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TiO_2/Ag_2O-Exfoliated Graphite as Visible Light-Responsive Nanostructure for Improved Photoelectrochemical Degradation of BPA

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Abstract

In this paper, exfoliated graphite (EG), titanium dioxide (TiO_2), silver oxide (Ag_2O) and TiO_2-Ag_2O/ EG have synthesized, fabricated and characterized. An electrolyte used in this work was Bisphenol A (BPA). Degradation was carried out under electrochemical oxidation, photolysis and photoelectrochemical. Characterization techniques utilized were: ultraviolet–visible (UV) diffuse reflectance analysis, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX), Raman, thermal gravimetric analyzer (TGA), and X-ray diffractometry (XRD). SEM morphologies, EDX and the XRD patterns showed a good mix and disperse among nanocomposites in terms of the formation of TiO_2-Ag_2O/EG. Degradation analysis revealed TiO_2-Ag_2O/ EG as the best nanocomposite for degradation of azo dyes from the wastewater. On a relative view of engaged techniques, photoelectrochemical revealed to be worthwhile.

Keywords: *Ag_2O, TiO_2, Graphite, Bisphenol and photoelectrochemical.*

1. INRODUCTION

The development of clean and safe water is regarded as key to sustainability of life. Currently, the world is faced with a mounting challenge in saving the few available sources of "clean" water due to pollution. Continuous pollution has led to an increase in the rate of deteriorating water quality. Rapid industrialization has led to high discharge of persistent organic pollutants into the environment, causing serious damage to aquatic life as well as human well-being [1]. Among the pollutants causing deterioration in water quality are a unique class of compounds known as emerging pollutants. Bisphenol A (BPA), a synthetic organic compound which is widely used in several applications, for example, has been reported to act as an endocrine disruptor [2, 3]. It can enter the aquatic system through industrial wastewater discharge or leaching from the products. BPA has a wide range of industrial applications, including, its utilization as a raw material for the manufacture of pesticides, polycarbonate and epoxy resins [1]. It is also utilized in the manufacture of flame retardants, plastic products, toys, medical equipment, and tubing. It has been reported to mimic or oppose the biological functions of natural hormones [4].

Hitherto, various methods have been proposed for the removal of BPA from wastewater. These include adsorption, biological treatment, chemical oxidation and advanced oxidation processes. However, advanced oxidation processes have been widely reported as potential

procedure to remove persistent organic pollutants, including, BPA from aqueous medium [5, 6]. Further, electrochemical advanced oxidation techniques have established themselves as efficient approaches for the decontamination of organic pollutants-containing wastewater, owing to their high efficiency as well as environmental compatibility [2]. The efficacy of these procedures are attributed to the formation of highly reactive species such as hydroxyl radical (•OH) with high redox potential that can mineralize organic pollutants [7].

TiO_2 is one of the most employed catalysts reported in literature for wastewater treatment. However, its practical application has been hindered by a number of challenges, including, high recombination rate of the photogenerated electron-hole pairs. In addition, this catalyst exhibits a wide band gap of 3.2 eV which restricts its application to UV light. To alleviate these challenges, combination with semiconductor possessing strong visible-light absorptivity owing to reduced band gap has been reported [8-14]. Ag_2O is an attractive and good visible-light responsive semiconductor that has previously been reported to exhibit synergetic effect on nitrogen doped TiO_2 for superior catalytic degradation of organic pollutant [15].

Photoelectrochemical procedure, known as the combination of photocatalysis and electrochemical oxidation technique has proven to be a rapid and highly efficient approach for organic pollutants degradation [9, 16, 17]. Exfoliated graphite on the other hand, has broadly been also reported as promising support for photoelectrochemical application owing to its electrical conductivities, large surface area, flexibility, corrosion resistance and enhanced [18-20].

The current investigation describes the preparation and evaluation of TiO_2/Ag_2O @EG electrode for electrocatalytic degradation of toxic BPA in aqueous environment under sunlight irradiation. Moreover, a plausible mechanism for BPA degradation was anticipated through high performance liquid chromatography (HPLC) technique.

