ABSTRACT: Silver nanoparticles (AgNPs) were synthesized separately and loaded onto the expanded layers of exfoliated graphite (EG) to form a silver nanoparticle-exfoliated graphite nanocomposite (AgNPs-EG). The AgNPs-EG was compressed into a pellet (0.6 cm in diameter) and used to prepare an electrochemical sensor for bisphenol A (BPA) in standard samples and in thermal paper. The synthesized materials were characterized by ultraviolet–visible spectrophotometry, X-ray diffraction spectroscopy, scanning electron microscopy, and energy-dispersive X-ray. The electrochemical behavior of BPA on the AgNPs-EG sensor was investigated by cyclic voltammetry and square wave voltammetry. Under optimized experimental conditions, the oxidation peak current was linearly proportional to bisphenol A concentrations in the range from 5.0 to 100 μM, with a coefficient of determination ($R^2$) of 0.9981. The obtained limit of detection of the method was 0.23 μM. The fabricated sensor was able to overcome electrode fouling with good reproducibility (RSD = 2.62%, $n = 5$) by mechanical polishing of the electrode on emery paper. The proposed method was successfully applied to determine bisphenol A in thermal paper samples and demonstrated good accuracy of 93.1 to 113% recovery.

INTRODUCTION

Bisphenol A (BPA) is one of the highest volume chemicals produced globally due to its extensive industrial use, such as in the manufacturing of polycarbonates, epoxy resins, and thermal papers. In the latter applications, the compound is used as a color developer, together with a thermochromatic dye and an organic solvent, to create a print on faxes, ATM receipts, bus tickets, receipts, and labels stuck on retail products. Scientific evidence shows that BPA is an estrogenic hormone and an endocrine disruptor, which can easily transfer from the thermal paper (either occupationally or via everyday handling) to fingers and penetrates to a point where it reaches the bloodstream, thereby inducing endocrine disruption. Even at trace levels, human exposure to BPA leads to adverse health issues such as infertility, diabetes, brain damage, and various kinds of cancer. Despite these facts, recent studies have shown that BPA is still used in thermal paper printing all over the world. This risky exposure and the toxicity of BPA in general, necessitate BPA detection and monitoring.

Until recently, BPA detection was achieved through chromatographic methods such as high-performance liquid chromatography (HPLC), liquid chromatography-mass spectrometry (LC–MS), and gas chromatography coupled with mass spectrometry (GC–MS). These methods are associated with a number of drawbacks that limit their applications. For example, they require skilled operators, large sample volumes, and are time consuming and expensive to maintain. On the other hand, electrochemical methods have extensively been reported in the literature and have proven to offer various advantages toward BPA detection due to their high sensitivity, selectivity, low cost, and rapid response. This is because BPA detection...
presents two hydroxyls moieties in its molecular structure, which can be oxidized at the electrode’s surface, rendering the possibility for its electrochemical detection.9

The oxidation of BPA, however, is an irreversible process that produces polymeric films, which foul electrode surfaces, and thus, resulting in diminished oxidative peak currents. It has been proposed that these polymeric films are due to electrochemical polymerization, and this phenomenon is considered as the main problem in the electrochemical detection of all phenolic compounds in general.7,10,11 Hence, the development of electrochemical sensors with better properties such as low costs, minimal, or no fouling effects is still a challenge. To avoid or minimize this issue, several approaches that include the use of catalytic, anti-fouling nanomaterials have been reported. For instance, Wannapob et al. proposed a porous gold-based electrochemical sensor for BPA detection and their electrode provided enhanced surface area and exhibited good electrolytic activity toward the oxidation of BPA. This work exhibited a detection limit as low as 2.0 nM.12 Furthermore, a more comprehensive study by Ragavan et al., reported a vast range of nanomaterials including quantum dots, graphene, carbon nanotubes, and molecularly imprinted polymer-based electrochemical sensors for BPA.13 Unfortunately, the issue of electrode fouling still remains a concern that needs to be mitigated.

