Silver nanoparticles-supported graphitic-like carbon nitride for the electrochemical sensing of nitrobenzene and its derivatives

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ABSTRACT

Nitrobenzene (NB) is toxic even at low concentrations and hence its contamination in the environment is a pervasive concern. The electrochemical techniques have emerged as rosy method to sense and degrade NB and graphitic carbon nitride (\(\text{g-C}_3\text{N}_4\)) catalysts are found to be promising for this. In this study, silver nanoparticles (AgNPs)-decorated \(\text{N-}[3-(\text{trimethoxysilyl})\text{propyl}]\text{ethylenediamine} \) (EDAS)-modified graphitic carbon nitride nanocomposites [EDAS/(\(\text{g-C}_3\text{N}_4\)-Ag)\(_{\text{NC}}\)] having various silver concentrations are prepared through a facile method and applied for the electrochemical sensing of NB derivatives. UV–vis absorption edge at 430 nm together with a broad surface plasmon resonance (SPR) peak at 450 nm indicates the existence of AgNPs on the \(\text{g-C}_3\text{N}_4\) nanosheets. FTIR spectra endorse the presence of \(\text{g-C}_3\text{N}_4\) nanosheets in the composite. The presence of Ag in EDAS/(\(\text{g-C}_3\text{N}_4\)-Ag)\(_{\text{NC}}\) is confirmed by transmission electron microscopy, energy dispersive X-ray analysis, and cyclic voltammetry (CV). The nanocomposite prepared with 2 mM Ag\(^+\) shows superb electrocatalytic activity toward the reduction of nitrobenzene and its derivatives. Sensitivity of the modified electrode and limit of detection (LOD) for NB assessed by square wave voltammetry are found to be 0.594 A M\(^{-1}\) cm\(^{-2}\) and 2 \(\mu\)M, respectively, in the linear range of 5–50 \(\mu\)M.

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1 Introduction

Mutagenic and carcinogenic behavior of nitroaromatics can cause health issues in human being and hence it is necessary to detect and degrade nitroaromatic compounds for the sake of human safety and security [1, 2]. The byproducts generated from explosives, herbicides, insecticides, and leather industries are mainly nitroaromatic compounds and are discharged into the environment [3, 4]. The presence of nitro group in benzene ring has stronger electron withdrawing tendency which attracts the electron density toward itself and makes the molecule more stable. The stable nature of nitrobenzene and its derivatives makes them as the unavoidable pollutant when they enter the soil or water. The nitrobenzene reduction has gained much importance for the creation of safer environment [5]. However, nitrobenzene oxidation can produce picolinic acid as dead end product which is more toxic [6]. Considering the toxic products in the oxidation of nitrobenzene, reduction technologies have received greater attention than oxidation [7]. Based on the different principles and techniques, various methodologies have been adopted for the detection of nitroaromatic compounds [8]. Various analytical techniques, such as spectrophotometry [9, 10], gas chromatography [11], capillary electrophoresis [12], and high-performance liquid chromatography [13], have been carried out for the determination of nitroaromatics. Owing to their high sensitivity, selectivity, simplicity, and low-cost instrumentation, electrochemical-techniques-based sensors are found to be promising for the detection of nitroaromatics [14–16]. Another advantage of employing electrochemical technique is that the electrochemical reduction of nitrobenzene generates less toxic compounds, such as aniline, phenylhydroxylamine, azoxybenzene, azobenzene, and nitrosobenzene [17]. Metal nanoparticles like silver nanoparticles (AgNPs) [14, 18] and gold nanoparticles (AuNPs) [19] and modified electrodes have been employed as electrochemical sensors for the detection of nitrobenzene (NB) and nitrobenzene derivatives. Bimetal Au/Ag nanorods-modified electrodes are also used for the electrocatalytic reduction of nitrobenzene [20].

Transition metal nanoparticles exhibit excellent catalytic and electrocatalytic activity than the corresponding bulk materials [21]. The size and shape of metal nanoparticles determine the exceptional physical and chemical characteristics and their applicability in catalysis and sensors. Among the various transition metals, silver has the advantages like high electrical conductivity and low cost than others [22, 23]. Hence, silver nanoparticles are extremely beneficial in catalytic and electrocatalytic applications. However, the stability of nanoparticles is a big issue due to the unsuitable high surface energy of the particles, which results in agglomeration of smaller nanoparticles. Various support materials such as SiO2 [24], graphene oxide [25], reduced graphene oxide [26], carbon nanotubes [27], and TiO2 [28] are investigated. Graphite-like carbon nitride (g-C3N4), a medium bandgap semiconductor nanomaterial, draws wide consideration owing to its interesting nature. The low density, thermal constancy, and medium bandgap of g-C3N4 make it as a potential candidate for light-induced processes [29], hydrogen storage [30], lithium-ion battery [31], electrogenerated chemiluminescence [32], and fluorescent sensor [33]. But the bulk g-C3N4 with poor water solubility and large size is not suitable for electrochemical sensing application. However, the large surface area (≈ 300 m2 g−1) and good chemical stability of nanostructured g-C3N4 make it as a good support material and suitable candidate for electrochemical applications. AgNPs-deposited g-C3N4 sheets were employed as electrocatalyst in the non-enzymatic detection of hydrogen peroxide and glucose [34] as well as in the reduction of oxygen [35].

