Silver-Loaded Carbon and Phosphorous Co-Doped Boron Nitride Quantum Dots (Ag@CP-BNQDs) for Efficient Organic Waste Removal: Theoretical and Experimental Investigations

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1. INTRODUCTION

In recent years, much emphasis has been paid to the use of photocatalysts to remove undesirable organic and/or inorganic contaminants. Aromatic structures of most drugs, pesticides, and dyes are highly hazardous, carcinogenic, and mutagenic. Several attempts have been made to improve the activity of the photocatalyst, including loading of other atoms. Noble metals, such as Ag, have been widely employed to improve photocatalytic activity in visible light. Here, the interaction between the electrons of Ag and incident photons occurs (plasmonic effect) and, hence, enhances the visible light harvesting properties of the photocatalyst. Thus, the addition of silver atoms is to increase light absorption in the visible region, delay recombination time, and provide extra orbitals (bands), which facilitate the movement of electrons between electron–hole (exciton) and traps the fast recombination. It is clear from the literature that a hybrid photocatalyst suppresses the movement of photogenerated exciton pairs in heterojunctions, that is, it is possible to reduce the recombination of electron–hole pairs, extend their lifetime, and considerably improve photocatalytic performance.

Another advantage of the hybrid junction photocatalyst is providing an n–p junction. When the heterojunction photocatalyst is irradiated by photons with energy higher than or equal to the gap energy of both photocatalysts, the electrons can move to the conduction band of the n-type photocatalyst and the holes move to the valence band of the p-type photocatalyst due to the formation of the inner electric field. As a result, it can reduce the recombination rate of photogenerated exciton pairs and enhance photodegradation performance. The reason behind this is that an internal electrostatic field in the region of p–n junction is formed, which separates and moves e− and h+ in the opposite directions and this reduces the rate of recombination. It also accelerates...
the separation rate of electrons between the valance band minimum (VBM) and conduction band maximum (CBM) and, hence, the rate of hydroxyl (OH•) and super oxide (O₂⁻) radical production increases.²⁻²³

Boron nitride quantum dots (BNQDs) are a class of zero-dimension nanoparticles. BNQDs appear in a variety of sizes ranging from 5 to 10 nm.²⁵⁻²⁶ Jung et al. measured the average thickness of the BNQDs to be 3.2 nm, indicating that the BNQDs had a few-layered structure.²⁷ The ability to exhibit quantum confinement, the functional edge effect, and high water dispersibility provide BNQDs with photoluminescence properties.²⁸⁻²⁹

The band gap of BNQDs ranges from 4.5 to 6 eV, is large, and not suitable for visible light applications.³⁰⁻³² On the other hand, Angizi et al. found that functionalized boron nitride has a band gap, for example, below 4.5 eV, which mainly depends on the type of functional group; for instance, hydroxyl-functionalized BNQDs gives, for example, 2.3–3.6 eV, methyl functionalized is 3.2–4.2 eV, and amine functionalized is 3.1–4 eV. Thus, functionalization of BNQDs makes them have potential use in the photocatalysis research.³³⁻³⁴

In our previous work, we co-doped phosphorous and carbon into boron nitride quantum dots (CP-BNQDs).² Then, we applied photodegradation of toluidine blue using UV light (274 nm) as a light source. The rate constant was competitive, this is may be due to the fast recombination of excitons. Additionally, gap energy of the nanocomposite was 4.2 eV, which is a wide band gap and cannot harvest in the visible region.

In the present work, we report loading Ag on CP-BNQDs using a hydrothermal method (Figure 1). Ag@CP-BNQDs are synthesized Ag@CP-BNQDs have been characterized and studied utilizing field-emission scanning electron microscopy (FE-SEM) (SEM 4500-Quanta, FEI, USA) and the chemical composition of synthesized nanostructures was measured by energy-dispersive X-ray spectroscopy (EDX) performed in FE-SEM. X-ray powder diffraction (XRD) was used to measure the crystal structure using X’Pert PRO (PANalytical, Netherlands) using Kα for copper element (Cu Kα = 1.5406 Å at 40 kV, 30 mA) in the 2θ range of (20–70°) with a rate of scanning of 1°/min, respectively. For monitoring the photodegradation process, absorbance spectra were recorded using a Lambda 25 Perkin-Elmer UV–vis spectrophotometer (Perkin-Elmer, USA). FTIR spectra were taken using an FTIR spectrometer (Thermo Scientific, USA).