2. MATERIALS AND METHODS

2.1. Synthesis of Rod-Like TiO_2

TiO_2 nanoparticles were synthesized using a hydrothermal process. In a typical preparation procedure, 5 mL of titanium (IV) isopropoxide was dissolved in 10 mL of a mixture isopropyl alcohol/water (5:3). 10 mL of 15 M NaOH aqueous solution was then added and the mixture was stirred at room temperature for 3 h. Next, the reaction was transferred to a Teflon-lined autoclave and heated to 180 °C for 24 h before being allowed to naturally cool to room temperature. The product was washed several times with ethanol and distilled water until pH 7. In the end, the wet precipitate was dried in an oven at 60 ℃ and calcined at 500 °C in a muffle furnace in air.

2.2. Synthesis of TiO_2/Ag_2O

0.64 g of $AgNO_3$ and 0.3 g of TiO_2 nanorod were mixed in 20 mL ethylene glycol. The solution mixture was sonicated for 30 min for good dispersion purpose. Then 0.1 M NaOH solutions were added dropwise so as to modify the pH value to 13, and stirred for 2 h. The product was isolated by filtration, washed many times using deionized water, and ultimately dried at 60 °C for 12 h.

2.3. Synthesis of EG

As based on literature, 150 mg of EG was compressed to form EG pellet of 1 cm diameter, and one end of a coiled Cu wire using a glass tube with conducting silver paint was attached to a small size of the prepared EG pellet and was covered with epoxy resin [21].

2.4. Characterization

For a proper observation on barely synthesized semiconductors and modified nanocomposites in terms of their

structures, phases and crystallinities present within them, X-Ray powder diffraction (XRD) was utilized. The engaged software was Philips PAN Analytical X'Pert System. The operational settings were voltage of 40 kV, 40 mA current and Cu-Kα radiation of the 0.154 nm. The record of diffraction data started from 4^o to 80^o (step size: 0.02^o, step time: 1min) at the normal 2θ angles which is mostly utilized on XRD measurements. For the surface morphologies and elemental compositions of the samples, scanning electron microscopy (SEM) coupled to energy dispersive X-Ray (EDX) operating at 20 kV electron acceleration voltage was applied. A relative absorbance of the light on engaged nanocomposites was carried out using Shimadzu UV-2450, UV-vis spectrophotometer in the range of 200-800 nm. The micro-Raman spectrometer (NRS-3100) with a 532 nm solid-state primary laser as an excitation source in the backscattering configuration at room temperature was furthermore involved on matching JCPDS standard files peak positions, and also on recording of the phonon vibrational study of the different nanostructures and nano-composites.

2.5. Degradation Experiments

In comparison of degradation efficiency from the techniques applied photolysis, electrochemical oxidation and photoelectrochemical curves were drawn up. For these experiments, a potentiostat/ galvanostat operated at a voltage range between 2 V-5 V and a corresponding current range of 1mA-15mA was applied on degradation of the dye in 0.1 M sodium sulphate as a complementary electrode. Besides fabricated photoanode as working electrodes, two other electrodes were generally engaged: Ag/AgCl (3.0 M KCl) as a reference electrode and a platinum foil as a counter electrode. Pertinent surfaces of utilized photoanode were aligned to receive the beam of light directly from the solar simulator. Overall, an electro-chemical cell was used to carry out all degradation experiments containing the photoanode and the BPA. Under solo-photolysis and electrochemical oxidation, light was applied for photolysis, while potential without solar simulation was applied for electrochemical oxidation. On synergistic photoelectrochemical degrade-ation, potential and light were applied to the cell. Within that setup, a distance between the New Port 9600 Full Spectrum solar simulator equipped with 400 W and the experimental was measured at a distance of 10 cm, to study the degradation and the degradation kinetics of the BPA. The beam power was equivalent to 1 sun. Aliquots (5 ml) of the suspension were withdrawn using a disposable syringe and filtered through 0.4 µm PVDF membrane filter at 10 min intervals for about 1 h. For the determination of supernatant solution, Shimadzu UV-2450 spectrophotometer of the concentration of methylene blue dye remaining after degradation. The aforementioned techniques were then used to investigate the degraded dye.

