkage [27]. Further a band at 660 cm^{-1} in Raman spectrum is due to symmetric C-S-C stretch while absence of absorption peak near 522 cm^{-1} clearly indicates absence of S-S bond in coordination polymer DMTD-Au. The results from FTIR and Raman spectroscopy reveal that gold ions get coordinated between DMTD molecules throughout the polymer chain.

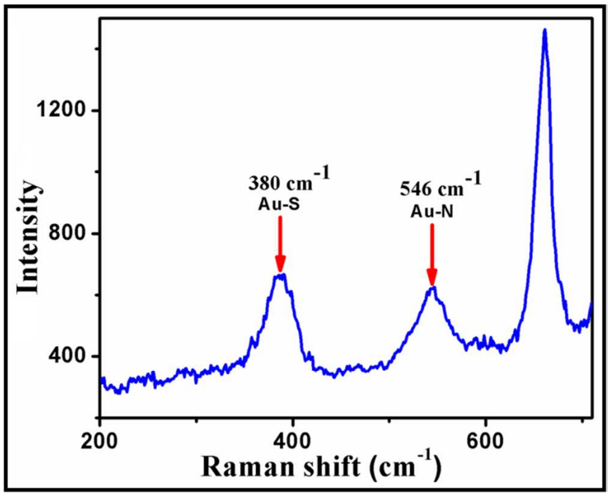


Fig. 2 Raman spectrum of coordination polymer DMTD-Au.

The crystal structure of DMTD-Au as investigated by powder X-ray diffraction (XRD) is shown in Figure 3. Figure (a) and (b) shows the diffraction pattern of DMTD-Au and DMTD respectively while figure (c) corresponds the diffraction pattern of fully reduced gold taken from JCPDS file CAS number 7440-57-5. Indexing for diffraction peaks of DMTD-Au were performed by Dicvol software and were analyzed that the diffraction features appearing at 2θ values 28.28°, 40.44°, 50.10°, 58.58°, 66.30° and 73.56°corresponded to the (100), (110), (112), (200), (202) and (114) planes, respectively for tetragonal system. Sharp diffraction peaks show crystalline characteristics of polymer DMTD-Au. Present study reveals not only the crystalline nature of coordination polymer but also it demonstrates the absence of fully reduced gold within coordination sphere supporting XPS results.

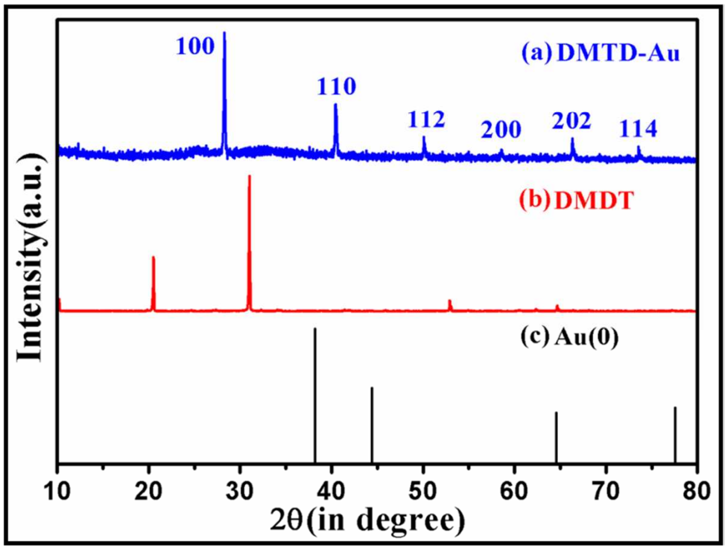


Fig. 3 XRD of DMTD-Au (a), DMTD (b) and Gold (c), taken from JCPDS file CAS number 7440-57-5.

XPS study of DMTD-Au (figure 4) reveals binding energy values 85.41 eV and 89.11 eV as shown in figure 4(a) corresponding to Au(I) $4f_{7/2}$ and Au $4f_{5/2}$ respectively [28-29]. The Au $4f_{7/2}$ binding energy is shifted in DMTD-Au. The direction of this shift clearly corresponds to Au being oxidized state in DMDT-Au and its magnitude is similar to that observed for Au(I).

