Synthesis of Ag/GO nanocomposite with promising photocatalytic ability for reduction reaction of \( p \)-nitrophenol

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Abstract

\( p \)-Aminophenol (PAP) is an important intermediate reagent in the synthesis of paracetamol, widely used as an analgesic and antipyretic drug. Therefore, finding an effective catalyst to improve PAP synthesis efficiency is worth studying. Among those studies, nanocomposite is the most promising material. In this study, Ag/GO nanocomposites were synthesized by reducing silver nitrate on graphene oxide (GO) with sodium borohydride as a reducing agent and characterized by SEM, EDX, XRD and UV–vis methods. The catalytic ability was investigated based on the hydrogenation reaction of \( p \)-nitrophenol (PNP). We successfully synthesized Ag/GO nanocomposite with relatively homogeneous distributions and similar particle sizes. The results showed that Ag/GO nanocomposite has an excellent catalytic activity with the yield of reduction reaction at 97\%, 3 min. Moreover, this photocatalyst can easily be recovered and reused three times without any reaction efficiency reduction. We also successfully synthesized and crystallized PAP with high purity and the total yield of 45.82\%. The results show that Ag/GO nanocomposite is an excellent catalyst for high-performance reactions with many useful properties, such as easily recovered and repetitive used. On top of that, Ag/GO nanocomposite is safe, less toxic and environmentally friendly.

Nomenclature

| Abbreviation | Description |
|--------------|-------------|
| PAP          | \( p \)-Aminophenol |
| PNP          | \( p \)-Nitrophenol |
| AgNPs        | Silver nanoparticles |
| GO           | Graphene oxide |
| DI           | Deionized water |
| UV–vis       | Ultraviolet-Visible spectroscopy |
| SEM          | Scanning electron microscope |
| EDX          | Energy dispersive x-ray spectroscopy |
| XRD          | X-ray diffraction |
| rGO          | Reduced graphene oxide |
| FTIR         | Fourier transforms infrared spectroscopy |
| TLC          | Thin layer chromatography |

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1. Introduction

In pharmaceutical industry, p-aminophenol (PAP) is known as an important intermediate to synthesize paracetamol. Global demand for paracetamol has been estimated at around 100 000 tons year\(^{-1}\), indicating the commercial importance of PAP [1]. Conventionally, PAP is manufactured by the reduction of p-nitrophenol (PNP) using the iron-acid. However, the major drawback of this method is the generation of a large amount of Fe-based sludge, which causes a serious environmental problem [2]. Therefore, studies on efficient and reusable catalysts are necessary when synthesis efficiency’s factors, economic and environmental benefits are considered. In which, metal nanoparticles have attracted lots of attention due to their strong catalytic ability [3]. Indeed, the precious metal nanoparticles such as silver nanoparticles (AgNPs) have been used as catalysts for the hydrogenation of PNP [4]. Because AgNPs are small in size, their surface area to volume ratio is larger. Under light illumination, conduction electrons of AgNPs are collectively oscillated on the surface, i.e., surface plasmon resonance (SPR). SPR can generate an electron-hole pair with sufficient energy that enables hot electrons to extend away onto the surface and easily transfer from the AgNPs surface to the reactants. These hot electrons can be transferred into their electronic states causing weakening as well as dissociating of reactant bonds, resulting in the activation of \(\text{H}_2\) molecules [5]. Nevertheless, the agglomeration of nanoparticles and recovery ability are two main challenges of employing AgNPs.

Graphene oxide (GO) is a well-known derivative of graphene with a two-dimensional sheet of sp\(^2\) carbon atoms packing into the unique honeycomb structure. Several functional groups including hydroxyl (\(-\text{OH})\), alkoxy (\(-\text{O}-%\)), carbonyl (\(-\text{O}-%\)), carboxylic acid (\(-\text{COOH}\)), and other oxygen-based group were found on the GO surface [6]. GO possesses various good physico-chemical properties such as large surface area, easy solubility, low toxicity, high mechanical strength, and capacity of functionalization [7, 8]. GO is identified as a good candidate for support materials that improve the dispersion of AgNPs and for materials with higher mechanical strength. In addition, the economy would be highly benefitted from using GO due to its low production costs and easy handling [9]. The composite form will integrate both advantages of AgNPs and GO, particularly the \(\pi-%\) charges on the GO surface that absorb the reactants via \(\pi-%\) stacking interaction, providing a higher concentration of agents near the AgNPs on the surface and therefore leading to more efficient contact between reactants [8].