In the present investigation, silver nanoparticles (AgNPs)-decorated N-[3-(trimethoxysilyl)propyl]ethylenediamine (EDAS)-modified graphitic carbon nitride (g-C3N4-Ag) nanocomposites (EDAS/(g-C3N4-Ag)NC) are prepared through a simple reduction method. The electrochemical performances of the nanocomposites toward the electrocatalytic reduction of nitrobenzene and nitrobenzene derivatives have been investigated through cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques.

2 Experimental section

2.1 Chemicals

Urea, N-[3-(trimethoxysilyl)propyl]ethylenediamine (EDAS), and silver nitrate (AgNO3) were obtained from Sigma-Aldrich, India. Sodium borohydride
(NaBH₄), sodium dihydrogen phosphate, disodium hydrogen phosphate, nitrobenzene (NB), nitroaniline (NA), nitrobenzoic acid (NBA), nitrophenol (NP), and nitrotoluene (NT) were purchased from Merck, India. The purities of chemicals were of analytical grades. All the glasswares were treated with Aqua regia [1:3 HNO₃/HCl (v/v)] before carrying out experiments.

2.2 Preparation of EDAS/(g-C₃N₄-Ag)ₙC

The procedure adopted for the preparation of g-C₃N₄ nanosheets is provided in Supplementary Information [36]. EDAS/(g-C₃N₄-Ag)ₙC was prepared as follows: 25 µL of EDAS was mixed with 2 mL of g-C₃N₄ nanosheets and stirred for 1 h. Into this mixture, 20 µL of AgNO₃ (0.1 M) solution were poured to maintain 1 mM concentration of AgNO₃ and stirred for another one hour. 100 µL of freshly prepared 0.1 M NaBH₄ was then added dropwise into the above mixture in order to reduce AgNO₃. When the Ag⁺ is reduced to Ag⁰, the color of the reaction mixture turned to brownish yellow and it was left overnight so as to uniformly deposit the AgNPs on g-C₃N₄ nanosheets. The aggregation of AgNPs on g-C₃N₄ is prevented through amine group stabilization by EDAS. The prepared nanocomposite was centrifuged and washed with double-distilled water to remove the unreduced AgNO₃ and NaBH₄.

Scheme 1  Pictorial description of the preparation of EDAS/(g-C₃N₄-Ag)ₙC

Fig. 1  Diffuse reflectance spectra of (a) g-C₃N₄ nanosheets, (b) EDAS/[g-C₃N₄-Ag(1 mM)]ₙC, (c) EDAS/[g-C₃N₄-Ag(2 mM)]ₙC, and (d) EDAS/[g-C₃N₄-Ag(3 mM)]ₙC.
Finally, the product was redispersed in 2 mL of distilled water. Other two composites with AgNO₃ concentration of 2 mM and 3 mM were prepared by adding 40 and 60 μL of 0.1 M AgNO₃ solutions, keeping all other procedure same, for getting EDAS/(g-C₃N₄-Ag)NC with various amounts of AgNPs. Pictorial description of the nanocomposite preparation is shown in Scheme 1.

2.3 Characterization techniques

Diffuse reflectance spectra of the films were carried out using a Shimadzu UV-2550 (Shimadzu, Japan) UV–Vis spectrophotometer fitted with ISR-2200 DRS accessory. The colloidal samples were coated on glass plate, dried completely, and used for diffused reflectance studies. The scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses were performed by employing a FEI-QUANTA 250 high-resolution scanning electron microscope. The high-resolution transmission electron microscopic (HRTEM) images were recorded in a JEOL 3010 (Jeol, Japan) high-resolution transmission electron microscope at an accelerating voltage of 200 kV. The specimen to be analyzed was dispersed in a solvent and coated onto carbon-coated copper grid and dried in vacuum condition. The IR spectra analysis was carried using Shimadzu IRTRACER-100 (Shimadzu, Japan) FTIR spectrophotometer. Cyclic voltammetry (CV) and square wave voltammetry (SWV) experiments were conducted in a single compartment three-electrode cell using an electrochemical workstation (CH Instruments, USA, Model 680) at 25 °C, by employing modified glassy carbon electrode (GCE) (CH instruments) as working electrode (area 0.07 cm²), Ag/AgCl electrode as reference electrode, and Pt wire as counter electrode.