2.2. Chemicals. All chemicals used were of analytical grades and used as purchased without further treatments. Silver nitride was purchased from Alpha Aesar GmbH (Karlsruhe, Germany). Boric acid, sodium oxalate, potassium bromates, 80% phosphoric acid, and congo red dye were obtained from CARL ROTH GmbH (Karlsruhe, Germany). Isopropyl alcohol was purchased from Fluka AG in Sigma Aldrich (Steinheim, Germany). Ascorbic acid was bought from Scharlau Chemicals (Barcelona, Spain) and folic acid was purchased from UNI-CHEM (China). Paracetamol was bought from PiONEER (Sulaymaniyah—Iraq). Toluidine blue, urea, and methyl orange were bought from labPak chemicals Ltd. (UK). The hydrochlorides of tetracycline were purchased from Sigma–Aldrich, St. Louis, MO, USA. 99% purity of amlodipine besylate was purchased from Awa medical (Hawler, Iraq). Chlorothanolin pesticide was supplied by Syngenta (Switzerland).

2.3. Synthesis of CP-BNQDs. For the fabrication of CP-BNQDs, 1.5 mg of urea in deionized water was mixed with 1.5 mg boric acid drop-by-drop in aqueous solution, along with 1 µL 1.0 M H₃PO₄. The solution was mixed for 30 min with a magnetic stirrer before being placed in a 250 mL Teflon-lined autoclave and heated to 200 °C for 24 h. The resulting solution was transparent and emitted a blue glow when illuminated by fluorescent lights. Next, the solvent was removed, and the solid was dried at 200 °C for 2 h until a white powder was obtained.

2.4. Synthesis of Ag@CP-BNQDs. To synthesize Ag@CP-BNQDs, 1:1 mole ratio was mixed from Ag⁺ along with CP-BNQDs; in brief, 0.5 g of CP-BNQDs was mixed with 0.1 M of silver nitrate drop-by-drop, the yellow-like turbid solution of Ag@CP-BNQDs was mixed using a magnetic stirrer for half-hour. The resulting colloidal solution was hydrothermally heated for 24 h 200 °C. Finally, the powder was purified and washed several times with deionized water, dried, and used in the photodegradation application. Figure 1 shows the scheme for the preparation of the nanostructure of Ag@CP-BNQDs.

2.5. Computational Study. The ab-initio computations were carried out utilizing the plane-wave basis and pseudopotential methods in the context of DFT. The CASTEP and Dmol3 codes have been used for all computations. We employed hybrid functionals, such as Becke-3 Parameter-Lee-Yang-Parr (B3LYP) ³⁵⁻³⁶ and Heyd–Scuseria–Ernzerhof exchange–correlation functional (HSE06). The kinetic energy cutoff for each exchange–correlation (XC) functional was 400 eV at norm conserving pseudopotentials. A 5 × 5 × 5 k-point Monkhorst–Pack grid was used to integrate the Brillouin zone, as well as the self-consistent field (SCF) tolerance was 2 × 10⁻⁶ (eV/atom).

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Figure 1. Schematic diagram demonstrates preparation and application of Ag@CP-BNQD.
2.6. Photocatalysis Experiments. Photocatalytic activities of Ag@BNQDs were evaluated by the degradation of tetracycline and nine other molecules tabulated in Table 1, under 5 W of blue LED (Light Bulb LED GU10 5W 400Lm Grow, GREENICE company, Madrid, Spain). Prior to illumination, a total of 25 mg of photocatalyst was dispersed into 25 mL of the solution containing the test compound and then magnetically stirred in the dark for 30 min to establish an adsorption−desorption equilibrium. At predetermined intervals, 3 mL of suspension was taken and centrifuged at 8000 rpm for 6 min to remove the photocatalyst. Then, the absorbance spectra of the tetracycline in the supernatants were analyzed by a UV−vis spectrophotometer at 367 nm.