The experimental photoemission curve of S 2p signal figure 4(b) can be fitted in two doublets i.e., two different atomic environments of sulfur with $2p_{3/2}$ components peaking at 161 and 162.5 eV. The first one can be assigned to aromatic sulphur while the second one is related to sulphur attached to gold atom [30-32]. Nitrogen 1s binding energy (BE) 400.0 eV in figure 4(c) corresponds to N-N binding energy [33-35]. The BE is referenced to C(1s) of C=N binding energy near 287 eV [36] in figure 4(d) since electronegative substituent decrease electron density of carbon atom causing a small increase in C (1s) binding energy.

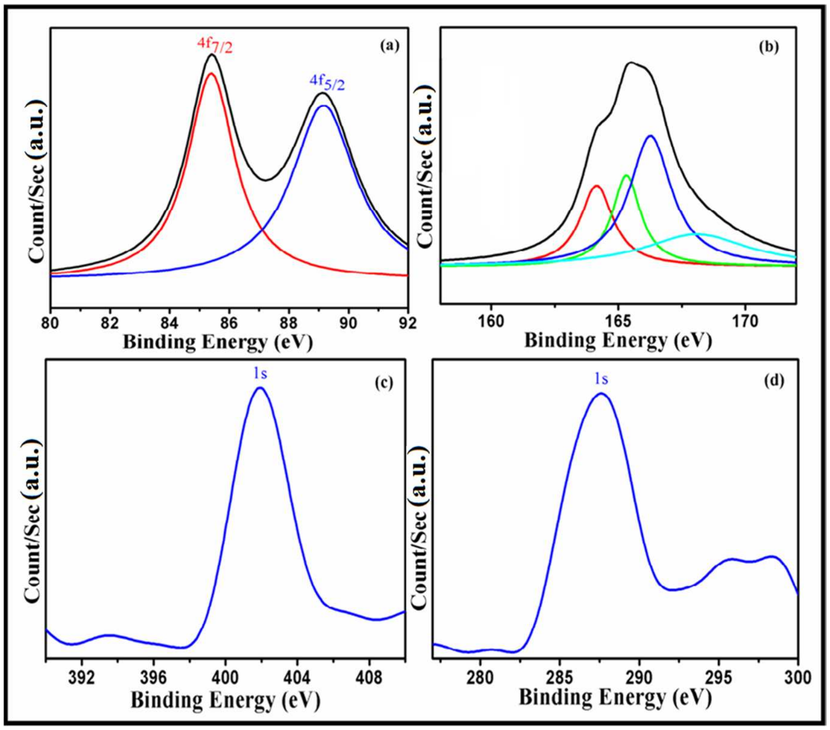


Fig. 4 XPS spectra of DMTD-Au for Au 4f (a), S 2p (b), N 1s (c) and C 1s (d) regions.

The HRTEM image in figure (SI-1) shows that the rigid molecules of Co-ordination Polymer DMTD-Au are arrayed itself in the coordination polymer sphere with an average diameter of about 170 nm having nanospheres. It may be assumed that the rigid coordination polymer DMTD-Au molecules arrayed in parallel due to the **π** –**π** stacking of adjacent molecular chains in the same plane. Corresponding SAED pattern clearly shows that synthesized coordination polymer has crystallinity which supports the XRD result as shown in figure 3. Synthesized coordination polymer DMTD-Au has a prominent peak at chemical shift value 206.95 (figure 5) showing strong deshielding of aromatic carbon as chemical shift value 177 is reported for DMTD [37]. Down field shielding in chemical shift value for DMDT-Au signifies the interaction of metal with DMDT molecule. It displays that aromatic carbon atoms are in strong electronegative environment and are same in nature.

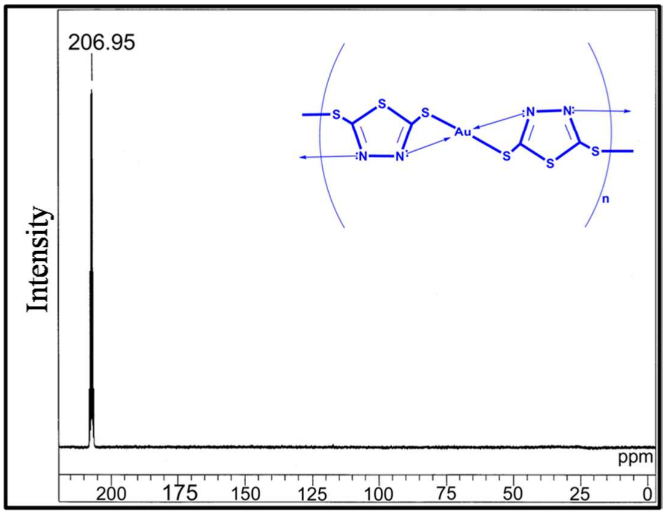


Fig. 5 ^{13}CNMR spectra of DMTD-Au in DMSO-d_6 at room temperature.