In this study, we synthesized Ag/GO nanocomposite-based photocatalysts, followed by investigating their photocatalytic activity in the hydrogenation reaction of PNP to PAP.

2. Materials and methods

2.1. Chemicals

30% Hydrogen peroxide H\(_2\)O\(_2\) (Xilong Scientific, China), 98% Sulfuric acid H\(_2\)SO\(_4\) (Xilong Scientific, China), 85% Phosphoric acid H\(_3\)PO\(_4\) (Xilong Scientific, China), 98% 5 \(\mu\)m Graphite flake (Xilong Scientific, China), 98% Potassium permanganate KMnO\(_4\) (Xilong Scientific, China), 35% Hydrochloric acid HCl (Xilong Scientific, China), Silver nitrate AgNO\(_3\) (Xilong Scientific, China), Sodium borohydride NaBH\(_4\) (Aladdin Industrial Corporation, China), p-Nitrophenol (Shanghai Zhannyn Chemical, China), Chloroform CHCl\(_3\) (Merck, China), Methanol CH\(_3\)OH (Merck, China), p-Aminophenol (Merck, China).

2.2. Instrumentation

Magnetic stirrer (Faithful, China), ABS220-4N Analytical balance (Kern, Philippine), MP55 Melting point system (Mettler Toledo, Switzerland), XUB10 Ultrasound tank (Gant, UK), EBA205 Portable centrifuge (Hettich, Germany), Shimadzu UV-1800 UV-vis Spectrophotometer (Shimazu, Japan), UNB200 Oven (Memmert, Germany), Agilent Cary FTIR 630 Spectrophotometers (Agilent, US), TESCAN MIRA 3 FEG-SEM Scanning electron microscope (Tescan, Czech), D8-Advance XRD (Bruker, Germany).

2.3. Synthesis of GO

The synthesis of GO followed a previous protocol described by Khai et al [10]. First, stirred a mixture of 98% sulfuric acid (46 ml, 0.841 mol) and 85% phosphoric acid (12 ml, 0.196 mol) for 10 min at room temperature. Then, added graphite powder (1 g, 0.083 mol) and continued stirring for 10 min. Next, slowly added potassium permanganate (12 g, 0.076 mol) into the mixture and immediately increased the reaction temperature to 35 °C and continued stirring for 3 h. Then added 90 ml of deionized water (DI) and increased the temperature to 90 °C for 5 h. Let the mixture cool down to room temperature and added 30% hydrogen peroxide (20 ml, 0.256 mol). When the reaction mixture turned into a yellow suspension, let precipitate form for 12 h. After the removal of liquid, centrifuged the mixture at 1 000 rpm for 10 min and rinsed with 8% HCl followed by DI water until...
pH 6 ~ 7. Continued centrifuging at 5 000 rpm for 10 min to remove excess graphite and thick GO plates. Finally, sonicated the mixture for 7 h to obtain GO solution.

2.4. Synthesis of Ag/GO nanocomposite

Ag/GO nanocomposite was synthesized using the method developed by Lei et al with slight modification [11]. AgNPs were synthesized by reducing silver nitrate on the surface of GO using sodium borohydride as a reducing agent. Added silver nitrate (0.15 g, 0.88 mmol) into GO (30 ml, 0.5 mg ml$^{-1}$) and stirred the mixture for 20 min at room temperature. Then, slowly added 0.2 M of sodium borohydride (10 ml, 2.00 mmol) into the mixture. Continued stirring for 2 h. Finally, centrifuged at 3 000 rpm for 10 min, then washed the mixture with distilled water several times, and finally slightly sonicated to disperse Ag/GO nanocomposite. The process is illustrated in figure 1.