To determine the ROS, isopropyl alcohol (IPA) was used as hydroxyl radical scavenger, ascorbic acid as O$_2$••• trapping species, sodium oxalate and potassium bromate was added as a scavenger for h$^+$ and e$^-$ accordingly. FTIR spectra were characterized to investigate the formation of Ag@CP-BNQDs. Figure 2C shows the FTIR spectra of Ag@CP-BNQDs. The signals at 552 cm$^{-1}$ could be detected for BNQDs and symmetric stretching vibration mode of P−O−P. Another peak was observed at 1010 cm$^{-1}$ due to the B−N−O vibration mode and it is also similar to the related results of BNQDs elsewhere, it may also be due to the P−O−Ag vibration mode., Moreover, the signal at 1384 cm$^{-1}$ resulted from the stretching vibration of C−O or due to the bending mode of B−OH and stretching mode of B−N., In addition, the peak at 1659 cm$^{-1}$ resulted from the vibration mode of the Ag−N bond Another peak was observed at 3242 cm$^{-1}$ due to the Ag−N vibration mode as well. The two peaks between 1300 and 1700 cm$^{-1}$ are assigned for the heterocyclic C−N stretching vibration mode as well. The crystal structure of Ag@CP-BNQDs was analyzed utilizing XRD spectra. Figure 2D shows the XRD pattern of Ag@CP-BNQDs with the diffraction peaks of 2θ equal to 29.45, 33, 36.2, 37.9, 44, 47.5, 52.6, 54.8, 57.1, 61.4, 64.3, 71.7, and 77.3$^\circ$ with the corresponding crystal planes indexed to

| organic waste     | conc. ppm | rate constant/min$^{-1}$ | rate constant/mol L min$^{-1}$ |
|-------------------|-----------|--------------------------|--------------------------------|
| amlodipine        | 10        | 0.047                    | 0.0002                         |
| caffeine          | 25        | 0.0053                   |                                |
| chlorothalonil    | 25        | 0.0033                   |                                |
| congo-red         | 15        | 0.011                    |                                |
| eosin yellowish   | 25        |                          |                                |
| folic acid        | 5         |                          | 0.138                          |
| methyl orange     | 10        | 0.0072                   |                                |
| paracetamol       | 10        | 0.0071                   |                                |
| toluidine blue    | 5         | 0.0106                   |                                |
| tetracycline      | 10        |                          | 0.207                          |

3. RESULTS AND DISCUSSION

3.1. Characterizations of Ag@CP-BNQDs. As shown in Figure 2A, the morphology of Ag@CP-BNQDs was imaged using SEM. It can be observed that a sheet-like morphology is synthesized, and the size according to the SEM image is roughly 27 nm. The SEM results were in a good agreement with the data obtained by XRD using Scherrer and Williamson−Hall equations. It was found that the average particle size of Ag@CP-BNQDs is roughly equal to 21 nm according to the Scherrer equation and 29 nm according to the W−H equation (see Supporting Information).

Figure 2. (A) SEM images of Ag@CP-BNQDs, (B) EDX spectrum of Ag@CP-BNQDs, (C) FTIR spectra of Ag@CP-BNQDs, and (D) XRD pattern of fabricated photocatalyst for Ag@CP-BNQDs.
In terms of how Ag atoms were formed on the surface of CP-BNQDs, a yellow colloid solution was first created by mixing Ag\(^+\) ions and CP-BNQDs. Due to loading of Ag\(^+\) ions to the lone pair of N in the CP-BNQD nanostructure, the Ag\(^+\) ions could be reduced to Ag atoms. This redox reaction may have been triggered by the presence of functional groups OH\(^-\) and NH\(^2\)\(^+\) that are present on the surface of CP-BNQDs.\(^{57,58}\) An illustration of the procedures followed in the synthesis of Ag@CP-BNQDs is provided in Figure 1.