On account of various characterization techniques, possible chemical structure of DMDT-Au has been proposed as shown in figure 6 which is in accordance with ^{13}CNMR, FTIR, RAMAN, HRTEM and XPS results.

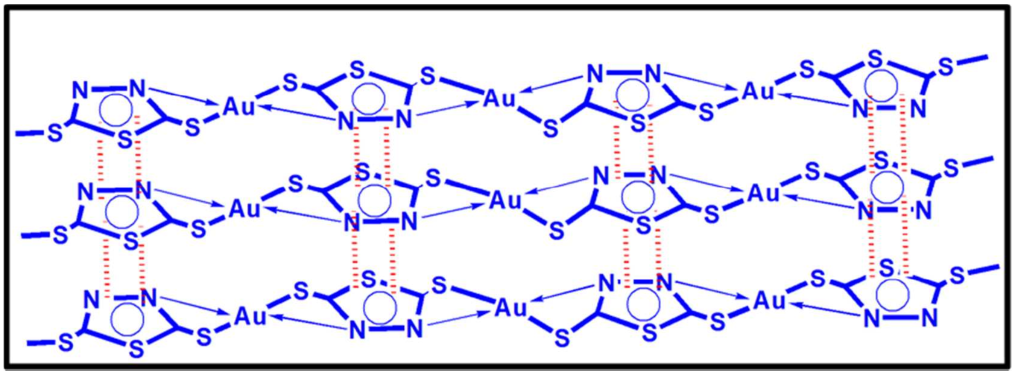


Fig. 6 Proposed structure of synthesized Coordination Polymer DMDT-Au.

The average molecular weight (approximate) distribution of coordination polymer DMTD-Au has determined by gel permeation chromatography using PMMA as a standard. Figure (SI-2) shows the chromatogram which clearly indicate that average molecular weight of dominant fraction is located around Mn = 370000 gmol^{-1} (PDI- 2.32). The minuscule humps are due to fragmentation of polymeric chains and traces of lower molecular weight polymeric fragments. The UV-vis spectrum of Co-ordination Polymer DMDT-Au has been shown in figure 7. The maximum absorption peak at around 433 nm with shoulder peak at 323 nm are attributed due to π-π^* and MLCT (metal to ligand charge transfer transition) (Au→π^*) transition respectively [38]. Thermal analysis of polymeric sample has examined by thermal gravimetric analysis (TGA) (figure 10) under a N_2 atmosphere by varying the temperature to 800 °C at heating rate of 20 °C min^{-1}. The first weight loss (2%) occurred in the temperature range 40-140 °C accounts for the uncoordinated water molecules which includes the lattice and adsorbed water molecules.

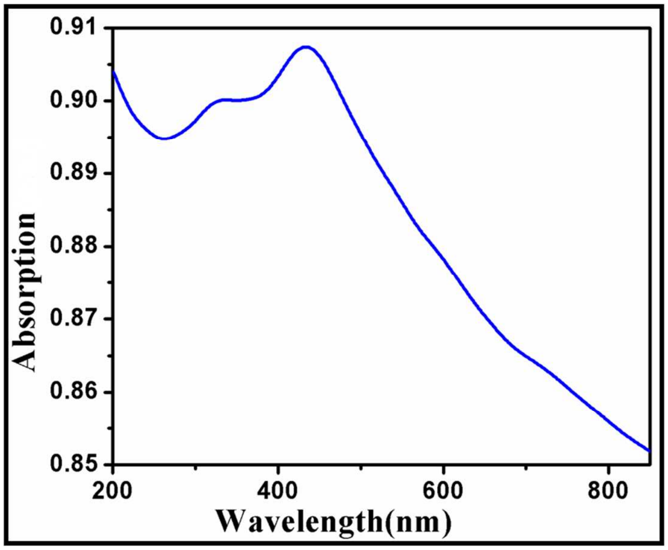


Fig. 7 UV-visible spectrum of coordination polymer DMDT-Au.

