Sunlight Photodeposition of Gold nanoparticles onto Graphitic Carbon Nitride (g-C₃N₄) and Application Towards the Degradation of Bisphenol A

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Abstract. Gold (Au) nanoparticles (NPs) were successfully deposited onto the surface of graphitic carbon nitride (g-C₃N₄) by using natural sunlight. Bisphenol A (BPA) were adopted as a pollutant with different pH condition to indicate the photocatalytic performance under natural sunlight. The presence of Au NPs (8.8 nm) was confirmed by TEM and XPS characterization. The duration for degraded BPA in pH 3 was 30 minutes faster than the normal degradation rate which is pH 7. This is due to the point of zero charge (PZC) properties of g-C₃N₄, contributing to better adsorption capacity efficiency and promoted the contact between photocatalysts and pollutants. The pH condition of BPA will affect the degradation efficiency, hence lower down pH condition of BPA can increase the photocatalytic performance.

1. Introduction
With the betterment of technology, rapid development of industry and rise in population, the environment pollution caused by organic pollutant is considering as a significant problem for the global. Endocrine disrupting chemicals (EDCs) are kind of organic pollutants that have the ability to interfere with natural hormonal mechanisms and alter the function of the endocrine system and thus lead to adverse health effects in an organism [1]. BPA is a well-known EDCs and it is widely utilized as an antioxidant or a stabilizer for various types of plastics [2]. Improper disposal of not readily biodegradable EDCs are highly toxic to environment and will produce some potential carcinogens. They are extremely resistant to degradation due to its high degree of chemical and biological stability properties. Consequently, direct discharge of EDCs into water sources will be harmful to the aquatic life, humans, animals and whole ecosystems. However, the traditional treatment methods are non-destructive and only turn the pollutant to another phase, producing secondary pollutant and requiring further treatment [3].

Since the first discovery of photocatalytic water splitting with titanium dioxide (TiO₂) electrodes by Honda and Fujishima (1972), extensive researches have undergone to comprehend the principles of photocatalysis and enhance the photocatalytic performance. The photocatalytic process harvests the light illumination as the energy source. It is known that the sunlight is abundant, sustainable and green resource. However, TiO₂ is active only under Ultraviolet (UV) light and can only absorb about 5% of
sunlight in the UV region [4]. Graphitic carbon nitride (g-C_{3}N_{4}) has recently attracted tremendous attention due to its high thermal and chemical stability, visible-light driven band gap (2.7 eV) and facile synthesis method [5]. However, the main shortcoming of g-C_{3}N_{4} is the poor electron-hole pairs separation, contribute to the slow photocatalytic reaction rate [6]. The electron-hole pairs recombination rate of g-C_{3}N_{4} need to be suppress in other to make g-C_{3}N_{4} become a promising and adaptable photocatalyst for sunlight harvesting. Recently, doping with a noble metal is recognized as one of the most promising alternatives to overcome the recombination issue. Xie and co-workers [7] reported that doped Au NPs onto g-C_{3}N_{4} will widen visible light response range and increased the hydrogen evolution rate. According to Cheng and co-workers [8], the Au/g-C_{3}N_{4} composite demonstrated superior photocatalytic activities towards the degradation of methyl orange under visible light irradiation. Furthermore, a pH experiment was used to find the optimum condition for photocatalytic degradation of BPA due to the pH of the solution could affect the surface charges on the photocatalyst [9].

2. Experiments And Characterizations

2.1. Synthesis of g-C_{3}N_{4} and Au/g-C_{3}N_{4}

30g of urea (R&M Chemicals) was dried in an oven at 80°C for 24h and then pyrolysed in a Muffle Furnace at 550°C for 3h. The obtained yellow-colored product was washed with nitric acid (0.1 M) and deionized water for several times to remove any residual alkaline species. For Au/g-C_{3}N_{4}, the prepared g-C_{3}N_{4} (0.5 g) was added to 20 mL of ethylene glycol containing a chosen amount of gold (III) chloride trihydrate (HAuCl_{4}, Sigma–Aldrich). Then the resulting suspension was exposed under natural sunlight for 60 min with continuous stirring to promote photodeposition. The schematic diagram and photograph of experimental setup is shown in Fig. 1(a). Then the obtained precipitate was washed repeatedly with ethanol and deionized water and followed by dried in an oven for overnight at 80 °C.

2.2. Characterization

The surface chemical composition of samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI Quantera II, Ulvac-PHI, Inc.) with Al Kα radiation source. The morphology of the samples was observed using a field emission scanning electron microscope (FESEM, JSM-6701F, JEOL). High-resolution transmission electron microscope (HRTEM, FEI-TECNAI F20) images were obtained at 200 kV. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were performed using UV-vis NIR spectrophotometer (UV-260, SHIMADZU) with a wavelength range of 200–800 nm.