When compared with other noble metals, silver has received special attention due to its high electrical conductivity, good catalytic activity, low toxicity, simple synthesis, and low

Figure 1. SEM images of (a) EG and (b) AgNPs-EG, (c) EDX of AgNPs-EG, and XRD patterns of (d) EG and (e) AgNPs-EG (Inset shows amplified Ag peaks suppressed by high intensity EG peaks).
These properties have led to a vast number of studies reporting on the electrodetection of BPA using silver nanoparticle (AgNPs) composites. For example, Campos et al. modified a glassy carbon electrode with a nanocomposite of SiO₂/GO/AgNPs to develop an electrochemical sensor for BPA. The presence of AgNPs led to enhanced BPA oxidation currents and significantly lowered the detection limit of the sensor. Baccarin et al. decorated a graphite-polyurethane composite electrode with silver nanoparticles to fabricate a pen-based electrochemical sensor for BPA detection. Improved electrokinetics of the sensor was obtained under optimized AgNPs contents, and the sensor exhibited a BPA detection limit of 0.24 µM. Other materials composited with silver nanoparticles for enhanced electrochemical detection such as carbon black-silver nanoparticles and Printex nanocarbon-silver nanoparticles have also been reported.

The above works motivates this paper, where silver nanoparticles were composited with exfoliated graphite (EG) for the fabrication of an electrochemical sensor for BPA detection. EG, possessing properties such as high electrical conductivity and electron transport, mechanical strength, and high surface area, has made a niche for itself as a suitable candidate for various applications, particularly as a substrate in electrochemistry. With compressibility and mechanical strength, EG can be easily compacted into a working electrode that allows surface regeneration by polishing on emery paper, as a way of tackling fouling. Based on these inherent properties of both EG and AgNPs, as well as the motivation from the above works, we report the use of an AgNPs-EG nanocomposite-based electrode for the development of an electrochemical sensor for BPA detection in thermal paper samples.
RESULTS AND DISCUSSION

Characterization of the AgNPs-EG Nanocomposite. The successful synthesis of AgNPs was confirmed by a characteristic strong absorbance peak at around 393 nm (Figure S1b),28,30 and an average particle size (prior to intercalation into the EG) of 20 nm was estimated from zetasizer. The field emission scanning electron images of EG and AgNPs-EG nanocomposite are shown in Figure 1a,b, respectively. From Figure 1a, an accordion-like structure and the expanded layers of graphite with open cavities suitable for the entrapment of particles, can be seen. The presence of AgNPs on EG after modification was evidenced as evenly distributed high-contrast nanoparticles on the surface of the layers of graphite on EG (Figure 1b). However, some agglomerations were observed on the AgNPs-EG nanocomposite at a higher SEM magnification (Figure S1a). To further confirm the loading of AgNPs and formation of the nanocomposite, EDX analysis was conducted (Figure 1d). The presence of the Ag peak confirmed the presence of AgNPs on the surface of EG.

The XRD pattern of the pristine exfoliated graphite (Figure 1d) shows two prominent diffraction peaks at 2θ = 26.33 and 54.52°, corresponding to the (002) and (004) planes, respectively. These XRD peaks are attributed to the characteristic diffraction peaks of graphite and crystal phase, which are in agreement with previous reports.24,31 For the AgNPs-EG nanocomposite (Figure 1e and inset), well-defined peaks were observed at 2θ = 37.74, 44.27, 64.10, 77.25, and 86.83°, corresponding to (111), (200), (220), (311), and (222) planes of the face centered cubic (fcc) structure of metallic silver, respectively (JCPDS 04-0783)11,32–34 while still retaining the characteristic peaks of EG.