2.5. Characterization of Ag/GO nanocomposite

2.5.1. Scanning electron microscope-energy dispersive x-ray spectroscopy (SEM-EDX)

The Ag/GO nanocomposite and the GO after dispersed in distilled water was dripped onto a 1 cm × 1 cm clean glass plate, then let the sample dried at 60°C for about 2 h. Magnified images were taken at different positions on the glass surface with an acceleration voltage of 10.0 kV, magnification of 2.00 kx; 5 kx; 20 kx and 30 kx, respectively. Resolution 1.2 nm at 30 kV and 2.3 nm at 3 kV. The functions of the microscope were controlled by the computer using the MiraTC software.

2.5.2. X-ray diffraction (XRD)

Crystallographic studies of synthesized GO and Ag/GO nanocomposite were analyzed using an x-ray diffractometer with Cu Kα ($\lambda = 1.5405$ Å, 40 kV, 40 mA) as a radiation source within 2$\theta$ = 10°–70° at the scan speed 0.4° min$^{-1}$. The size of AgNPs (D) was calculated by using Debye-Scherer’s equation:

$$D = \frac{K \times \lambda}{\beta \times \cos \theta}$$

Where: $\beta$ is the full width at half maximum height expressed in radians, $\theta$ is half diffraction angle, $\cos \theta$ value is in radians, $\lambda$ is the wavelength of the incident x-ray ($\lambda = 0.154$ nm), and K = 0.9 is the Scherrer factor.

2.5.3. Ultraviolet-visible spectrum (UV–vis)

The absorption spectrum of the Ag/GO nanocomposite dispersed in distilled water was measured using a Shimazu 1800 UV–vis spectrometer with range of wavelength from 600–200 nm.

2.6. Measuring PNP reduction reaction kinetics using Ag/GO photocatalyst

The Ag/GO nanocomposite was recovered by centrifuging at 5 000 rpm for 10 min, washing with distilled water, and then slightly sonicating to re-disperse Ag/GO. The Ag/GO-X nanocomposites (X = 1, 2, 3; where X was the number of time cycles) were obtained to investigate the reusable property.

Taken exactly 0.2 mM PNP (4 ml, 0.008 mmol), 0.2 M NaBH₄ solution (2 ml, 40 mmol), and 1 ml of the Ag/GO nanocomposite diluted 20-fold with distilled water. Immediately measured the UV–vis absorbance of the solution mixture with kinetic mode at 400 nm, the maximum absorption wavelength of p-nitrophenolate ions. Data were recorded every second for Ag/GO-1 samples and every 10 s for Ag/GO-2 and Ag/GO-3 samples. Because the concentrations of NaBH₄ were much higher than those of the PNP, the reduction reaction of PNP had a rate constant that follows the first-order reaction [4]. The catalytic reduction efficiency of PNP of the as-
A synthesized sample was calculated by the formula as follows:

\[
\text{Reduction or conversion(\%)} = \frac{A_0 - A_t}{A_0} \times 100\%
\]

Where: \(A_0, A_t\) are the absorbance of \(p\)-nitrophenolate at 0 (s) and \(t\) (s), respectively.

The reaction rate constant \((k)\) was determined from the linear plot of \(\ln\left(\frac{A_t}{A_0}\right)\):

\[
\ln\left(\frac{A_t}{A_0}\right) = -kt
\]

2.7. Synthesis of PAP using Ag/GO photocatalyst

Added sodium borohydride (1.14 g, 30 mmol) to 20 mL of Ag/GO-X nanocomposite and stirred this mixture for 3 min at room temperature. Gradually added PNP (1.00 g, 7.2 mmol) and stirred for 5 min. Filtered to obtain the solution. Crystallized PAP by cooling at 5 °C for about 72 h, then filtered the crystalline solid and dried at 50 °C.

The process is summarized in figure 2.

2.8. Statistical analysis

The diameter of AgNPs on GO surface was processed by using ImageJ software version 1.8.0_172. Particle size distribution graphs, XRD patterns of the GO and Ag/GO nanocomposite graphs, UV–vis molecular absorption spectrum, catalytic reaction kinetics were plotted by Origin 2021 software. The value of \(\ln\left(\frac{A_t}{A_0}\right)\) was calculated using Microsoft Excel 2016.
Figure 4. SEM micrographs of Ag/GO nanocomposite.

Figure 5. Particle size histogram of Ag/GO nanocomposite found on the SEM micrograph.

