Boron nitride quantum dots (BNQDs) were synthesized hydrothermally using boric acid and urea. High-resolution transmission electron microscopy (HR-TEM) analysis confirmed the formation of BN quantum dots with the lattice size of 0.227 nm. Fourier-transform infrared (FT-IR) and Ultraviolet–visible (UV-Vis) spectroscopies revealed the B-N, O-H and N-H bond formation in the BNQDs and the maximum absorption wavelength at 269 nm. BNQDs exhibited strong fluorescence emission at a wavelength of 330 nm. Furthermore, BNQDs were coated onto a glassy carbon electrode (GCE). Followed by, poly(luminol) (Plu) was electrochemically deposited onto BNQDs/GCE from 0.1 M H2SO4 containing 0.5 mM luminol in order to prepare nanocomposite (hybrid film) coated electrode with improved stability and electrochemical activity. Due to unique nature and synergistic effect between BNQDs and Poly(luminol), as-prepared hybrid Plu/BNQDs film coated GCE showed improved electrocatalytic activity for vitamin C (ascorbic acid, AA) oxidation at 0.2 V. The calibration graph was obtained from 10 to 100 μM AA by amperometry and limit of detection (LOD) was found to be 1.107 μM. The interference effects were also carried out in the presence of uric acid (UA), dopamine (DA) and glucose (Glu). Interestingly, UA, DA and Glu did not produce significant responses on the Plu/BNQDs/GCE which indicated good selectivity of the sensor for AA. Moreover, Plu/BNQDs/GCE based sensor showed reproducible and repeatable analytical performances. We propose that the Plu/BNQDs based hybrid film can be used as a selective sensor probe for the detection of the AA.

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properties of Plu/BNQDs hybrid film were studied which showed high catalytic activity for AA in physiological condition.30,39–47

**Experimental**

**Materials and reagents.**—Boric acid, ammonia solution (25%), urea, sulfuric acid, luminol, AA were purchased from Sigma-Aldrich, India and used without further purification. Vitamin C (Limcee) tablets were purchased from a local drug store in Tamilnadu. Distilled water was obtained from a Millipore ultrapure water system (18.2 MΩ·cm @ 25 ± 2 °C). Solutions and buffers were prepared according to the usual laboratory procedures. Before each electrochemical experiment, solutions were deoxygenated by purging with a pre-purified nitrogen gas.

**Apparatus.**—Electrochemical measurements such as cyclic voltammetry and amperometry were carried out by using the electrochemical workstation (CHI Instrument; Model: CHI-760E, USA). Bare GCE or modified GCE (Plu/BNQDs/GCE) were used as a working electrodes. Ag/AgCl (3 M KCl) and platinum wire were used as a reference and counter electrode, respectively. The absorption spectra of the BNQDs were recorded by using UV-Vis spectrophotometer (Perkin Elmer). Fourier-transform Infrared spectrometer (FT-IR; NICOLET3 80) was used to analyze the functional groups using KBr pellet technique. BNQDs dispersion was directly mixed with KBr to make a pellet for FT-IR spectrum measurements. The morphology and crystal structure of BNQDs were characterized by transmission electron microscope (TEM) (FEI-Tecnai F20 microscope) and HR-TEM (JEM-2100 Plus Electron Microscope, Japan). For HR-TEM analysis, the sample was prepared by coating of “Cu” grid using 10 μL of purified BNQDs dispersion and dried in the room temperature. Zeta potential measurements were done using Nanotrac Wave II; Microtrac Inc, USA. All fluorescence measurements were recorded by using a fluorescence spectrophotometer (Hitachi, Japan) with excitation slit set at 2 nm under ambient conditions. BNQDs dispersion was directly used to measure fluorescence without further dilutions.