Electrochemical Characterization the Prepared Electrodes. Cyclic voltammetry (CV) and square wave voltammetry (SWV) were used to compare and investigate the electrochemical behaviors of bare EG and AgNPs-EG electrodes in [Fe(CN)₆]⁢⁻⁴³⁻ as a redox probe and in phosphate buffer solution (PBS). SWV was chosen because it is a more sensitive and faster technique than differential pulse voltammetry. It is especially sensitive to surface-confined reactions. Thus, it is often preferred for organic detection owing to its ability to limit/omit adsorption effect (such as BPA electro-oxidation).35 The pristine EG electrode (Figure 2a) displayed a peak potential separation (ΔEₚ) of about 290 mV, which reduced to about 180 mV after loading with AgNPs. This indicates that the kinetics of the electron transfer of the redox probe is faster at the modified EG electrode as a result of the AgNPs. The SWV responses of the two electrodes in BPA solution are presented in Figure 2b. A 44.54% current enhancement and shift toward lower peak potential on the AgNPs-EG electrode compared to that of the EG electrode can be observed. The marked increase in the electro-oxidation peak of BPA shows the electrocatalytic nature, large surface area, and excellent conductivity conferred on EG by the AgNPs. The reduction of anodic potential denotes an increase in the electron transfer rate constant from BPA.36 Furthermore, the reduction in the peak potential of BPA at the AgNPs-EG electrode suggests that a lower energy is needed to oxidize BPA; this is a further evidence of the electrocatalytic nature of AgNPs. A reduced peak potential can also help in eliminating some interference from other electroactive species. The presence of AgNPs in the AgNPs-EG electrode was further proven electrochemically by CV using PBS as the electrolyte (Figure 2c). The Ag⁺/Ag redox behavior of the AgNPs-EG electrode was observed at potentials 380 and 620 mV for the oxidation of AgNPs and at ~80 mV for the reduction of Ag cations. These redox peaks were not observed on the pristine EG electrode. These results corroborated those in Figure 1, in the sense that AgNPs were successfully grafted on the EG substrate. Figure 2d shows successive scans at the AgNPs-EG electrode surface to study electrode surface fouling. The obtained results showed that the intensity of oxidation peaks of BPA declines cycle after cycle. These results clearly show that even though the modified electrode responded better than pristine EG toward BPA (as shown in Figure 2b), the electrode is still susceptible to fouling. This observation can be explained as a result of an electrode fouling phenomenon, in the sense that oxidative and polymeric products of BPA-oxidation are deposited on the electrode surface, which blocks further access of BPA to the electrode.37 The oxidation current signal declined by 74% on the second scan and further declined by 81% on the third scan. Moreover, an 83% current decline was recorded on the seventh scan (relative to the first scan), thus indicating a continuous and progressive deactivation of the electrode. As a way of tackling this problem, we propose mechanical polishing of the electrode surface between scans to counteract fouling. The fouled electrode was polished on P1200-grit emery paper, and the results showed successful regeneration of the electrode since similar BPA oxidation peak currents were obtained after every polishing, as shown in Figure 2e. This electrode regeneration method was reproducible, with electrochemical responses having a relative standard deviation (RSD) of 2.62%. The minor peaks observed (in Figure 2b,d,e) at potentials between 0.20 and 0.25 V are possibly attributed to byproducts of the electro-oxidation of BPA.38

Effects of Electrolyte pH on BPA Electro-Oxidation. SWV was used to study the effects of electrolyte pH on the peak current and peak potential in 10 mM PBS, pH 7.0 to 12, containing 5 mM BPA. As shown in Figure 3, an increase in
9.0 was selected as the optimum pH value for all subsequent electrochemical experiments. Furthermore, under this study, the anodic peak potential ($E_{pa}$) shifted negatively with an increase in pH, conforming to the equation: $E_{pa} (V) = -0.05569 \text{pH} + 1.10112$ ($R^2 = 0.9925$). The obtained slope of 0.05569 V/pH is approximately close to the theoretical value of 0.0576 V/pH and indicates that the electron transfer was accompanied by an equal number of protons on the AgNPs-EG electrode. Therefore, it can be inferred that the electrochemical oxidation of BPA at the AgNPs-EG electrode is a two-electron and two-proton process and this is illustrated in Scheme 1.