3.2. Photocatalytic Degradation. 3.2.1. Organic Waste Removal. Ag@CP-BNQDs as a photocatalyst was applied to remove different pollutants, including pesticides, dyes, and pharmaceuticals. All experiments were performed at room temperature 25 °C. Ag@CP-BNQDs could photodegrade some pharmaceuticals, dyes, and other common molecules with different rate constants, as illustrated in Table 1 and Figure 3. The difference of rate constants is attributed to ROS, which is the product of photocatalysis, as different molecules react differently with ROS and as a result, they have different mechanisms and so different kinetics.\(^{60–63}\)

As illustrated in Figure 3A, typical UV–vis spectra and integral kinetic model for the removal of amlodipine, chlorothalonil, eosin yellowish, and tetracycline each with the degradation pathway were monitored by a spectrophotometer. Tetracycline was chosen for further study in this research as it shows good degradation and has a clear spectrum among all other pollutants.

3.2.2. Effect of Temperature and pH. Photodegradation of tetracycline was studied as a function of temperature. The effect of temperature on the apparent rate of photodegradation is shown in Figure 4B. It can be observed that the optimum temperature is 35 °C and the rate constant drops as the temperature rises. When operating above 35 °C (like 45 and 55 °C), the desorption of the produced product restricts the photocatalytic process because it reduces surface degradation.

Figure 3. Change of UV–vis spectra as a function of time (A) tetracycline, (C) amlodipine, (E) eosin yellowish, and (G) chlorothalonil. Integral kinetic plot of (B) second-order tetracycline, (D) first-order Amlodipine, (F) first-order Eosin yellowish, and (H) first order chlorothalonil at 25 °C and LED blue light.
and reactant adsorption.\textsuperscript{64-67} It also reduces dissolved oxygen as well as the decreased saturation value of oxygen, which is important because it maintains the photocatalytic mechanism by trapping the photogenerated electrons. However, at lower temperatures, adsorption of pollutants onto the photocatalyst surface is the restriction stage.\textsuperscript{64-67} In addition, the photocatalytic activity decreases at elevated temperatures because the electron–hole recombination rate increased.\textsuperscript{68}

Figure 4C shows the effect of pH on the degradation efficiency. Based on our results, relatively a range of pHs from 4 to 11 was good for degradation of tetracycline, while the best one was pH 9. We can conclude that the isoelectric point (the point of zero charge pH(Pzc)) is just above pH 9 and at this point Ag@CP-BNQDs is positively charged, since tetracycline is negatively charged in aqueous solution, therefore at pH 9 maximum concentration of tetracycline is adsorbed at the surface of photocatalyst and maximum rate of degradation is obtained.\textsuperscript{14,69-73}

3.2.3. Effect of Concentration and Kinetics of Degradation. To study the kinetics of photocatalytic degradation, the tetracycline molecule was chosen first, and then the experiment was carried out under the same conditions and with the same radiation source. The rate of tetracycline degradation was estimated by examining the order of degradation at peak 375 nm. For this reason, the log–log graphical approach, as well as integral and differential rate laws, have been used. The validity of the kinetic order can also be assessed using the correlation coefficient ($R^2$) obtained from fitting curves, especially when $R^2$ is close to unity.\textsuperscript{4,5,67} It shows that the degradation of tetracycline 375 nm is the second order with a $R^2$ value of 0.99 as shown in Figure 3B.