**Synthesis of BNQDs.**—BNQDs were synthesized by a single step hydrothermal method. In a typical procedure, the boric acid (0.5 g) was dissolved in ethanol (10 mL) and deionized water (5 mL). After that urea (0.97 g) was dissolved in 10% of liquid ammonia (10 mL) and added to the boric acid/ethanol mixture. This mixture was heated hydrothermally in a Teflon-equipped stainless-steel autoclave at 200 °C for 12 h. After that, the mixture solution was cooled to room temperature (25 °C ± 2). Finally, BNQDs dispersion was vacuum filtered using a filter paper with a pore sizes of 0.22 μm and centrifuged at 6500 rpm for 30 mins. After centrifugation, top supernatant liquid (~70%) was collected and stored for further characterization and electrochemical measurements (Scheme 2).

**Preparation of Plu/BNQDs sensor.**—Glassy carbon electrode (GCE) was polished on a polishing cloth using alumina powder (Al₂O₃, particle size ~0.05 μm) in order to get a mirror like surface and bath sonicated for 5 min in distilled water. To get a hydrophilic surface, GCE was electrochemically activated in 0.1 M H₂SO₄ solution by potential cycling between −0.5 and 1.0 V for 10 cycles at a scan rate of 0.05 V s⁻¹. Afterwards, 10 μL BNQDs dispersion was coated on the pretreated GCE and dried for 3 h in the absence of light. The BNQDs/GCE was rinsed using deionized water. Then, polymerized luminol film was coated onto BNQDs/GCE by electrochemical polymerization method. For this, BNQDs/GCE was potential swept (between −0.5 and 1.0 V for 10 cycles at a scan rate 0.05 V s⁻¹) in 0.1 M H₂SO₄ solution containing 0.5 mM luminol (lu). As obtained, Plu/BNQDs/GCE was thoroughly rinsed with double-distilled water and then dried at room temperature for an hour in the absence of light. It was noted as Plu/BNQDs/GCE and then used for further studies. For comparison measurements, BNQDs/GCE and Plu/GCE were prepared similarly and used for further investigations. (Scheme 3).

**Results and Discussion**

**FT-IR, HR-TEM, UV-Vis and PL studies.**—The FT-IR could confirm the nature of functional groups and chemical bonds present on the sample. The FT-IR spectrum of as-synthesized BNQDs showed absorption bands at 1329,1450,1638 cm⁻¹ due to the B-N stretching
then started to decrease with excitation wavelengths. The emission intensities of BNQDs were first increased and fluorescence under the illumination of 365 nm UV light. The PLE data showed blue tails about optical properties of the BNQDs. From UV-vis spectrum, the maximum absorption wavelength of BNQDs was found to be 269 nm as shown in Fig. 3a. The inset of Fig. 3a showed blue fluorescence under the illumination of 365 nm UV light. The PLE data of BNQDs under different excitation wavelengths were also recorded (Fig. 3b). The emission intensities of BNQDs were first increased and then started to decrease with excitation wavelengths. The maximum fluorescence emission was recorded at 330 nm excitation wavelength. It was suggested that edges and point defects of BNQDs (BO2−, zigzag carbene edges and 1,3-B centers) were responsible for the observed luminescence effects. In addition, the surface charge of the BNQDs was investigated by measuring the respective ζ potential, which was found to be −19.3 mV. This indicated that charged functional groups present on the surface of the BNQDs which formed a stable dispersion.

Preparation of Plu/BNQDs/GCE.—Fig. 4 shows the electropolymerization of luminol on BNQDs/GCE. The first anodic oxidation peak was observed for oxidation of the primary amino group of luminol monomer at +0.84 V (Pa1). In the reverse scan, a cathodic peak observed at +0.44 V (Pc1). With further successive potential scans, a new anodic peak was observed at +0.55 V (Pa2). This reversible redox peak (Pa2/Pc1) begins to grow on the subsequent cycles which was due to the growth of poly(lu) film on the BNQDs/GCE. Polymer film growth was faster for the first eighteen cycles. After the 20th cycle, polymer film growth got stopped which showed the saturation. For further studies, we deposited Plu film by controlling electro-polymerization up to 20 cycles. However, Plu deposition was carried out up to 50th cycle, but the redox peak current of Plu did not change significantly, so we used only 20 cycles (for polymerization) in order to control the Plu film thickness on BNQDs/GCE. The anodic and cathodic peak potentials of Poly(lu) (Plu) were in good agreement with the reported redox potential for Plu. The chemical composition, and redox mechanism of Plu might be similar to polyaniline as reported elsewhere.