3. RESULT AND DISCUSSIONS

3.1 SEM Analysis

SEM surface morphologies shown in Fig. 2 reveal each concerned solo nanocomposite and the corresponding synergistic nanocomposite synthesized in this study. In Fig. 2(a), EG is characterized by an absolute well-arranged plane of graphite, while porous TiO_2 morphology can be observed in Fig. 2(b). With an exhibition of a regular spherical morpho-logy an existence of the Ag_2O was noted as can be seen in Fig. 2(c). Overall, a synergistic nanocomposite is shown in Fig. 2(d). There, all engaged solo nano-composite morphologies can be seen in a mixed structure. This is evidenced by the EDX spectrum with: C for EG, Ti from TiO_2, Ag from Ag_2O and the O from obvious three nanocomposites. As these elements are therein from singular nanocomposite, this shows successful

synthesis of TiO_2-Ag_2O/EG from singular nanocomposite [17, 22].

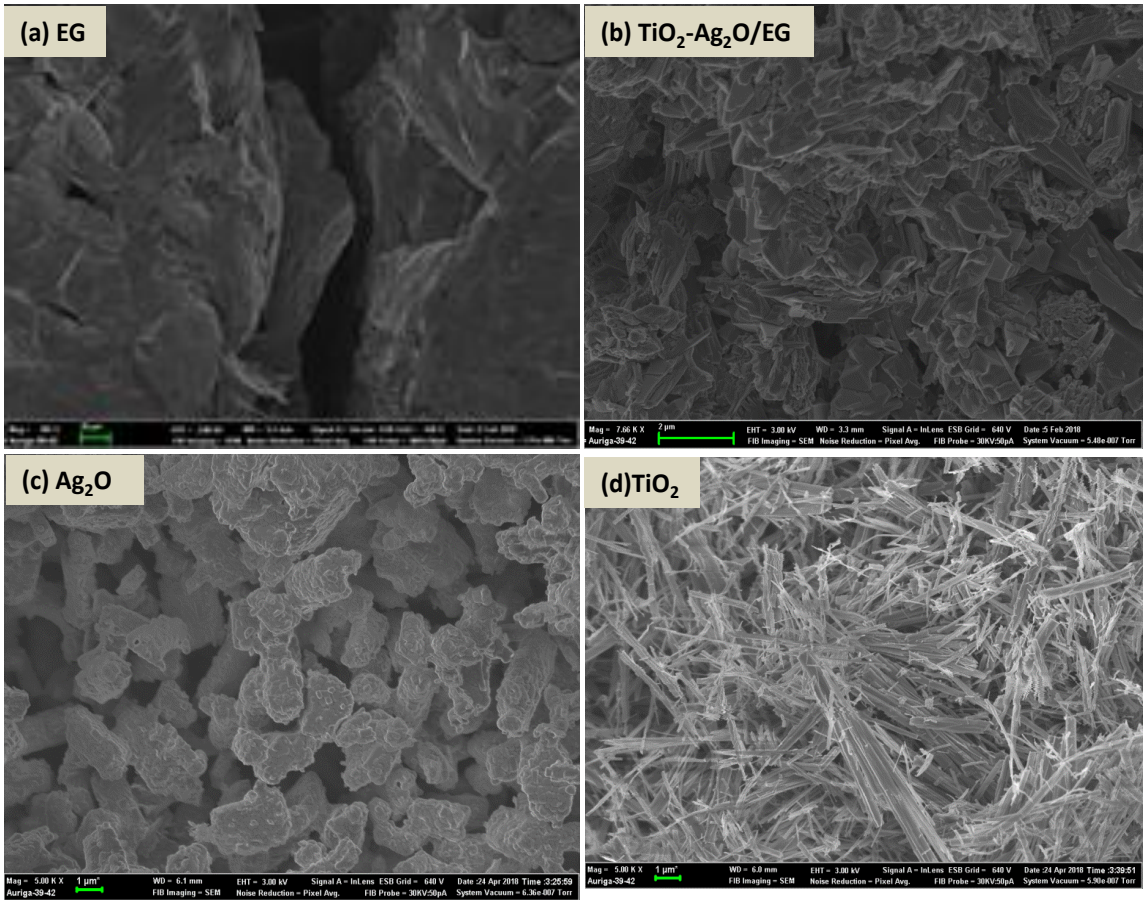
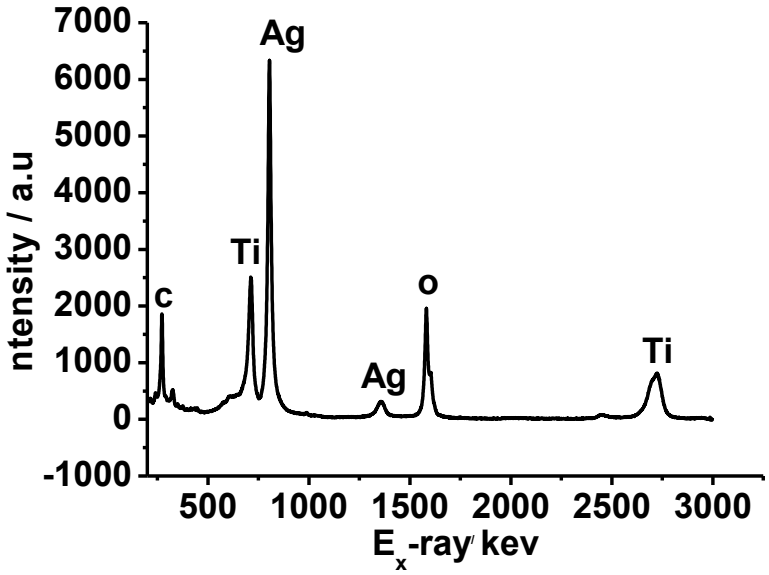