Figure 6. EDX of Ag/GO nanocomposite.
3. Results

3.1. Characterizations of and Ag/GO nanocomposite

3.1.1. Scanning electron microscope

Figure 3 shows SEM images of GO flakes and layers, indicating them to have a wavy, folded shape and to be in thin layers. The SEM images also showed that the GO material consists of individual sheets closely associated with each other (figure 3(A)). Additionally, the high-magnification image of the GO clearly reveals that it consisted of several layers stacked on top of one another like silky sheets of paper (figure 3(B)). These results suggest that thin layers of nanosheets formed the GO dispersion.

![Figure 3 SEM images of GO flakes and layers](image)

Figure 3. SEM images of GO flakes and layers.

| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| C       | 3.934      | 24.939     |
| O       | 0.668      | 3.179      |
| Na      | 1.387      | 4.595      |
| Cl      | 0.641      | 1.376      |
| Ag      | 93.370     | 65.910     |

Table 1. Elemental composition of Ag/GO nanocomposite.

![Figure 7 XRD patterns of the GO and Ag/GO nanocomposite](image)

Figure 7. XRD patterns of the GO and Ag/GO nanocomposite.

![Figure 8 UV–vis spectra of Ag/GO nanocomposite](image)

Figure 8. UV–vis spectra of Ag/GO nanocomposite.
SEM micrographs of Ag/GO nanocomposite are shown in figures 4(A) and (B). AgNPs have rather circular shapes that adhere onto the GO plates. However, AgNPs tend to be slightly bundled into groups.

The diameter of AgNPs on GO surface was evaluated using ImageJ software. Based on the SEM micrographs of Ag/GO nanocomposite, the distribution sizes of AgNPs ranged from 30–100 nm with an average diameter of about 65.75 nm (figure 5).

3.1.2. Energy dispersive x-ray spectroscopy
According to figure 6, the peaks at 2.99 keV and 3.17 keV correspond to the binding energy of the Ag atom, while the observed peak near 1.0 keV corresponds to the carbon atom [12].

As shown in table 1, the major elements in Ag/GO nanocomposite including C, O, Ag with 65.91% of AgNPs deposited on the GO surface. In addition, O atoms account for only small percentage, 3.18%.

3.1.3. X-ray diffraction
The x-ray diffraction analysis of the GO and Ag/GO nanocomposite was shown in figure 7. As it can be seen, the XRD pattern of GO shows a (002) sharp peak at $2\theta = 12^\circ$, corresponding to an interlayer distance $(d$-spacing) of about 0.73 nm, indicating that the graphite was well-exfoliated into individual GO sheets.

3.1.4. Ultraviolet-visible spectroscopy
UV–vis spectrum of Ag/GO nanocomposite display two absorption peaks at 268.5 nm and 410.5 nm (figure 8). The former of which is attributed to the surface plasmon resonance of AgNPs. The latter one is assigned to the electronic transition of GO.

3.2. PNP reduction reaction kinetics using Ag/GO photocatalyst
During the monitoring process, the absorption intensity of $p$-nitrophenolate at 402 nm decreased and a new peak at 300 nm appeared due to the formation of PAP (figure 9).

The catalytic reaction kinetics of PNP hydrogenation using Ag/GO nanocomposite and its recycled forms were shown in figure 10.

The reaction time and the reaction rate constant $k$ (s$^{-1}$) were calculated from the slope of the line. The results are summarized in table 2.

As shown in figure 11(A), the two peaks at 268.5 nm and 410.5 nm are not only different from the intensity but also from the shape. According to figures 10(B), (D), and (F), data were summarized in figure 11(B) to illustrate the linear slope decreased in line of Ag/GO-1, Ag/GO-2, and Ag/GO-3, respectively.

The ratio of two adsorption peaks related to Ag/GO nanocomposite changed remarkably depending on how many times the catalyst was recycled as shown in table 3.

