Facile synthesis of solar active charcoal passivated Ag$_3$PO$_4$ and their two-channel mechanisms for H$_2$O$_2$ formation in aerated water

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Abstract

This work presents the use of activated charcoal passivated-Ag$_3$PO$_4$ (CAgP) and bare Ag$_3$PO$_4$(AgP) nanoparticles (NPs) as effective photocatalysts for the generation of hydrogen peroxide (H$_2$O$_2$) in air-saturated water containing either formic acid (FA) or silver nitrate (AgNO$_3$). The synthesized CAgP and pristine AgP were characterized using various state-of-the-art optical and electron microscopy techniques. The CAgP composites showed remarkable photocatalyzed H$_2$O$_2$ formation compared to bare AgP NPs. The CAgP photocatalyzed-assisted H$_2$O$_2$ formation from O$_2$-saturated water under sunlight was achieved via two-channel mechanisms. First, in the presence of FA as a hole scavenger, enhanced H$_2$O$_2$ formation was facilitated by decomposition of FA to produce proton (H$^+$), followed by a spontaneous reduction of dissolved molecular oxygen by the photo-excited electrons. The second photocatalytic pathway involves the formation of H$_2$O$_2$ in the absence of electrons (using AgNO$_3$ as an electron scavenger) which occurred via oxidation of H$_2$O by photo-induced holes to generate hydroxyl radicals ($^\bullet$HO) and the combination of photogenerated $^\bullet$HO to produce H$_2$O$_2$. The most notable feature of CAgP composite as a photocatalyst is the ease of H$_2$O$_2$ formation in O$_2$/H$_2$O and O$_2$/H$_2$O/FA system, as well as the ability to reuse the recovered CAgP catalyst for a few reaction cycles without losing substantial catalytic activity or mass.

Keywords: Ag$_3$PO$_4$ nanoparticles; hydrogen peroxide formation; hole scavengers; photocatalysis; electron scavengers; charcoal passivated Ag$_3$PO$_4$.

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Introduction

Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) is a colourless liquid that easily mixes with water or other organic solvents to produce non-toxic reagents [1]. Because of its nontoxicity and greener nature, H\textsubscript{2}O\textsubscript{2} is a superior energy transporter or storage system than H\textsubscript{2} and may be safely moved from one location to another [2,3]. For many decades after its discovery and isolation in 1818 by Louis Jacques Thenard [4], H\textsubscript{2}O\textsubscript{2} has consistently played a central role as a versatile oxidant in a variety of applications, including deodoriser for wastewater purification, disinfectant or antiseptic for wounds dressing and mouthwash, organic chemical synthesis and transformation, and as a bleaching agent in the textile and paper industries [5]. H\textsubscript{2}O\textsubscript{2} spontaneously decomposes into water and oxygen (2H\textsubscript{2}O\textsubscript{2} → 2H\textsubscript{2}O + O\textsubscript{2}) as the two major products when exposed to ultraviolet (UV) or visible light, thus adding to the safety of its use in industry and at home [2,3]. To increase small-scale synthesis and satisfy expanding demand, researchers are exploring other cost-effective and sustainable methods of producing H\textsubscript{2}O\textsubscript{2} utilizing low-cost catalytic materials [2].

The current large-scale industrial production of H\textsubscript{2}O\textsubscript{2} relies on a BASF-developed anthraquinone auto-oxidation (AO) technology, in which alkylanthraquinone (AAQ) sequentially undergo hydrogenation reactions in the presence of palladium catalysts to form dihydroanthraquinone (DAQ) (AAQ + H\textsubscript{2} \rightarrow DAQ), followed by oxygenation of the resultant DAQ to yield H\textsubscript{2}O\textsubscript{2} and AAQ (DAQ + O\textsubscript{2} → H\textsubscript{2}O\textsubscript{2} + AAQ) [2,5]. The AO technique requires large energy consumption for the hydrogenation and oxidation stepwise reactions and therefore not cost-effective or practicable for small-scale H\textsubscript{2}O\textsubscript{2} synthesis [2]. The direct mixing of H\textsubscript{2} and O\textsubscript{2} gases on the other hands, which has been proposed as an alternative approach to anthraquinone oxidation method for H\textsubscript{2}O\textsubscript{2} production over noble metal catalysts, is also regarded to be environmentally unsafe due to the possibility of explosions from the mixing of H\textsubscript{2} and O\textsubscript{2} gases [6,7]. As a result of the evaluations of the available technologies, the advanced oxidation process (AOP) driven by UV or visible light radiation in the presence of a suitable photocatalyst is a sustainable and cost-effective option for producing H\textsubscript{2}O\textsubscript{2} using water and atmospheric oxygen as the only primary ingredients [8].