Scheme 1. Possible Reaction Mechanism for BPA Oxidation on the AgNPs-EG Electrode

![Scheme 1](image)

**Analytical Performance of the AgNPs-EG Sensor toward BPA Detection.** Under the optimal experimental conditions, the prepared AgNPs-EG sensor was employed to detect a series of BPA solutions with different concentrations by SWV and responses are presented in Figure 4a. The peak currents increased linearly with an increase in BPA concentrations in the range from 5.0 to 100 $\mu$M with a linear regression equation as $I (\mu A) = 0.95988 \text{ [BPA]} (\mu\text{M}) + 11.8201$ ($R^2 = 0.9981$) (Figure 4b). The detection limit of the method was calculated according to the equation, $\text{LOD} = 3 \times SD/b$, where $SD$ is the standard deviation of three blank measurements and $b$ is the slope of the calibration plot. From Figure 4b, a detection limit of 0.23 $\mu$M was calculated for this work. For the control study, SWV measurements of the EG electrode were also conducted within the same linear concentration range, under the same optimized electrolyte pH. The calibration plot of the EG electrode shows a lower sensitivity (as interpreted by a lower slope, and was not as linear in the concentration range analyzed (as interpreted from a lower correlation coefficient value of 0.8272)) due to its ineffectiveness in the electro-oxidation of BPA. Table 1 compares the performance of the AgNPs-EG sensor with those reported previously. It can thus be inferred that the AgNPs-EG-based sensor exhibits either comparable or even better response toward BPA detection.

**Interference and Stability Studies of the AgNPs Electrode.** The influence of interferences on the detection of BPA was studied in a 10 mM PBS (pH 9.0) electrolyte solution containing BPA in the presence of possible interfering species like 4-nitrophenol, 3-chlorophenol, phenol, and 4-phenylphenol. Figure 5a shows that no marked interference was caused by the presence of these interfering molecules. Intensity current changes of only 9.89, 16, 0, and 0.55% were observed when 3-chlorophenol, 4-nitrophenol, 4-phenylphenol, and phenol were present, respectively. This is an indication that the AgNPs-EG sensor exhibits relatively reasonable ability to detect BPA without the interference of the chosen species. Furthermore, the stability of the electrode was conducted for a period of 2 weeks. After detection of 30 $\mu$M BPA in 10 mM PBS (pH 9.0), the electrode was polished, rinsed with deionized water, and stored for 14 days. The oxidation of the same BPA concentration after this storage period retained more than 85% of the initial current response, as shown in Figure 5b. Hence, the AgNPs-EG sensor exhibits good stability for BPA detection.

**Analysis of Real Thermal Paper Samples.** To evaluate the performance of the AgNPs-EG electrode in practical analytical applications, the determination of BPA in thermal paper samples was carried out through a recovery study and the results are shown in Table 2. The recovery of BPA was from 93.1 to 113%, indicating that the proposed electrochemical sensor is reliable, effective, and accurate for practical applications.

### Table 1. Comparison of Different Electrochemical Sensors for BPA Detection

| electrode configuration | linearity range ($\mu$M) | detection limit ($\mu$M) | references |
|-------------------------|--------------------------|--------------------------|------------|
| (3D-GN)/CuFe$_2$O$_4$   | 7.2–18                   | 1.70                     | 41         |
| PEDOT-GCE               | 40–410                   | 22.0                     | 42         |
| AuNP@MOF               | 200–1000                 | 37.80                    | 43         |
| CNHs-Nafion/GCE        | 2.0–1000                 | 1.80                     | 44         |
| SWCNT/GCE              | 10–100                   | 7.30                     | 45         |
| Gr-AuCuNP/AuE          | 0.1–30                   | 1.31                     | 46         |
| Gr-AuCuNP/AuE          | 0.1–100                  | 1.91                     | 46         |
| MWCNTs/GCE             | 2.0–30                   | 0.5                      | 47         |
| AgNPs-EG               | 5.0–100                  | 0.23                     | this work |