It can be seen from figure 8 that degradation of DMTD-Au starts at 260 °C which may be due to the cleavage of metal-sulphur and metal-nitrogen linkage indicating a good extent stability of synthesized coordination polymer. Corresponding DTA plot exhibits four peaks at 280 °C, 600 °C, 510 °C and 730 °C.

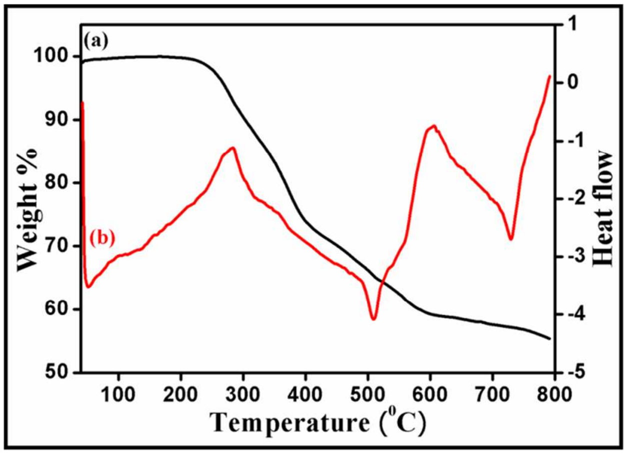


Fig. 8 TGA (a) and DTA (b) plot of DMTD-Au.

Broido et al. [39] demonstrated a method to evaluate the activation energy related with decomposition. The equation developed for calculation of activation energy (E_a) is as follows:

$$\ln\ln (1/Y) = -(Ea/R)\ 1/T + \text{constant}$$

where $Y = W_t - W_\infty / W_0 - W_\infty$

Y is fraction of number of initial molecules not yet decomposed; W_t is weight at anytime t, W_∞ is weight at infinite time (= zero) and W_0 is initial weight. A plot of lnln (1/Y) vs 1/T gives an excellent approximation to a straight line. The slope is related to activation energy. Activation energy using Broido model as shown in figure (SI-3), is measured as 25.20 kJmol^{-1} with R^2 value 0.984.

3.2. Electroanalysis of CPE/DMTD-Au modified electrode

The cyclic voltammetry of DMTD-Au modified carbon paste electrode has examined in presence of 0.02 M Fe(II) /Fe(III) redox couple in 0.1 M phosphate buffer solution (PBS) pH 7.

Three electrode configuration consisting of carbon paste electrode as working electrode, Pt foil as counter electrode and Ag/AgCl as reference electrode has been used for RS sensing as shown in figure 9.

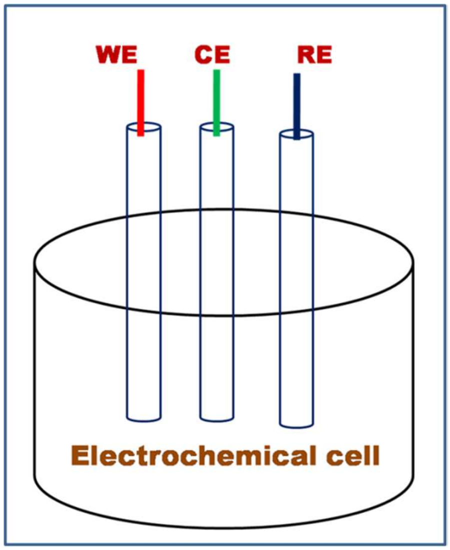


Fig. 9 Schematic diagram of three electrode system.

Significant increase in peak current of Fe(II) /Fe(III) redox couple has observed with DMTD-Au modified carbon paste electrode as compared to unmodified carbon paste electrode for the same amount of Fe(II) /Fe(III) redox couple as shown in figure 10 which reveals that DMTD-Au polymeric material facilitates electron transfer and can be used as an excellent electrocatalytic material.