As indicated in Table 2, the influence of initial concentration on the rate constant, the rate constant of waste removal does not remain constant when the initial concentration is changed. The reason behind this is due to secondary photochemical processes that occur during photocatalytic degradation and also a change caused by the quenching process due to excimer formation, in which some intermediates absorb light and re-emit it as heat without initiating semiconductor photocatalysts, resulting in photons not reaching the photocatalyst’s surface.\textsuperscript{4,5,69-73}

3.2.4. Effect of Light Source and Efficiency of Degradation. Various light sources available in our laboratories were studies to find the best photocatalytic performance. Our aim is toward a visible light source and avoid using UV light. Table 3 illustrates the degradation rate constant as a function of the light source. With regard to degradation efficiency, the sample was irradiated 30 min each time and the cycle was repeated six times, as shown in Figure 4. It can be concluded that the efficiency was close to 80% in the first cycle of irradiation and then fluctuates between above and just below 70%. In an efficiency experiment, 10 ppm of tetracycline was irradiated using 5 watt blue LED light and the temperature was kept constant 25°C. It is worth mentioning that the photocatalyst Ag@CP-BNQDs is applied in a one-pot degradation and no further activation is performed. Prior to the photocatalytic

| conc. ppm | rate constant/mol⁻¹.L.min⁻¹ |
|-----------|-----------------------------|
| 10        | 0.207                       |
| 25        | 0.0854                      |
| 50        | 0.033                       |
| 75        | 0.016                       |

| light source | intensity | rate constant/mol⁻¹.L.min⁻¹ |
|--------------|-----------|-----------------------------|
| fluorescent 380 nm | 4 (mW/cm²) | 0.01            |
| blue (420–480 nm) | 5 (W/cm²) | 0.207                 |
| white (520–560 nm) | 4 (W/cm²) | 0.08            |
| yellow (560–590 nm) | 4 (W/cm²) | 0.0529         |
| red (625–750 nm) | 5 (W/cm²) | 0.018            |
experiment. It is worthy to mention that the solution is kept in the dark to gain adsorption–desorption equilibrium to minimize the adsorption effect on the photocatalytic experiments.

3.3. Photocatalytic Mechanism and Scavenger Trapping Experiments. Scavenger trapping analyses were conducted using a procedure equivalent to photodegradation in order to verify the main active species that was involved in the photodegradation process as well as the photocatalytic mechanism. As illustrated in Table 4, the rate constant of tetracycline degradation was influenced by all trapping agents that means all active species are involved in the photocatalytic process. However, the degradation was more significantly affected by the addition of KBrO3 as it traps e− movement; as a result, the recombination rate of electrons between the VBM and CBM slowed down.

With respect to the band structure of Ag@CP-BNQDs, the Tauc plot was plotted from the data obtained from UV–vis absorption spectra. As shown in Figure 5A, the DOS intensity for 2s orbitals are very low compared to 2p-orbitals. As it is found in Figure 5A, the DOS is concentrated at 2p orbitals, broad multiple peaks in the range of 12.5 to 0.9 eV at the CBM have been observed, the DOS intensity of s orbitals for both Ag and N atoms is low, so that the band edge energy of conduction band (ECB) is −0.4 eV. The Mulliken electronegativity rules were utilized in this calculation.

As illustrated in Figure 4D, the level of energy of the band edge at EVB of Ag@CP-BNQDs was estimated 2.1 eV, which is more positive than that of (OH−/OH) (1.99 eV vs NHE); so that, h+ at VBM is able to oxidize OH− to produce OH. At the same time, the CBM potential is measured to be −0.4 eV versus NHE, which is more negative than that of O2/O2− (−0.33 eV vs NHE). So the electrons at the CBM band edge can be injected to O2 to form O2−; these results are in good agreement with the scavenger trapping experiments, which strongly indicate that all active species are involved in the photodegradation of tetracycline over Ag@CP-BNQDs. Hence, the loading of silver atoms provides extra orbitals (bands), which facilitate the movement of electrons and they provide a p−n junction, which slows down the recombination rate. The applied trapping agents with their rate constants are tabulated in Table 4.