![Figure 4](image)

Figure 4. (a) SWVs of the AgNPs-EG sensor in 10 mM PBS, pH 9.0 containing different concentrations of BPA (5.0, 20, 30, 50, 80, and 100) and (b) calibration plot of response currents of AgNPs-EG (solid line) and EG (broken line) electrodes as a function of BPA concentrations.

![Figure 5](image)

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We have developed a simple anti-fouling electrochemical sensor for the quantitative detection of BPA using a silver nanoparticle-modified exfoliated graphite electrode. The anti-fouling property of the sensor is by a simple step of mechanical polishing of the electrode for surface renewal. Relative to the pristine EG electrode, the silver nanoparticles incorporated the electrode allowed for the oxidation of BPA in less basic conditions and further improved/lowered the detection limit of the sensor. The proposed sensor was further applied in the detection of BPA in thermal paper real samples and exhibited good recoveries. Furthermore, the sensor exhibited insignificant interferences from potential BPA co-existing molecules and also showed good stability. Therefore, this easy to fabricate electrochemical sensor offers a potential application for BPA environmental monitoring while mitigating the problem of electrode fouling by BPA.

### EXPERIMENTAL SECTION

#### Chemicals and Reagents.
Bisphenol A (≥99%), natural graphite flakes, sulfuric acid (99.98%), trisodium citrate (AR), 4-nitrophenol (98%), phenol (99%), 4-phenylphenol (97%), 3-chlorophenol (98%), and potassium chloride (≥99%) were all obtained from Sigma-Aldrich (South Africa) and were used as received. Nitric acid (≥55%) was obtained from Honeywell Fluka (South Africa). Silver nitrate (99%) was obtained from ACE Chemicals (South Africa). Sodium borohydride (AR) was purchased from Sisco Research Laboratories Pvt. Ltd. (India). Phosphate buffer solutions (PBS, 10 mM) of different pH values were prepared with 10 mM sodium dihydrogen phosphate (AR, Sigma-Aldrich) and 10 mM disodium hydrogen phosphate (AR, Sigma-Aldrich), and their pH values were adjusted using sodium hydroxide (AR, Sigma-Aldrich) and hydrochloric acid (32%, Sigma-Aldrich). All the solutions were prepared using ultrapure water (18.2 MΩ·cm at 22 °C).

#### Instrumentation and Apparatus.
Scanning electron microscopy (SEM) analysis and elemental composition analysis were conducted by a Zeiss Gemini 2 Crossbeam 540 FEG SEM with an EDX detector (United Kingdom). A Malvern Zetasizer (South Africa) was used for the particle size distribution of AgNPs. The ultraviolet—visible (UV—Vis) spectra were recorded with an Agilent UV—Vis spectrophotometer (Malaysia). X-ray diffraction patterns were examined under an X-ray diffractometer (XRD, Rigaku Ultima IV, Japan). Electrochemical measurements were conducted using an Ivium compactstat potentiostat (Netherlands) system connected to a three-electrode system. The electrode system comprised of an AgNPs-EG (and EG) compressed pellet on copper wire as a working electrode, a platinum wire as a counter electrode, and Ag/AgCl (in 3 KCl) as a reference electrode. All solutions were sparged with argon gas before electrochemical measurements.