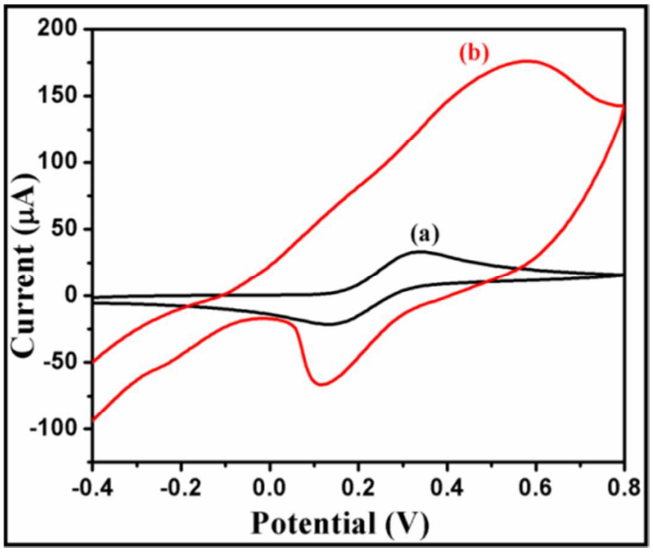


Fig. 10 CV for 0.02 M Fe(II) / Fe(III) in 0.1 M PBS (pH 7)at unmodified carbon paste electrode (a) and (DMTD-Au) modified carbon paste electrode (b).

3.3 Voltammetric Sensing of Resorcinol

The synthesized coordination polymer has been further utilized in voltammetric sensing of resorcinol by DMTD-Au modified carbon paste electrode in phosphate buffer solution. For voltammetric sensing of resorcinol we have selected potential window region 0 to 0.9 V as oxidation of resorcinol is expected in this region. Resorcinol in PBS did not show any peak at bare carbon paste electrode at trace concentration and also not any peak of modified carbon paste electrode has observed as such as shown in the figure 11. Resorcinol addition shows anodic peak at potential 0.55 V vs Ag/AgCl over modified electrode as shown in figure 11. The electrochemistry behind this electro-sensing of resorcinol is probably because of the catalytic effect of DMTD-Au which exhibit high electron transfer kinetics via interaction of diazole nitrogen with hydroxyl group of resorcinol through hydrogen bonding as shown in schematic representation in figure 12. The potential utility of present modified electrode has further examined by recording the voltammetric response on successive addition of resorcinol in PBS (pH 7.0). A systematic change in current has noticed after each addition of resorcinol into supporting electrolyte solution as shown in voltammogram of figure 13 (a). This DMTD-Au modified carbon paste electrode does not suffer electrode fouling and poisoning problem for resorcinol detection which is major limitation of other existing modified electrodes. Stability of the electrode is also very much important for biosensing applications and has tested repeatedly more than 5 times by using the same modified carbon paste electrode. Calibration plot of resorcinol concentration vs. peak current has been shown in figure 13(b) having sensitivity and limit of detection as 0.019 µA/nM and 29.77 nM respectively at R^2 value 0.999 and S/N (signal-to-noise ratio):3.

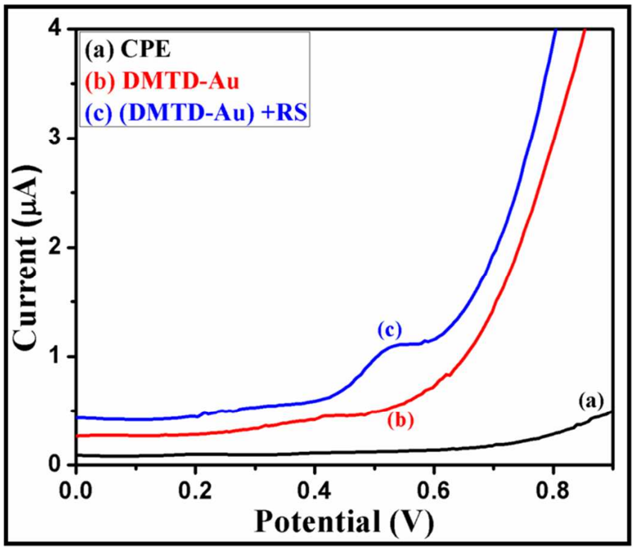


Fig. 11 Differential Pulse Voltammetric response of unmodified carbon paste electrode (a), (DMTD-Au) modified carbon paste (b) and DMTD-Au modified carbon paste +RS (c) in phosphate buffer solution.