Figure 1. *SEM Image of (a) EG (b) TiO_2-Ag_2O/EG (c) Ag_2O (d) TiO_2.*



EDX of TiO_2-Ag_2O/EG

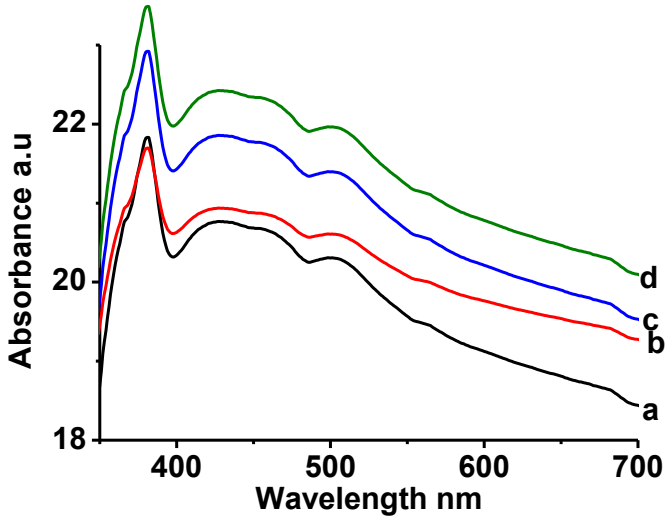


Figure 2. *UV-Vis Absorbance Spectra of (a) EG (b) Ag_2O (c) TiO_2 (d) TiO_2-Ag_2O/EG.*

Fig. 3 shows a comparative XRD patterns of engaged nanocomposites in this study. This was particularly for the characterization of the structure, phase and crystallinity from singular nanocomposite to the modified synergistic nanocomposite: The engaged nanocomposites were as follows: a) EG, (b) Ag_2O (c) TiO_2 (d) TiO_2-Ag_2O/EG. The first pattern shows a known monoclinic structure of TiO_2. A face centred cubic (FCC) and characteristics of lattice vibration can be seen in Fig. 3 (ii). On the vivid observation of the whole Figure, a shift on solo nanocomposite in comparison to the TiO_2-Ag_2O/EG sample can be seen. Firstly, AgO_2 first peak which appears around 25.2˚ shifted a bit to an increased peak, and that is attributed to the inclusion of EG [3]. EG involvement is also associated with the reduction of the intensity of photoactive nanocomposites, and that is significant on degradation of dyes [23]. Furthermore, all Ag_2O peaks which are found at 2θ values of 32.5˚, 37.6˚, 55.0˚,65.0˚ and 68.5˚ oscillated to (111), (200), (220), (311) and (222) shifted to the higher values. For the calculation of average crystallite size for the TiO_2-Ag_2O/EG, the popular utilized equation from Debye-Scherrer's was applied. Details of the equation can be found elsewhere [24]. Moreover, a propensity broadening peak on Ag_2O was reduced on the synergistic sample (TiO_2-Ag_2O/EG) as can be seen in Fig. 3(iii).All these show that all engaged nanocomposites were mixed and dispersed evenly well.