Electrochemical impedance spectroscopy (EIS) studies.—Fig. 5 shows EIS plots of the various modified electrodes. EIS could give information about the solid-liquid interface system of the modified electrodes. In the impedance spectrum, the semicircle portion represents the electron transfer limited process at the higher frequency and the linear plot represent the diffusion process at the lower frequency. The semicircle diameter at the higher frequency represents the charge transfer resistance (Rct) of the electrode. Fig. 5 shows Nyquist plots obtained for Plu/BNQDs/GCE (curve a), Plu/GCE (curve b), BNQDs/GCE (curve c) and bare GCE (curve d) in 5 mM [Fe(CN)6]3−/4−/4−/4− + 0.1 M KCl solution. A small semicircle plot and tail may indicate the diffusion controlled process. The Nyquist impedance spectra of Plu/GCE (196.3 Ω) (curve b), bare GCE (275.1 Ω) (curve d) and the modified BNQDs/GCE (671.5Ω) (curve c) were compared with each other and found that there was increase in Rct values after deposition of BNQDs compared to bare GCE (curve d). This may be due to point defects of BNQDs (dielectric interface) structure which could result in a wide bandgap with insulating behavior. However, after Plu deposition on the BNQDs/GCE surface, linear plot at the higher frequency indicated a faster redox reaction due to the presence of conducting Plu film. For Plu/BNQDs/GCE, Rct was decreased to 103.6 Ω, this may be due to the high conductive nature of the hybrid Plu/BNQDs film as an effective proton transfer medium.

Electrocatalytic oxidation of AA.—Fig. 6 represents the CVs of Plu/BNQDs/GCE (curve a), Plu/GCE (curve b), BNQDs/GCE (curve c) and bare GCE (curve d) in 0.1 M PBS (pH 7.4) with 1 mM AA. In contrast to other coated electrodes, Plu/BNQDs/GCE showed higher oxidation current (~2.5 times higher than BNQDs/GCE) for 1 mM AA at reduced overpotential of 0.2 V which confirmed that the hybrid film

![Figure 1. FT-IR spectrum of synthesized BNQDs.](image-url)
Figure 2. (a and b) HR-TEM images of synthesized BNQDs and (c) particle size distribution histograms of BNQDs.

Figure 3. (a) UV-Vis spectrum of BNQDs (Inset: visual images of BNQDs under normal and UV light). b) Fluorescence emission spectra of BNQDs at different excitation wavelengths from 300 to 400 nm.
Scheme 4. Redox reaction of Poly-luminol (Plu).

Figure 4. CVs of the Plu film growth on BNQDs/GCE from the 0.1 M H2SO4 containing 0.5 mM luminol monomers. Scan rate = 0.05 V/s.

Figure 5. EIS data for Plu/BNQDs/GCE (curve a), Plu/GCE (curve b), BNQDs/GCE (curve c) and bare GCE (curve d) in 5 mM [Fe(CN)6]3−/4− + 0.1 M KCl solutions by applying an AC voltage with 5 mV amplitude in a frequency range from 100 MHz to 100 kHz.

Figure 6. CVs of Plu/BNQDs/GCE (curve a), Plu/GCE (curve b), BNQDs/GCE (curve c) and bare GCE (curve d) in (pH 7.4) 0.1 M PBS containing 1 mM AA and (curve e) represents the CV of Plu/BNQDs/GCE in the absence of AA (Scan rate = 10 mV/s).

has electrocatalytic properties (curve a). AA oxidation was appeared at 0.25 V with lower current on bare GCE and BNQDs/GCE (curves d and c). In addition, if we observe closely, AA oxidation current was higher for BNQDs/GCE than bare GCE (curves c and d). This proved that as-synthesized BNQDs has electrocatalytic activity. This improved electrocatalytic activity was due to that AA diffuses to the Plu/BNQDs/GCE surface effectively and in turn, it produced higher oxidation current for AA compared to bare and BNQDs/GCE. It was suggested that due to synergistic effect between Plu and BNQDs, this new hybrid film showed higher catalytic current for AA oxidation (curve a). AA electro-oxidation reaction at the Plu/BNQDs/GCE could be explained as given in the Equation 2 (Scheme 5).