2.4 Preparation of modified electrode and electrochemical studies

The electrochemical detection of nitrobenzene derivatives were conducted in a three-electrode cell system containing phosphate buffer (pH 7.4) as a supporting electrolyte in nitrogen environment. 5 μL of EDAS/(g-C₃N₄-Ag)NC was coated on a polished and pre-cleaned glassy carbon (GC) electrode (disk shaped, 3 mm dia, area 0.07 cm²). The modified
electrode was dried for an hour at room temperature (≈ 32 °C) and utilized as a working electrode. Thin films on GC electrode were prepared using 2, 4, 5, 6, and 7 μL of EDAS/(g-C$_3$N$_4$-Ag)$_{NC}$ sol for optimization. As the electrode prepared using 5 μL exhibited continuous stable film (5 μL gave discontinuous films; 7 μL showed aggregation) and maximum cyclic voltammetric current response, it was chosen for further studies. Platinum (Pt) wire and Ag/AgCl electrode were chosen as counter and reference electrodes, respectively. The square wave voltammograms were recorded (using CH Instruments, Model 680) by applying a step potential of 4 mV, amplitude of 25 mV, and a frequency of 15 Hz. Experiments were done in triplicates and the average values are reported.

3 Results and discussion

3.1 Characterization of EDAS/(g-C$_3$N$_4$-Ag)$_{NC}$

The formation of EDAS/(g-C$_3$N$_4$-Ag)$_{NC}$ was initially verified through UV–visible diffused reflectance spectra. The spectra of g-C$_3$N$_4$ nanosheets and EDAS/(g-C$_3$N$_4$-Ag)$_{NC}$ are depicted in Fig. 1. The presence of g-C$_3$N$_4$ nanosheets in the nanocomposite is confirmed from the typical UV–vis absorption edge near 430 nm. A new band appeared around 450 nm along with the typical absorption of g-C$_3$N$_4$ in EDAS/(g-C$_3$N$_4$-Ag)$_{NC}$ samples which confirmed the formation of AgNPs on g-C$_3$N$_4$ nanosheets. The new band is attributed to the surface plasmon resonance (SPR) absorption characteristic of AgNPs.

Figure 2 shows the FTIR spectra of g-C$_3$N$_4$ nanosheets and EDAS/[g-C$_3$N$_4$-Ag(2 mM)]$_{NC}$ in the wave number range of 500–4000 cm$^{-1}$. The peak obtained in the range of 1240–1643 cm$^{-1}$ is attributed
to the characteristic stretching modes of C–N heterocycles. The broad absorption peaks that appeared in the range of 3040–3300 cm\(^{-1}\) are ascribed to the N–H vibration and H\(_2\)O adsorption, respectively [37, 38]. The FTIR data inferred that the attachment of Ag nanoparticles does not affect the structural features of the g-C\(_3\)N\(_4\) nanosheets.

Figure 3 shows TEM images of the prepared EDAS/[g-C\(_3\)N\(_4\)-Ag(2 mM)]\(_{\text{NC}}\) NC. The sheet-like structure of g-C\(_3\)N\(_4\) suggests the presence of exfoliated g-C\(_3\)N\(_4\) (Fig. 3A). A large number of spherical AgNPs with size range of 10–15 nm are found on the g-C\(_3\)N\(_4\) nanosheets surface, which confirmed the formation of AgNPs-loaded g-C\(_3\)N\(_4\) nanosheets (Fig. 3B). The lattice fringes with interplanar distance of 0.235 nm assigned to Ag(111) facet was found on the AgNPs. The elemental characterization of EDAS/[g-C\(_3\)N\(_4\)-Ag(2 mM)]\(_{\text{NC}}\) was performed through EDX analysis (Fig. S1). The spectrum confirmed the presence of the elements C, N, O, Si, and Ag by showing their X-ray lines. The elemental mapping of EDAS/[g-C\(_3\)N\(_4\)-Ag(2 mM)]\(_{\text{NC}}\) showed the uniform distribution of AgNPs in the nanocomposite and confirmed the formation of g-C\(_3\)N\(_4\)-Ag nanocomposite in EDAS sol–gel network (Fig. S1). Cyclic voltammogram of EDAS/(g-C\(_3\)N\(_4\)-Ag)\(_{\text{NC}}\)-modified electrode (Fig. S2) shows an anodic peak representing Ag oxidation at 0.23 V, which affirm the Ag presence in the composite material [39].