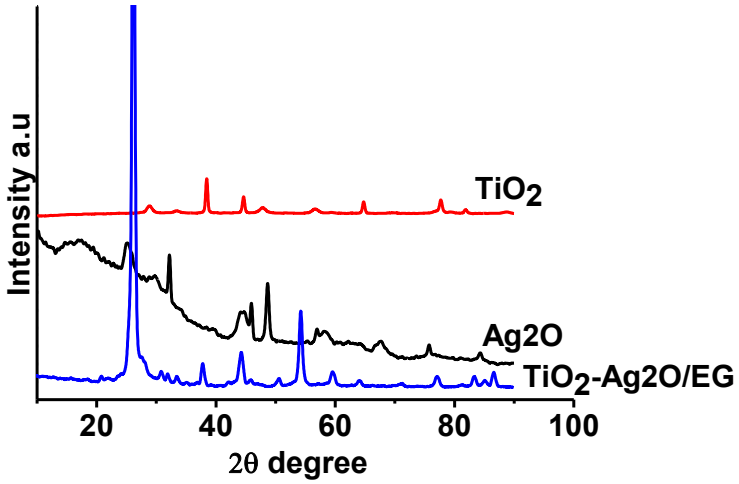


Figure 3. *XRD Pattern of (b) Ag_2O (c) TiO_2 (d) TiO_2-Ag_2O/EG.*

On a further characterization of the modified TiO_2-Ag_2O/EG electrode for surface area and pore volume, BET surface analysis was conducted through nitrogen adsorption-desorption isotherm. As can be seen from Table 1, EG has both lowest surface area and pore volume, while TiO_2 has the highest surface area. On the other hand, Ag_2O has a pore volume higher than all three solo materials. Hence, a necessitation of improvement became paramount. Significantly, it can be seen that the surface area reduced to be in between of all the engaged solo-photoanodes, while the pore volume became highest.

Table 1. *Show the BET result of (a) TiO_2-Ag_2O/EG (b) EG (c) TiO_2-Ag_2O.*

Sample	BET surface area / m^2 g g^{-1}	Pore volume/cm^3 g g^{-1}
EG	11.98	. 0.0369
TiO_2	18.22	0.0452
Ag_2O	12.31	0.6130
TiO_2-Ag_2O/EG	16.99	0.07996

Photoelectrochemical degradation of BPA Evaluation

3.2. Degradation Measurements

Fig. 3 shows UV curves obtained from UV spectrometer that was recorded within the wavelength range of 280-440 nm as function of absorbance of light. The operational setting were as follows: pH of 7 and 2.5 V potential. As can be seen in the figure, the removal of the BPA occurs as time goes by, and can particularly be observed between 280 and 320 nm. This observation is an indication that the TiO_2-Ag_2O/EG is an appropriate photoanode for effective photoelectrochemical degradation of BPA from the organic waste.

Synthesized EG, TiO_2, Ag_2O and TiO_2-Ag_2O/EG on degradation measurements are displayed in Fig. 4, while the Fig. 5 shows relative degradation efficiency of utilized techniques. Vividly, it can be seen that TiO_2-Ag_2O alone possesses low efficiency on degradation of the dye. However, an incorporation of the EG into the TiO_2-Ag_2O significantly improves degradation kinetics as can be seen in Fig. 4 (a). This is attributed to the magnificent properties of the EG with its structure with electrons trap sites [19]. Furthermore, the inclusion of TiO_2 within synergistic material is also attributed to a further generation of hydroxyl radicals which turns up with an excitation consists of photons with energy higher than or equal to its band gap, and thus leading to efficient degradation. Overall, degradation profile of the engaged techniques shown in Fig. 5, it can be seen that synergistic photoelectrochemical is worthwhile. Therefore, a combination of both photolysis and electrochemical oxidation is effective on removal of the azo dyes from the wastewater. The improved occurrence is associated to the limitations of photolysis which are covered by electro-chemical oxidation and limitations of electrochemical oxidation. The details on both advantages and limitations of solo technique can be found elsewhere [25].