Effect of scan rate on AA oxidation.—The effect of scan rates on the oxidation peak current (Ipa) of AA at Plu/BNQDs/GCE was studied in 0.1 M PBS from 10 to 100 mV/s as shown in Fig. 7a. The Ipa of AA was increased with square roots of scan rate (ν1/2). According to Ipa ∝ ν1/2 curve, the oxidation peak current increased linearly (r² = 0.99) with the scan rates. This indicated a diffusion controlled electron transfer process of AA oxidation on Plu/BNQDs/GCE (Fig. 7b).
Amperometric detection of AA.—Fig. 8a shows the amperometric response of Plu/BNQDs/GCE for oxidation of AA (different concentrations) at an applied potential of 0.1 V. In this experiment, 10 mL of 0.1 M PBS was used as an electrolyte (pH 7.4). After each addition of AA, Plu/BNQDs/GCE responded linearly in current steps. A calibration plot was made against concentration of AA vs. oxidation current which revealed that there was a linear relationship from 10 to 100 μM with a correlation coefficient (R²) of 0.985 (Fig. 8b). The response time was 1.8 s, (Fig. 8a). The limit of detection (LOD) for AA was estimated as 1.107 μM using the following equation:

\[
LOD = \frac{3SD}{S}
\]

The slope of the calibration graph was (S) \(5.846 \times 10^{-11}\) A μM⁻¹ and the standard deviation (SD) of blank was \(2.15 \times 10^{-11}\) A. The calculated LOD (1.107 μM) was lowest compared to other reported methods (Table I). The improved electrocatalytic activity of the hybrid film (Plu/BNQDs) may be due to the fast electron transfer between the analyte and the electrode surface.

Interference and repeatability studies.—Since, dopamine (DA), uric acid (UA) and glucose (Glu) have similar oxidation potentials compared to AA. They may interfere on the oxidation of AA in physiological pH. The addition of these biomolecules such as 5 μM DA, 5 μM UA and 5 μM Glu were investigated in 0.1 M PBS using Plu/BNQDs/GCE as a sensor at an applied potential of 0.1 V in amperometry. These interfering molecules did not produce any observable current at this condition. This indicated that the Plu/BNQDs/GCE have good selectivity for AA (Fig. 9a). There is no significant current change observed in CV studies as shown in Fig. 9b which also proves that, there is no interference of DA, UA and Glu. This selectivity toward AA may come from the specific interaction between Plu/BNQDs hybrid film and AA in neutral media. As reported, luminol exist as fully protonated (reduced) form in neutral medium, so it gets attracted to negatively charged AA molecules.

Moreover, the repeatability was also tested by recording CVs in the presence of 100 μM AA in PBS using Plu/BNQDs/GCE. CV responses were repeated in fresh PBS with 100 μM AA using same Plu/BNQDs/GCE at 60 min time intervals. The relative standard deviation (RSD) of the current measurements was 2.2%. This proved
Table I. Comparison of analytical performance of Plu/BNQDs/GCE sensor with other reported AA sensors.