### 3.2 Electrocatalytic reduction of nitrobenzene (NB)

The electrocatalytic reduction of NB at the EDAS/[g-C\(_3\)N\(_4\)-Ag(2 mM)]\(_{\text{NC}}\)-modified electrode (thin films over flat bottom of 3 mm dia GC electrode) was investigated through cyclic voltammetry. The cyclic voltammograms (CVs) recorded for 500 \(\mu\)M of NB at bare GC, GC/(EDAS/g-C\(_3\)N\(_4\)), and GC/EDAS/[g-C\(_3\)N\(_4\)-Ag(2 mM)]\(_{\text{NC}}\)-modified electrodes at a scan rate of 50 mV s\(^{-1}\) are shown in Fig. 4. In the reductive scan with the GC/EDAS/[g-C\(_3\)N\(_4\)-Ag(2 mM)]\(_{\text{NC}}\)-modified electrode, the reduction peak for nitrobenzene was observed at \(-0.68\) V, whereas the corresponding oxidation peak was observed at 0.6 V. The reduction peak of NB in the bare GC and GC/(EDAS/g-C\(_3\)N\(_4\)) were observed at \(-0.78\) V and \(-0.74\) V, respectively. The reduction peak current of nitrobenzene for GC/EDAS/[g-C\(_3\)N\(_4\)-Ag(2 mM)]\(_{\text{NC}}\), GC/(EDAS/g-C\(_3\)N\(_4\)), and bare GC were found to be
The above results imply that the GC/EDAS/[g-C₃N₄-Ag(2 mM)] NC possesses enhanced electrocatalytic activity toward reduction of nitrobenzene. The electrocatalytic reduction of nitrobenzene in different electrodes, the plots of cathodic peak current ($I_{pc}$) vs. concentration of nitrobenzene obtained for various electrodes are shown in Fig. 5d. It can be clearly visible that, the GC/EDAS/[g-C₃N₄-Ag(2 mM)] NC-modified electrode showed improved electrocatalytic activity than those of GC/EDAS/[g-C₃N₄-Ag(1 mM)] NC and GC/EDAS/[g-C₃N₄-Ag(3 mM)] NC-modified electrode. Upon increasing the concentration of nitrobenzene, linear increase in the cathodic peak current is observed.

Figure 5 depicts the CVs of GC/EDAS/[g-C₃N₄-Ag(1 mM)] NC, GC/EDAS/[g-C₃N₄-Ag(2 mM)] NC, and GC/EDAS/[g-C₃N₄-Ag(3 mM)] NC-modified electrodes in 0.1 M PBS with various concentrations of NB (0 μM to 600 μM) and (d) corresponding calibration curves.

Fig. 5 Cyclic voltammograms of (a) GC/EDAS/[g-C₃N₄-Ag(1 mM)] NC, (b) GC/EDAS/[g-C₃N₄-Ag(2 mM)] NC, and (c) GC/EDAS/[g-C₃N₄-Ag(3 mM)] NC-modified electrodes in 

22.22 μA, 7.2 μA, and 8 μA, respectively. For comparing the
activity, it was used for further electrochemical experiments.

Figure S3 demonstrates the effect of pH on the electroreduction of 0.5 mM nitrobenzene at GC/EDAS/[g-C3N4-Ag(2 mM)]NC-modified electrode. The peak potential for nitrobenzene reduction is shifted toward negative potentials on increasing the pH of the solution. It is evident that the negative shift of peak potential advocates that the electron transfer and proton transfer occurs simultaneously. An increasing trend is observed in the cathodic peak current up to pH 7.4 and tends to drop beyond that pH (pH > 7.4). As the maximum peak current was attained at pH 7.4, it was fixed for sensor applications. The variation of scan rate on the electrocatalytic reduction of 0.5 mM nitrobenzene at GC/EDAS/[g-C3N4-Ag(2 mM)]NC electrode is displayed in Fig. S4. While increasing the scan rate from 10 to 300 mV s⁻¹, well-defined cathodic peak appears at −0.64 V. The value of current increased with increasing scan rate. Due to the irreversible nature of nitrobenzene reduction, the cathodic peak shifts toward more negative potential with increasing scan rate. A linear plot is obtained between the peak current and square root of the scan rate, which is depicted in Fig. S4 and it suggests that the reduction of nitrobenzene was a diffusion-controlled process.