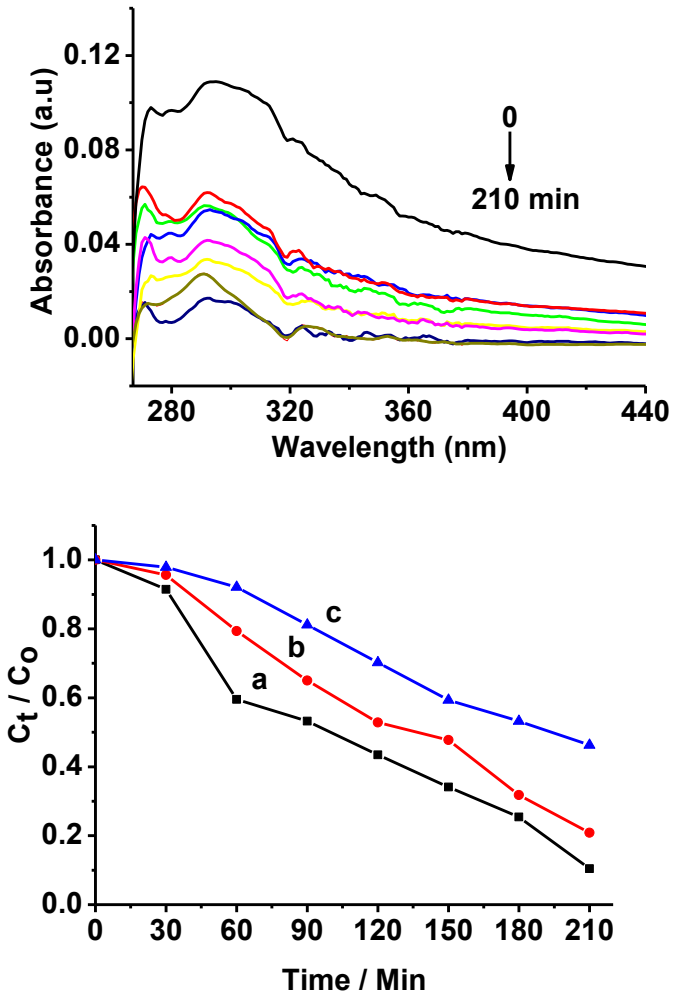


Figure 4. *Degradation profile of (a) TiO_2-Ag_2O/EG (b) EG (c) TiO_2-Ag_2O.*

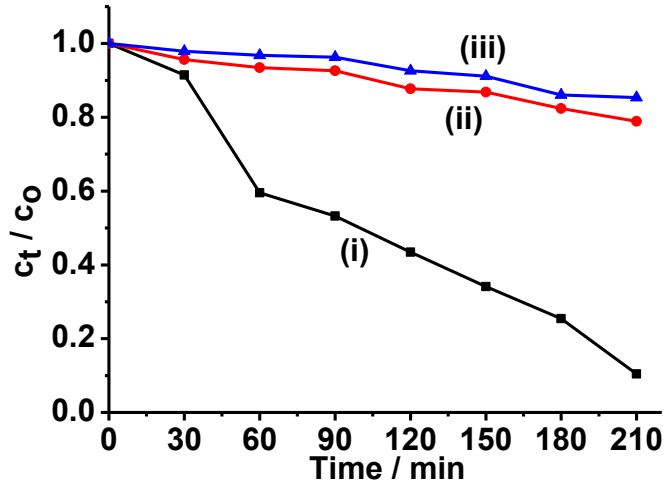


Figure 5. *Degradation of (i) Photoelectrochemical (ii) Electrochemical oxidation (iii) Photolysis.*

On characterization of probable multiple usage of TiO_2-Ag_2O/EG on photoelectron-chemical degradation of dyes from wastewater, five consecutive cycles of photoelectrochemical degradation were run from 0 to 210 min. From the curves shown in Fig. 6, the good photoelectrochemical re-usage can be observed. This occurrence is absolutely ideal for quasi-nil of secondary pollution, and this is efficient on the entire photoelectrochemical degrade-ation utilization [12].