3.3. Synthesis of PAP using Ag/GO photocatalyst
Purified PAP was checked by Thin Layer Chromatography (TLC) Silica gel 60 F254 (Merck) with chloroform: methanol solvent system (8:2, etc). The TLC assay showed only one spot with $R_f = 0.51$, corresponding to the standard PAP.
Figure 10. The catalytic reaction kinetics measurement of PNP reduction using Ag/GO and recycled Ag/GOs with kinetic mode at 400 nm. A, C, E: Time dependent UV–vis spectra of the PNP reduction reaction in the presence of the Ag/GO-1 and Ag/GO-2, Ag/GO-3. B, D, F: Plot of ln$(A_t/A_0)$ against the reaction time using Ag/GO-1, Ag/GO-1 and Ag/GO-3. The induction periods (t) are indicated by arrows; the apparent reaction constants (k), correspond to the linear slope in each curve.

Table 2. The results of the PNP reduction catalytic reaction kinetics measurement using Ag/GO nanocomposite.

| Photocatalyst | Time (min) | Reaction constant k (s$^{-1}$) | Half-life $T_{1/2}$ (s) | Yield (%) |
|---------------|------------|--------------------------------|------------------------|-----------|
| Ag/GO-1       | 3          | $18.19 \times 10^{-3}$          | 38                     | 96.45     |
| Ag/GO-2       | 30         | $1.31 \times 10^{-3}$           | 529                    | 97.94     |
| Ag/GO-3       | 48         | $0.92 \times 10^{-3}$           | 753                    | 96.67     |
The melting point of the product was 193.4 °C – 194.6 °C. The Fourier transforms infrared spectroscopy (FTIR), \( \nu_{\text{max}} \) (cm\(^{-1}\)): 3 329, 3 270 (NH\(_{\text{amid}}\)); 1 604, 1 461, 1 375 (C = C\(_{\text{ring}}\)); 955 (C–O) (figure 12). The UV–vis: \( \lambda_{\text{max}} = 297 \text{ nm} \) (figure 13).

## 4. Discussion

### 4.1. Synthesis and characterizations of Ag/GO nanocomposite

According to figure 7, as reported earlier, an increase in interlayer spacing is mainly due to the intercalation of water molecules and the presence of various oxygen-containing functional groups on the basal plane of the graphene sheet [13, 14]. For the Ag/GO nanocomposite, the three diffraction peaks were observed at 2\( \theta \) values of

![Figure 11](image1.png)

**Figure 11.** The correlation between UV–vis spectra and catalytic ability of Ag/GO nanocomposite after each time of recycling catalysts. A: The UV–vis spectra; B: Plot of ln(A\(_t\)/A\(_0\)) against reduction time using Ag/GO-1, Ag/GO-2, and Ag/GO-3.

![Figure 12](image2.png)

**Figure 12.** UV–vis spectra of the PAP standard and the PAP synthesized by the reduction of PNP using Ag/GO nanocomposite.

| Catalyst   | Ag/GO-1 | Ag/GO-2 | Ag/GO-3 |
|------------|---------|---------|---------|
| Ag/GO      | 1.1     | 1.08    | 1.01    |

Table 3. The ratio of two absorbance peaks at 410.5 nm and 268.5 nm related to Ag atom and GO after the reduction reaction of PNP by using Ag/GO-1, Ag/GO-2, and Ag/GO-3.
38.4°, 44.5° and 64.6° which are indexed to (111), (200), and (220) planes, respectively according to JCPDS card No. 04-0783 that it confirms to the growth of AgNPs based on the face-centered cubic structure [15, 16]. The XRD results clearly show that the AgNPs synthesized by the present method are crystalline in nature. The characteristic diffraction peak of GO was not detected in the Ag/GO sample, which might be because of the few amounts of GO. The size of obtained AgNPs is estimated at around 30 nm from the breadth of the (111) reflection. It has found that the nanoparticle size observed in SEM is larger than the nanoparticle in XRD, proving the agglomeration of nanoparticles. It should also be noted that in SEM (~ 30–100 nm), the grain size was measured by the difference between the visible grain boundaries, while in XRD the measurement was extended to the crystalline region that diffracted x-rays coherently. Therefore, the XRD measurements resulted in smaller size. The Ag/GO nanocomposite synthesized in our study has a small size, more uniform size distribution on the GO surface with the average particle size of AgNPs estimated at around 30 nm.