2.3. Photocatalytic degradation of organic pollutants

0.1 g Au/g-C3N4 was adopted as photocatalyst in the degradation of BPA (5 ppm) under different pH condition as shown in Fig. 1(b). pH experiment was used to find the optimum condition for
photocatalytic degradation of BPA. 0.1 M of sodium hydroxide (NaOH) was used for alkali condition and 0.1M of nitric acid (HNO₃) was used for acidic adjustment. The BPA solution was set at pH 3, 5, 7, 9 and 12 to identify the degradation efficiency at certain pH condition. The pH of BPA solution was adjusted and verified using HI2210-01 Benchtop pH Meter with 0.01 pH resolution. The experiment was carried out for 2 h under natural sunlight and sample was collected for high-performance liquid chromatography (HPLC, PerkinElmer Flexar) analyzer. The HPLC was equipped with fluorescence detector, a separation column used was Ascentis C18 column (Supelco Analytical, USA) (15 cm × 4.6 mm × 5 µm). The mobile phase was 40 % acetonitrile (ACN), 60 % water and the flow rate was 1.0 mL/min.

3. Results And Discussions

SEM and TEM were used to characterize the morphologies of synthesized samples and the obtained images are shown in Fig. 2. The obtained FESEM images for Au/g-C₃N₄ showed a characteristic lamellar structure, which is assembled of massed irregular nanosheets of g-C₃N₄ [10]. The dark contrast in TEM images indicated the presence of Au NPs (0.235 nm lattice fringes) and uniform distributes over the g-C₃N₄ nanosheets with average particles size 8.8nm.

Figure 2a. SEM images of Au/g-C₃N₄
Figure 2b. TEM images of Au/g-C₃N₄
Figure 2c. TEM images of Au/g-C₃N₄

Figure 3. XPS Spectra of Au/g-C₃N₄ (a) C1s, (b) N1s, (c) O1s and (d) wide scan.
XPS was used to examine the chemical composition and chemical state of Au/g-C₃N₄. The XPS spectra in Fig. 3 reveal the existence of C, N, O and Au in the composite with the weight percentage of 37.74, 53.74, 2.13 and 5.56 wt%, respectively. The C1s peak was deconvoluted into four peaks which is C-C (284.69 eV), C-O (286.20 eV), C=O (287.70 eV) and COOH (288.51 eV). In the N1s spectrum, the main peak observed at 398.18 eV is ascribed to CN=CN coordination which originates from the sp²-bonded N in triazine rings, while the other two weak peaks observed at binding energies 398.91 and 400.44 eV can be attributed to N-(C)³ and C-N-H species [11]. In Fig. 3(c), the peak observed at 531.59 eV was assigned to some hydroxyl groups (OH) attached on the surface of g-C₃N₄ [12]. A peaks located at around 85 eV observed in wide scan (Fig. 3(d)) was assigned to the Au 4f, indicated the presence of metallic Au NPs.

The visible light absorption capability of the Au/g-C₃N₄ was determined by UV–vis DRS and shown in Fig. 4(a). The absorption range from 200 to 450 nm UV was ascribed to the optical band gap of g-C₃N₄. Nevertheless, a hump was observed at absorption band ~550 nm was attributed to Au NPs on surface of g-C₃N₄, this is acknowledged to LSPR effect delivered by Au NPs, thus broaden the absorption band towards the visible region. The existence of Au NPs had generated a disturbance on dielectric constant of the surrounding matrix and contributed for visible light absorption [13]. Furthermore, the band gaps of Au/g-C₃N₄ were estimated to be 2.95 eV by using the Tauc plot as shown in Fig. 4(b).

\[ \text{Absorbance (a.u.)} \]
\[ \text{Wavelength (nm)} \]

**Figure 4a.** UV-Visible Absorption Spectra of Au/g-C₃N₄.

\[ \text{(F(R)/hv)}^{1/2} \]
\[ \text{hv (eV)} \]

**Figure 4b.** Tauc plot

3.1. Photocatalytic Experiment

As the pH of the solution could affect the surface charges on the photocatalyst, the degradation of BPA was investigated under different condition. From Fig. 5, the highest degradation efficiency was pH 3 followed by pH 5, 7, 9 and 12. The BPA compound was negatively charged as it possesses two negative oxygen atoms at the hydroxyl groups and four negative carbon atoms ortho to the phenolic groups. The formation of hydroxyl radicals was due to the adsorption mechanism of BPA onto the surface of photocatalyst [14].

Furthermore, the dissociation constant of BPA pKa values within 9.6 and 10.2 where the dissociation constant representing the favorability of BPA separate into smaller molecules. When the pH > pKa, the ionic species was the predominant which means the surplus hydroxide ions in alkali inhibited the dissociation of BPA into simplier form. On the other hand, when pH < pKa the undissociated species of BPA became the predominant. Therefore, the degradation of BPA at pH 12 was much slower compared to pH 9 due to the hydroxyl radicals (•OH) scavenging by carbonate and bicarbonate ions [15].