The mechanism of electroreduction of nitrobenzene may be understood from the scrutiny of CV recorded for the reduction of NB (500 µM) on the GC/EDAS/[g-C3N4-Ag(2 mM)]NC-modified electrode shown in Fig. S5. The peak obtained at −0.65 V is corresponding to the reduction of −NO₂ group to −NHOH group and an anodic peak at +0.05 V is due to the oxidation of −NHOH to −NO group. A new peak observed at −0.11 V in the second cycle may be ascribed to the reduction of −NO to −NHOH (Fig. 6) [15, 17]. The electrocatalytic activity of GC/EDAS/[g-C3N4-Ag(2 mM)]NC was also evaluated in the presence of nitrobenzene derivatives. The well resolved peaks and very good electrochemical responses observed for the electroreduction of nitrobenzene derivatives at the modified electrode indicated that this modified electrode is capable of sensing nitrobenzene derivatives by its electroreducing property. The present GC/EDAS/[g-C3N4-Ag(2 mM)]NC showed peak potential of −0.8 V, −0.67 V, 0.78 V and −0.7 V for the reduction of nitroaniline, nitrobenzoic acid, nitrophenol and nitrotoluene, respectively (Fig. S6). Upon increasing the concentration of analytes, linear increase in peak current is observed, revealing good sensing response of the GC/EDAS/(g-C3N4-Ag)NC electrode.

3.3 SWVs of NB on GC/EDAS/[g-C3N4-Ag(2 mM)]NC

The sensing ability of the GC/EDAS/[g-C3N4-Ag(2 mM)]NC-modified electrode (thin films over flat bottom of 3 mm dia GC electrode) toward the detection of nitrobenzene and its derivatives was investigated by SWV. The square wave
voltammograms (SWVs) were recorded by applying a step potential of 4 mV, amplitude of 25 mV, and a frequency of 15 Hz. The SWV curve obtained for each addition of 5 μM nitrobenzene at the GC/EDAS/[g-C3N4-Ag (2 mM)]NC-modified electrode is shown in Fig. 7A. The cathodic peak for NB reduction appears at -0.58 V. While increasing the concentration of nitrobenzene, linear increase in the current is observed. The modified electrode also exhibits better responses for the addition of 2 μM nitrobenzene which is shown in Fig. 7B.

The SWV signals obtained for the determination of nitrobenzoic acid (NBA), nitroaniline (NA), nitrophenol (NP), and nitrotoluene (NT), employing the GC/EDAS/[g-C3N4-Ag (2 mM)]NC-modified electrode, at each increase of 5 μM nitrobenzene derivatives are shown in Fig. 8. The modified electrode performed well with moderate concentrations of NBA, NA, NP, and NT (Fig. 8). Due to the adsorption
of redox analytes at higher concentration of analytes, a split in square wave voltammograms is observed [40, 41].

Table 1 summarizes the results obtained with various electroanalytical techniques and different metal nanocomposite electrodes including EDAS/(g-C₃N₄-Ag)NC-modified electrode for the determination of NB and its derivatives [8, 24, 42–52]. The abbreviations of the modified electrodes in the table are given as provided in the appropriate references. The prepared EDAS/(g-C₃N₄-Ag)NC showed relatively low LOD and wide sensing range, mainly owing to the synergy of AgNPs and g-C₃N₄ nanosheets.

4 Conclusions

The EDAS/(g-C₃N₄-Ag)NC with different silver concentrations were prepared using a simple reduction method. The UV–Vis absorption edge at 430 nm together with a broad SPR peak at 450 nm confirm that the AgNPs are attached to the g-C₃N₄ nanosheets surface. The characteristic stretching modes of C–N
heterocycles observed in the FTIR spectra affirmed the presence of g-C$_3$N$_4$ nanosheets in the composite. The presence of Ag in EDAS/(g-C$_3$N$_4$-Ag)$_{NC}$ was further confirmed by EDX analysis and cyclic voltammetry. TEM analysis established that the so-formed AgNPs on g-C$_3$N$_4$ nanosheets are in the size range of 10–15 nm. The prepared nanocomposite forms a stable thin film over GC electrode to give highly active modified electrode. The EDAS/(g-C$_3$N$_4$-Ag)$_{NC}$ with 2 mM silver concentration showed very good electroactivity toward the reduction of NB and its derivatives, delivering lowest experimental detection limit of 2 nM for NB. Further improvement in the LOD for NB and its derivatives by incorporating bi-metal nanoparticles like Ag/Cu or Ag/Au into g-C$_3$N$_4$ shall be explored, as it has great potential in electrochemical sensing of trace nitrobenzene.

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Declarations

Conflict of interest The authors have no conflicts of interest to declare.

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