As shown in table 1, the elemental analysis of the Ag/GO nanocomposite was performed by EDX, which confirmed that the major elements in Ag/GO nanocomposite including C, O, Ag with 65.91% of AgNPs deposited on the GO surface. The peaks at 2.99 keV and 3.17 keV correspond to the binding energy of the Ag atom, while the observed peak near 1.0 keV relates to the carbon atom [12]. In addition, The O atom seized only small percentage, 3.18%, which could be explained by the reduction of GO to form rGO by the reducing agent sodium borohydride, according to Muda et al [17]. Results also indicate that AgNPs were efficiently formed on the GO surface. However, because the washing process of GO and Ag/GO nanocomposite did not completely remove impurities, the sample also has the presence of elements Na and Cl remaining after the reduction by NaBH4 and washing process of Ag/GO nanocomposite.

In figure 8, a strong intensity of the peak at 410.5 nm suggests that AgNPs were formed with high concentration, while the absorption peak at 268.5 nm corresponds to the π→π* transition of the aromatic C–C bond [18]. The absorption peak at 410.5 nm, due to the surface plasmon resonance effect of silver nanoparticles, reveals the presence of silver nanoparticles on the GO sheet [18].

### 4.2. The reaction kinetics of PNP reduction using Ag/GO photocatalyst

When sodium borohydride was added to the PNP solution, the pH of the solution altered from a weakly acidic condition to a strong base due to the presence of nitrophenolate ions [19]. After adding Ag/GO, electrons from BH4− were accepted by nitrophenolate ions and the reduction of PNP to PAP takes place rapidly on the surface of AgNPs adhering to GO background. Therefore, the absorption intensity of p-nitrophenolate at 400 nm decreased and a new peak at 300 nm appeared (figure 9).

According to figure 10, the PNP hydrogenation catalytic reaction time was longer after every time catalysts were reused. It is obvious that reaction time (t) increased while reaction constant (k) decreased when we used Ag/GO-1, Ag/GO-2, and Ag/GO-3. These results clearly showed that the catalytic activity of Ag/GO was slightly reduced after each time of reusing.

Figure 11(A) shows that the ratio of two adsorption peaks related to Ag/GO nanocomposite changed remarkably depending on how many times the catalyst was recycled. These two peaks not only differ from intensity but also from shape. In terms of the Ag/GO-1, the absorption spectrum has two clearly distinguished...
Table 4. Comparison efficiency of Ag/GO nanocomposite with some catalysts reported for reaction kinetics of PNP reduction.

| No. | Catalyst | Conditions                  | Time (min) | Yield (%) |
|-----|----------|-----------------------------|------------|----------|
| 1   | Fe₃O₄ Ni MNPs [25] | Glycerol, KOH, 80 °C         | 210        | 88       |
| 2   | PdCu/graphene [26]  | NaBH₄, EtOH: H₂O (1:2), 50 °C | 90         | 98       |
| 3   | Fe-phenanthroline/C [27] | N₂H₄·H₂O, THF, 100 °C      | 600        | 97       |
| 4   | Ni-Fe mixed oxide [28] | N₂H₄·H₂O·propan-2-ol, reflux | 105        | 93       |
| 5   | AgNPs [21] | NaBH₄·H₂O, t° room           | 75         | 96       |
| 6   | GO/AgNPs [20] | NaBH₄·H₂O, t° room           | 20         | 96       |
| 7   | Ag/GO [24] | NaBH₄·H₂O, t° room           | 8          | 79.5     |
| 8   | Ag/GO (This study) | NaBH₄·H₂O, t° room           | 3          | 97       |

MNP: magnetic nanoparticles, THF: tetrahydrofuran, AgNPs: silver nanoparticles.

peaks, whereas the absorption peaks related to Ag/GO-2 and Ag/GO-3 are broad and not well-defined. As shown in table 3, the amount of AgNPs on the GO surface decreases gradually after each time of recycling Ag/GO nanocomposite. Combined with the linear slope difference in figure 11(B), it can be concluded that the catalytic activity of Ag/GO nanocomposite was slightly reduced after each time of recycling when washing the photocatalyst by performing centrifugation and ultrasonication. Lu et al recovered Ag/GO nanocomposite by centrifugation, the catalytic activity of Ag/GO nanocomposite between times did not show any significant change [20]. Because during the catalysis process, the concentration of Na⁺ is high enough to cause Ag/GO nanocomposite to be aggregated, leading to a decrease in its large surface area, so it is better to use ultrasonication to re-disperse Ag/GO nanocomposite. However, using ultrasonication to re-disperse the Ag/GO nanocomposite may have separated the AgNPs from the GO surface as well as lost the amount of Ag/GO nanocomposite, thereby reducing the catalytic activity. Although the reaction time is increased by 10–16 times, the reaction efficiency is still high.