| Electrochemical detection methods | Transducer | Linear response | LOD | References |
|----------------------------------|------------|-----------------|-----|------------|
| Potentiometry                    | Two ion sensitive field effect transistors (ISFET) | 0.25–2.0 mM | –   | 71         |
| Potentiometry                    | MnO₂ modified nanoparticles ion sensitive field effect transistor (ISFET) | 0.02–1.27 mM | 0.01 mM | 72         |
| Cyclic Voltammetry               | Platinum electrode | 0.31–20 mM | 0.075 mM | 73         |
| Cyclic Voltammetry               | Carbon paste electrode | 0.07–20 mM | 0.062 mM | 73         |
| Cyclic Voltammetry and Differential Pulse Voltammetry | Gold nanoparticles/overoxidized polyimidazole composite modified GCE | 210–1010 μM | 2.0 μM | 74         |
| Differential Pulse Voltammetry   | Gold nanoparticles modified GCE | 0.3–1.4 mM | 90 μM | 75         |
| Amperometry                      | Clark oxygen electrode | 0.10–0.55 mM | 0.023 mM | 76         |
| Amperometry and cyclic voltammetry | Modified GCE with Palladium Nanoparticles supported on GO | 0.02–2.28 mM | – | 77         |
| Amperometry                      | Plu/BNQDs/GCE | 10–100 μM | 1.107 μM | This work |

Figure 9. a) Typical amperograms obtained with a Plu/BNQDs/GCE in 0.1 M PBS (pH 7.4) at an applied potential of 0.1 V, stirring rate = 1000 rpm. Successive additions of 10 μM AA (first two additions), 5 μM UA, 5 μM DA, 5 μM Glu and 10 μM AA (last three additions), b) CV responses of Plu/BNQDs/GCE to the addition of AA (100 μM) and different interfering species: DA (50 μM), UA (50 μM), and Glu (50 μM) in 0.1 M PBS (pH 7.4). Scan rate: 10 mV/s.

that Plu/BNQDs/GCE had high stability which retained 97.8% electrode response after storage of 6 h in the absence of light at room temperature.

Real sample analysis.—The real application of Plu/BNQDs/GCE was tested with 10 mg of vitamin C tablet using amperometric technique by standard addition method. The vitamin C tablet was finely powdered, from that 10 mg of the substance was dissolved in 10 mL of 0.1 M PBS solution.30,70 The diluted tablet samples were analyzed by using Plu/BNQDs/GCE with various spiked concentration of AA. In this analysis, amperograms were recorded in 0.1 M PBS with the addition of different concentrations of AA tablet samples after series of dilutions with and without spiked AA which indicated that other components/additives present in tablets did not affect the electrode response. The analyzed AA samples and their recovery values were calculated using vitamin C tablet samples on Plu/BNQDs/GCE (see Table II). The estimated AA concentrations were in the range of acceptable levels. The AA recovery varied from 98.8 to 102% in Vitamin C tablet samples (Table II).

Conclusions
In summary, we have synthesized BNQDs via a simple hydrothermal treatment method using boric acid and urea. As-synthesized BNQDs have been characterized using FT-IR, fluorescence emission spectra, HR-TEM, UV-Vis, and Zeta potential measurements. These studies confirmed the formation of BNQDs. The BNQDs showed a strong blue fluorescence under UV light. In addition, the electrochemical properties of Plu/BNQD were tested after coating on the GCE. Plu/BNQDs/GCE exhibited improved electro-catalytic performance.

Table II. The detection of AA in vitamin C tablet samples using Plu/BNQDs/GCE as a sensor.

| S.No. | Samples Content (μM) | AA added (μM) | Total AA found (μM) | RSD (%) | Recoveries % |
|-------|----------------------|--------------|---------------------|---------|--------------|
| Sample 1 | AA tablet solution | 10 | - | 9.88 | 1.24 | 98.8 |
| Sample 2 | AA tablet solution with spiked AA | 10 | 50 | 61.17 | 1.22 | 101.95 |
| Sample 3 | AA tablet solution with spiked AA | 10 | 60 | 69.9 | 1.31 | 99.8 |

*aMean value of three replicates.
toward AA, with linear range of detection from 10 to 100 μM. The LOD was estimated to be 1.107 μM. This Ptu/BNQDs/GCE exhibited rapid response (1.8 sec) time for AA, and highly selective in the presence of DA, UA and Glu. Real sample analysis was also performed to detect AA in vitamin C tablet samples with good recovery. We believe that this new hybrid sensor based on BNQDs and Ptlu could be a valuable tool for the detection of AA in biological and food samples.

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