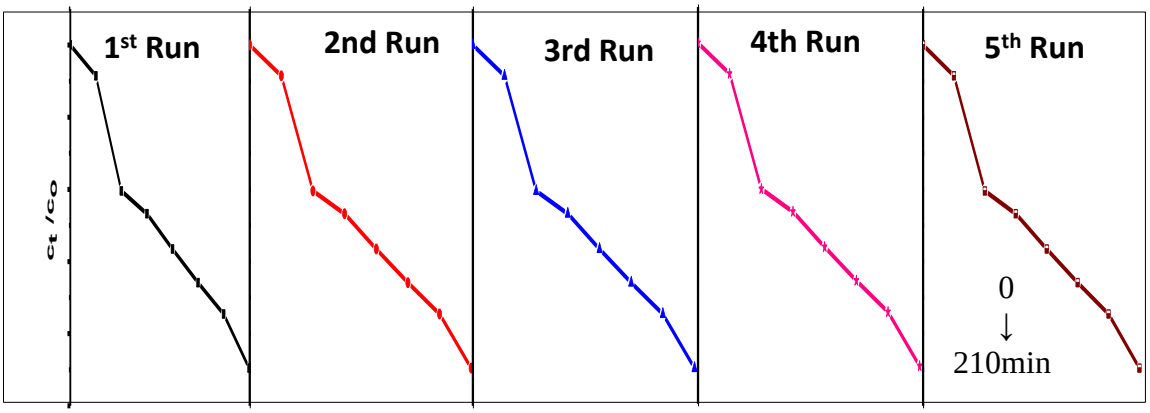


Figure 6. *Five cycle degradation test of the TiO_2-Ag_2O/EG electrode for the photoelectrochemical degradation of (dye name).*

Table 2 below compares semiconductors which consist EG in degradation of azo dyes from the wastewater. First, it can be seen from Table 2 that the presently fabricated EG/TiO_2-Ag_2O yields relatively good degradation efficiency. Second, on comparison which centres between bare Ag_2O/TiO_2 on and EG/TiO_2-Ag_2O, it can vividly be seen that Ag_2O/TiO_2 yielded 66% while EG/TiO_2-Ag_2O gave 87% degradation efficiency. This therefore suggests an incorporation of EG to the bare Ag_2O/TiO_2 is more worthwhile on degradation of azo dyes from wastewater.

Table 2. *Comparison of Catalysts used in Degradation of Exfoliated Graphite.*

Used Catalysts Reference	**Dyes Degradations**	**Efficiency**
PD-ZnO-EG [26]	Acid Orange	87%
WO_3/EG [27]	2-nitrophenol	82%
Ag2O/TiO2 [28]	Phenol	66%
EG/diamond [29]	Anthraquinone	81%
EG/TiO2-Ag2O The current study	Bisphenol A	87%

4. CONCLUSION

In this study, synthesis, fabrication and characterization of EG, TiO_2 and EG/Ag_2O-TiO_2 were carried successfully. The following conclusions were overall drawn up from characterization techniques

applied on engaged solution and electrolytes:

- XRD revealed a propensity broadening peak on Ag_2O to be reduced when it is mixed with EG and TiO_2.
- The SEM image showed coordination of all singular nanocomposites in synergistic $EG/Ag_2O.TiO_2$ nano-composite.
- The EG/ MnO2 exhibited improved visible light absorption compared to the singular nanocomposite, and that resulted to a higher Photoelectro-chemical degradation efficiency.
- The photoelectrochemical method of degradation was observed to be more efficient than photolysis and photochemical oxidation methods on their solo application.
- The photoelectrochemical degradeation method achieved 87% degradation efficiency within 240 min, and that underpins the fact that it is an appropriate electrode for the elimination of BPA dyes from the wastewater using $EG/Ag_2O.TiO_2$ as the photo anode.

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