Some reports used other photocatalysts shown in table 4. We can acknowledge that Ag/GO nanocomposite has much better catalytic ability in reaction time and efficiency than other catalysts such as Fe₃O₄ Ni MNPs, AgNPs, PdCu/graphene, Fe-phenanthroline/C, Ni-Fe mixed oxide. Using the same AgNPs but distributed on GO background showed superior time efficiency compared to the research conducted by Al-Marhaby et al, in which the reaction time was as high as 25 times [21]. This can be because GO contains many oxygen-containing functional groups such as hydroxyl, carbonyl, and carboxyl [22]. The carboxyl anions not only adsorb Ag⁺ ions but also make the GO sheets farther apart by electrostatic repulsion, enabling Ag⁺ ions to attach to the GO sheets. As GO and Ag⁺ ions are reduced, rGO layer structure and electron transfer between AgNPs and aromatic rings of GO can limit the movement of AgNPs [23]. Therefore, GO ensured the high dispersion of AgNPs and prevented their agglomeration, thereby providing a higher surface area and active absorption sites for the reaction [7]. In this study, the better catalytic efficiency is showed to correlate with higher Ag/GO nanocomposite concentration, and the reaction time is reduced more than six times compared to the study of Lu et al [20], and about three times compared to Li’s research [24] with a higher reduction efficiency.

4.3. Synthesis of PAP using Ag/GO photocatalyst

Conventionally, PAP was manufactured by the reduction of PNP using the iron-acid. The major disadvantage of this method was the generation of a large amount of Fe-based sludge [2]. To our best knowledge, no study has been conducted and published on the utilization of Ag/GO nanocomposite to photocatalysis the reduction of PNP to yield crystallized PAP. PAP was synthesized with high purity and the total crystallization yield of 45.82%.

5. Conclusions

In this study, we successfully synthesized Ag/GO nanocomposite and studied its photocatalytic properties in the hydrogenation reaction of PNP. The Ag/GO nanocomposite was prepared by reducing silver nitrate on graphene oxide (GO) using sodium borohydride as a reducing agent. The AgNPs on the surface of GO are relative homogeneity in distributions and particle sizes depicted on the SEM micrographs. The calculated results from the Scherrer formula indicate that the average particle size of AgNPs was around 30 nm. The catalytic ability was investigated based on the hydrogenation reaction of PNP. The results showed that Ag/GO nanocomposite has an excellent catalytic activity with reaction constant $k = 18.19 \times 10^{-3} \text{ s}^{-1}$ and the yield of reduction reaction at 97%. Moreover, this Ag/GO nanocomposite photocatalyst can be easily recovered and reused three times with no significant loss of reaction efficiency. Furthermore, Ag/GO nanocomposite is safe, less toxic, and environmentally friendly. Since we have also successfully synthesized and crystallized PAP with high purity and total yield of 45.82%, which could be used as an intermediate in the synthesis of paracetamol. In
short, Ag/GO nanocomposites can be used as a promising material for photocatalytic reactions. However, some issues are still existed, the catalytic ability of Ag/GO decreases gradually after each time of recycling due to the agglomeration of AgNPs on GO surface while synthesizing Ag/GO nanocomposite, and the decrease in the amount of Ag/GO nanocomposite after recycling by ultrasonication that separates the AgNPs from the GO surface. In future, it is essential to optimize the fabrication as well as the recycling process of Ag/GO nanocomposite to enhance the catalytic ability of recycled forms.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Competing interests

The authors declare that we have no competing interests.

Author’ contribution

All authors contributed to designing and conducting experiments, data analysis, and interpretation as well as drafting and revising the manuscript. The authors read and approved the final manuscript.

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