### Table 4. Scavengers Trapping Experiments as a Function of Rate Constant Using LED Light 25 °C, 10 ppm Tetracycline and 20 min Time Interval

| trapping agent | rate constant/mol−1.L.min−1 | degradation % | active species |
|----------------|-----------------------------|---------------|---------------|
| IPA            | 0.12                        | 49            | OH            |
| Na2C2O4        | 0.106                       | 50            | h+            |
| KBrO3          | 0.305                       | 85.1          | e−            |
| ascorbic acid  | 0.065                       | 34            | O2−           |
| no trapping    | 0.207                       |               |               |

3.4. Computational Simulation. To have a better understanding of the fabricated nanoparticles, theoretical simulations were carried out using B3LYP hybrid functionals. In these calculations, we supposed silver is bound to CP-BNQDs via a nitrogen atom. The band gap of the Ag@CP-BNQDs has been observed to decrease after loading with Ag, this is because of the n−p junction of outer electrons between Ag p-type and n-type of CP-BNQDs, Figure 5A shows a band structure and total density of state (TDOS) of Ag bound to CP-BNQDs via a nitrogen atom. The partial density of state (PDOS) of electronic levels of Ag@CP-BNQDs is plotted in Figure 5B. It can be noted that the Fermi level bisects the VBM and CBM that means the energy gap from CP-BNQDs is predominant in photocatalysis. With regard to Ag atoms, the 4d-orbital showed a high DOS covering the Fermi level at the valance band, which appears as multiple peaks in the range of −12.8−0.67 eV, explaining that most of the DOS of Ag atoms is located at 4d-orbitals. The bottom of the conduction band consists of a mixed 4p and 5s orbitals with medium intensity at 1.02 eV up to 10.7 eV, as shown in Figure 5B. With respect to nitrogen atoms, most of the DOS is concentrated at 2p orbitals, broad multiple peaks near at the VBM −12.5 to 0.9 eV at the CBM have been appeared, the DOS intensity for 2s orbitals are very low compared to 2p-orbitals. As it is found in Figure 5A, the intensity of s orbitals for both Ag and N atoms is low, so that

![Figure 5](https://doi.org/10.1021/acs.omega.2c04480)

**Figure 5.** (A) Band structure and TDOS Ag@CP-BNQD (Ag–N position) photocatalyst and (B) PDOS of the Ag@CP-BNQDs (Ag–N position) utilizing DFT/B3LYP/norm conserving.
Table 5. Calculated Lattice Parameters of Ag@CP-BNQDs.

| Photocatalyst | Lattice parameter (primitive centered) | Bond length (Å) |
|---------------|---------------------------------------|-----------------|
| Ag@CP-BNQDs   | a(Å) | b(Å) | c(Å) | V(Å³) | α (°) | β (°) | γ (°) | B-N | B-B | N-Ag | B-Ag |
|               | 3.61 | 3.61 | 7.23 | 94.48 | 90°   | 90°   | 90°   | 1.56534 | 2.55619 | 1.56534 | 2.55619 |

they have a minimum contribution to the DOS at the VBM and the CBM. As shown in Table 5, the optimized lattice parameter and bond length for Ag@CP-BNQDs was calculated using the PBE exchange functional.\(^2,8\) From theoretical calculations, we found that the band edges of CP-BNQDs have a maximum contribution in the photocatalytic process and Ag provides extra bands, which facilitate the electron movement. According to DFT calculations in the literature, boron nitride is considered an n-type semiconductor;\(^5\) therefore, there is an n–p junction, which enhances and delay recombination of excited electrons.

4. CONCLUSIONS

A novel photocatalyst nanocomposite was synthesized via loading of silver atoms on CP-BNQDs. Photocatalytic degradations were dramatically enhanced and can harvest a blue weak LED lamp for the degradation of 10 common compounds, including dyes, pesticides, and pharmaceuticals. Experimental and theoretical results showed that loading Ag atoms can decrease the energy gap of the nanocomposite and enhance the charge separation through the n–p junction and plasmonic effect. Theoretical simulation using the DFT calculation proved that Ag atoms share bands with CP-BNQDs, which enhances the charge separation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04480. EDX mapping of sample Ag@CP-BNQDs, UV–vis absorption spectra, Tauc plot of Ag@CP-BNQDs in DMF and H\(_2\)O, respectively, and band edge calculations (PDF)

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Notes

The authors declare no competing financial interest.

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