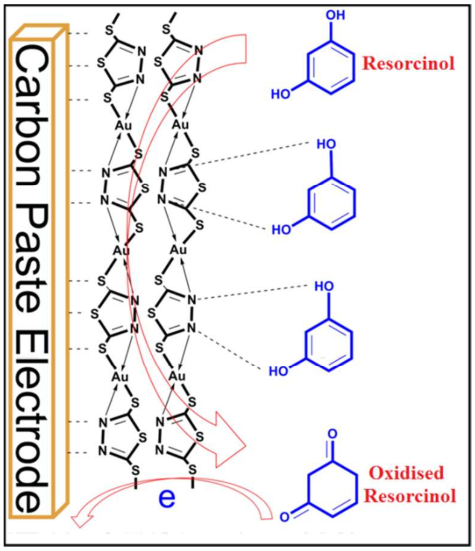


Fig. 12 Schematic representation of voltammetric sensing mechanism of resorcinol.

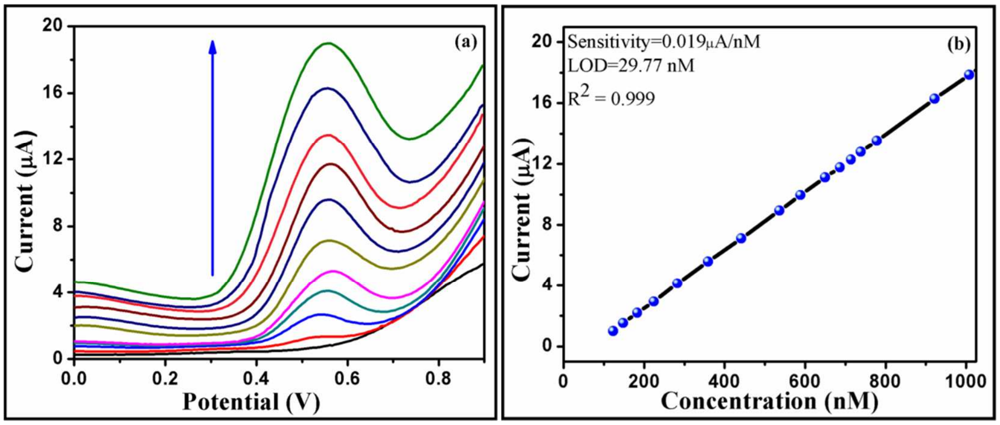


Fig. 13 Differential pulse voltammogram of RS at various concentrations (112.60 x 10^{-9} to 1.09 x 10^{-6} M) in 0.1 M phosphate buffer (pH 7.0) at DMTD-Au modified carbon paste electrode (a) and corresponding standard addition calibration plot of current vs. resorcinol concentration (b).

Conclusions

This work presents one pot facile synthesis of coordination polymer (DMDT-Au) at room temperature. The synthetic method described here is very simple, offers no requirement of catalyst to initiate the polymerization which can have commercial application in drug delivery, metal-organic frameworks (MOFs) for gas storage, catalysis and sensing applications. The average molecular weight of DMDT-Au has been found to be about 370000 gmol^{-1} (PDI-2.32) and activation energy of synthesized material has been evaluated using Broido model as 25.21 kJmol^{-1} at R^2 value 0.984. The DMDT-Au molecules are aligned parallel and polymeric layers are stacked on account of **π-π** stacking and hydrophobic interaction. Further the redox activity of DMDT-Au has been exploited in electrochemical determination of resorcinol up to nanomolar concentration with modified carbon paste electrode. Under the optimized conditions, DMDT-Au modified carbon paste electrode (DMDT-Au/CPE) shows the anodic peak current at lower positive potential (0.55 V) than other existing methods and exhibits linear response towards resorcinol concentration with sensitivity and limit of detection 0.019µA/nM and 29.77 nM respectively at S/N (signal-to-noise ratio):3. The developed coordination polymer based modified electrode possesses advantageous properties such as a high active surface area, stability and rapid electron transfer rate which cumulatively demonstrate high performance toward the electrocatalytic oxidation and detection of resorcinol. Notable conclusions of modified electrode surface demonstrate that DMDT-Au can be used to assemble a selective and sensitive sensor for resorcinol through the formation of intermolecular hydrogen bonding via hetro atom. With regard to future directions, we hope to broaden the scope for synthesis of such thiadiazole-gold coordination polymer encapsulated with other valuable metal ion and finding their potential application towards chemical sensors, biomedical applications, biosensors and other electrochemical purposes.

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The synthesized coordination polymer DMTD-Au has layered structure in which these layers are stacked via **π** –**π** stacking and hydrophobic interaction. It facilitates electron transfer kinetics which has been utilized in ultra trace sensing of Resorcinol.