The adsorption capacity eventually depends on the point of zero charge (PZC) of the photocatalyst. The PZC was an useful measurement in pH unit used to evaluate the net electric charges on the surface. From the report of Fronczak, et al. (2017) [16], the PZC of g-C₃N₄ tends to have better adsorption
capacity in pH less than 7. High pH with more negative charge could neutralize the surface charge of photocatalyst in causing the electrostatic repulsion of itself and the organic pollutants [17]. Additionally, the electrostatic repulsion also retarded the adsorption ability of photocatalyst and thus decreasing lower degradation efficiency.

![Figure 5. Photodegradation of BPA under Different pH Condition for Au/g-C3N4](image)

4. Conclusion
In summary, the Au/g-C3N4 composite was successfully synthesized via a simple and sustainable photodeposition method. The composite performed better photodegradation of BPA in low pH condition. This is mainly due to the PZC of g-C3N4 incline to have better adsorption capacity in pH less than 7. pH 3 have the smallest electrostatic repulsion compare with others pH condition. Thus promoted the adsorption ability of photocatalyst and thus increased the degradation efficiency. Moreover, BPA is more favorable to separate into smaller molecules when the pH is lower than 9.6 contributed to the dissociation constant of BPA pKa values are within 9.6 and 10.2. Therefore, the PZC of photocatalysts and the dissociation constant of pollutant played an essential part in boosting the photocatalytic performance.

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References
[1] J. C. Sin, S. M. Lam, A. R. Mohamed, and K. T. Lee, “Degrading Endocrine Disrupting Chemicals from Wastewater by TiO\textsubscript{2} Photocatalysis: A Review,” Int. J. Photoenergy, vol. 2012, 2012, doi: 10.1155/2012/185159.
[2] S. Imai, A. Shiraishi, K. Gamo, I. Watanabe, H. Okuhata, H. Miyasaka, K. Ikeda, T. Bamba, and K. Hirata, “Removal of phenolic endocrine disruptors by Portulaca oleracea,” J. Of Biosci. And Bioeng. vol. 103, Feb. 2007, pp. 420-426, doi: 10.1263/jbb.103.420.
[3] Z. Li, “Surface modified nanocarbons for photodegradation of organic pollutants,” Master thesis, Curtin University, 2016.
[4] H. Dong, G. Zeng, L. Tang, C. Fan, C. Zhang, X. He, and Y. He, “An overview on limitations of TiO\textsubscript{2}-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures,” Water Res., vol. 79, Aug. 2015, pp. 128-146, doi: 10.1016/j.watres.2015.04.038.
[5] H. Yan, Y. Chen, and S. Xu, “Synthesis of graphitic carbon nitride by directly heating sulfuric acid treated melamine for enhanced photocatalytic H\textsubscript{2} production from water under visible light,” Int. J. hydrogen energy, vol. 37(1), Oct. 2011, pp. 125-133, doi:
[6] J. Liu, H. Wang, and M. Antonietti, “Graphitic carbon nitride "reloaded": emerging applications beyond (photo)catalysis,” Chem. Soc. Rev., vol. 45(8), 2016, pp. 2308-2326, doi: 10.1039/c5cs00767d.

[7] L. Xie, Z. Ai, M. Zhang, R. Sun, and W. Zhao “Enhanced Hydrogen Evolution in the Presence of Plasmonic Au-Photo-Sensitized g-C3N4 with an Extended Absorption Spectrum from 460 to 640 nm,”, PloS one, vol. 11(8), Aug. 2016, e0161397, doi:10.1371/journal.pone.0161397.

[8] N. Cheng, J. Tian, Q. Liu, C. Ge, X. Sun, A. Qusti, A. Asiri, and A. Al-Youbi, “Au-nanoparticle-loaded graphitic carbon nitride nanosheets: Green photocatalytic synthesis and application toward the degradation of organic pollutants,” ACS Appl. Mater. Interfaces, vol. 5(15), July 2013, pp. 6815-6819, doi:10.1021/am401802r.

[9] M. Yasmina, K. Mourad, S.H. Mohammed, and C. Khaoula, “Treatment heterogeneous photocatalysis; factors influencing the photocatalytic degradation by TiO2,”, Energy. Proced., vol. 50, 2014, pp. 559-566, doi: 10.1016/j.egypro.2014.06.068.

[10] Y. Fu, T. Huang, L. Zhang, J. Zhu, and X. Wang, “Ag/g-C3N4 catalyst with superior catalytic performance for the degradation of dyes: a borohydride-generated superoxide radical approach,” Nanoscale, vol. 7(32), 2015, pp. 13723-13733, doi: 10.1039/C5NR03260A.

[11] C. L. Wong, Y. N. Tan, and A. R. Mohamed, “Photocatalytic Degradation of Phenol Using Immobilized TiO2 Nanotube Photocatalysts,” J. Nanotechno., vol. 2011(2011), April 2011, pp. 1–9, doi: 10.1155/2011/904629.