#### Synthesis of Silver Nanoparticles.
AgNPs were synthesized through the reduction of Ag ions from silver salts using sodium borohydride and trisodium citrate. Sodium borohydride and sodium citrate acted as primary and secondary reducing agents, respectively, and also as stabilizing agents. This was conducted at two different temperatures, 60 and 90 °C. The required amounts of freshly prepared aqueous solutions of sodium borohydride and trisodium citrate were mixed and heated to 60 °C for 30 min under magnetic stirring to produce a homogeneous solution. After this, the required amount of AgNO₃ was added to the reduction solution and the mixture immediately turned light yellow, confirming the formation of AgNPs. Thereafter, the temperature was increased to 90 °C and kept for 30 min under continuous stirring. The typical input amounts of each precursors were 5 mM sodium borohydride, 2 mM trisodium citrate, and 1.22 mM silver nitrate on a base of 500 mL of deionized water.

#### Preparation of EG and AgNPs-EG Electrodes.
The preparation of EG followed a two-step procedure: intercalation and exfoliation. The intercalation was achieved by soaking natural graphite flakes in a mixture of concentrated HNO₃ and H₂SO₄ (in a volume ratio of 1:3) for 72 h at room temperature. The intercalated material was washed with deionized water until a pH of 7 was attained and air dried. Exfoliation was then carried out by subjecting the dried material to a preheated furnace at 800 °C for 1 min.

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**Table 2. Detection of BPA in Thermal Papers using the AgNPs-EG Electrochemical Sensor**

| sample | added (μM) (%) | found (μM) | recovery |
|--------|---------------|------------|----------|
| sample 1 | 10 | 11.35 ± 0.45 | 113 |
| sample 2 | 10 | 17.66 ± 1.17 | 93.1 |

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**Figure 5.** (a) Effect of the presence of 50 μM 3-chlorophenol, 4-nitrophenol, phenol, and 4-phenylphenol on the signal responses obtained for 50 μM BPA in 10 mM PBS, pH 9.0, (b) stability study of AgNPs-EG electrode for a period of 2 weeks.
The preparation of a composite of EG and silver nanoparticles (AgNPs-EG) was based on the following procedure: the prepared exfoliated graphite was poured in the as-prepared silver colloidal solution and the mixture was subsequently transferred into a 100 mL Teflon-lined autoclave. The autoclave was sealed and heated in an oven at 110 °C overnight. After the reaction duration, the autoclave was allowed to cool to room temperature and the resulting product was collected by filtration and air dried.

About 500 mg of the AgNPs-EG nanocomposite was weighed and compacted without any binder into a pellet using a hydraulic press at a high pressure for 12 h. The pellet was employed in the construction of an electrode by using a copper wire, the conductive silver paint, and a glass tube. The copper wire was coiled at one end to form a flat surface, which was scrubbed on a P120-grit sandpaper to remove any oxides on the surface. The AgNPs-EG pellet was then placed on the coiled flat surfaced copper wire with the assistance of silver paint and allowed to dry overnight. The electrode was then inserted into a glass tube and the edges of the pellet were subsequently covered with Teflon tape so that the current is contributed by only the basal plane of the electrode. The same procedure was followed for the fabrication of the EG electrodes. The diameter of the EG electrode was 0.6 cm. Fouled electrodes were cleaned by polishing on P1200-grit emery paper after every scan, to have renewed and activated surfaces, as a way of tackling electrode fouling.

**BPA Extraction and Sample Preparation.** The determination of BPA in thermal printing paper is a two-step procedure. First, the compound is extracted from paper samples with polar organic solvents like methanol or acetone, etc., and second, detection is employed. For this work, two types of thermal papers (travel tickets and retail store receipts) were collected. The samples were referred to as sample 1 and 2. BPA was extracted according to a previously published method with slight modifications. Briefly, thermal papers were cut into 4 mm diameter circular pieces using a puncher. Then, 1.0 g from each sample was immersed into 10 mL of ethanol overnight at 60 °C for the extraction process. After centrifugation, supernatants were filtered with a 0.45 μm filter. Sample solutions were then diluted with PBS and detected by SWV.

**ASSOCIATED CONTENT**

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05836.

Electron microscope image of AgNPs-EG (at a higher magnification, X10 000) and the UV–Vis spectrum for AgNPs (PDF)

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Notes

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