Photocatalytic advanced oxidation processes utilizing visible-light-driven catalytic materials, including TiO\textsubscript{2}, g-C\textsubscript{3}N\textsubscript{4}, Ag\textsubscript{2}O\textsubscript{3}, AgX (X, Cl, Br, I), and other silver-based photocatalysts, have been reported by different research groups to produce significant amounts of H\textsubscript{2}O\textsubscript{2} from aerated water in the presence of hole and electron scavengers [2,9-11]. Silver-based photocatalysts, in
particular, have demonstrated outstanding photocatalytic performance to thermodynamically drive
the formation of H$_2$O$_2$ due to their conduction band edges being more negative ($<$ 0.6 eV vs. NHE, pH 7) than the redox potential of O$_2$/H$_2$O$_2$ at 0.68 eV vs. NHE, and their
valence band edges being lower (more positive) than the redox potentials of OH$^-$/OH and O$_2$/H$_2$
O at +1.99 and +1.23 eV (vs. NHE, pH 7), respectively [10,11]. The remarkable photocatalytic
performances of silver-based photocatalysts are however tainted by their uncontrollable
decomposition and photo-corrosion caused by the interaction of surface plasmon resonance of Ag$^+$
with photo-excited electrons, which transforms Ag$^+$ into black metallic Ag$_0$ particles when exposed
to UV or visible photons for long periods of time [12,13]. Yang and coworkers [14] reported that
using graphene (GR) and graphene oxides (GO) as stable coverage of Ag$_3$PO$_4$ effectively shielded
the Ag$_3$PO$_4$ from photo-decomposition and restrained the recombination of photo-induced electron
with holes during photocatalysis, resulting in improved photostability and performance of Ag$_3$PO$_4$-
graphene composites over bare Ag$_3$PO$_4$. The bare Ag$_3$PO$_4$ catalyst which is proposed in the current
work has high tendency to decompose into Ag$_0$ and PO$_3^{4-}$ (Ag$_3$PO$_4$ + 3e$^- \rightarrow$3Ag$_0$ + PO$_3^{4-}$) when
irradiated in the absence of photo-thermally stable solid supports such as carbon-based
nanostructures [14]. Thus, activated charcoal is proposed here as a solid support to passivate
Ag$_3$PO$_4$ in order to fabricate activated carbon-Ag$_3$PO$_4$ (CAgP) composite with overall improved
stability, catalytic activity, and performance for photocatalyzed H$_2$O$_2$ production.

Herein, raw coconut hardwood charcoal was first acidified in 0.1 M HCl to remove alkaline and
alkaline-earth metals from its surface and endow it with various oxygen functional groups that
provided active sorption sites for Ag$^+$ (aq. AgNO$_3$) via electrostatically driven interaction,
followed by the precipitation of Ag$_3$PO$_4$ using disodium hydrogen phosphate (Na$_2$HPO$_4$). Pal et
al. [11] fabricated magnetically recyclable photocatalysts for H$_2$O$_2$ formation using starch
functionalized Fe$_3$O$_4$@Ag@Ag$_2$O nanocomposites. They demonstrated that the best photocatalyst
(C1), with VB and CB edges at 2.63 and 0.4 eV, respectively, thermodynamically facilitated water
oxidation and 2e$^- \rightarrow$ reduction of molecular oxygen to produce H$_2$O$_2$ [11]. Interestingly, the photo-
induced holes in AgP/CAgP have a better thermodynamic driving force than C1 to generate •OH
radicals and water oxidation to produce H$_2$O$_2$, because the potentials of the top of VB of
AgP/CAgP are more positive at 2.79-2.84 eV than the VB edge of C1. Similarly, the edges of CB
of AgP/CAgP are more negative than 0.68 eV, indicating that photocatalytic formation of H$_2$O$_2$ in
O$_2$-saturated water is a high possibility. Thus, through 2e$^- \rightarrow$ reduction of O$_2$ and water oxidation,
both AgP and CAgP satisfy two-channel pathways for H$_2$O$_2$ formation. When the reaction is carried out in the presence of hole scavengers such as organic acids and alcohols, photo-excited electrons at the CB constitute the main driving factor for the production of H$_2$O$_2$ [11,15]. Photo-induced holes also drive the formation of H$_2$O$_2$ at the VB when an electron scavenger such as silver nitrate is added to the O$_2$-water system [10,15]. Premised on the above, the photocatalytic performances of bare AgP and CAgP for the generation of H$_2$O$_2$ in the presence of hole and electron scavengers were tested. Also, the two-channel plausible mechanisms for the formation of H$_2$O$_2$ in water at VB and CB were elucidated.

2.0. MATERIALS AND METHODS

2.1 Material

Silver nitrate (AgNO$_3$, > 99.7%), Potassium titanium oxalate dihydrate (PTO, K$_2$[TiO(C$_2$O$_4$)$_2$].2H$_2$O, formic acid (FA, 85%), benzoquinone (BQ), isopropyl alcohol (iPA) and sodium phosphate dibasic dodecahydrate (Na$_2$HPO$_4$.12H$_2$O) were purchased from Sigma Aldrich. Methanol, ethyl alcohol ethanol (%), Commercial H$_2$O$_2$(30% v/v) sodium hydroxide (NaOH), hydrochloric acid (HCl) and deionized water was purchased from Pascal Scientific Limited, Nigeria, and were used as received without purification.

2.2 Materials syntheses

2.2.1 Preparation of raw charcoal

The raw coconut hardwood charcoal (200 g) was graciously donated to our laboratory by Prime Coal Plant, Lagos, Nigeria, and the product description as provided by the supplier are listed in Table 1. The charcoal was washed three times with deionized water to remove sands and debris, and then dried in an oven at 60°C for 12 h. Thereafter, it was ground with a mortar and pestle, then pulverized into fine particle sizes using an electric blender (Model: HFB-3489, China). The pulverized charcoal was then sieved for uniform particle size distribution using a 0.25nm sieve and stored for further use.

Table 1: Supplier description of coconut hardwood charcoal
<table>
<thead>
<tr>
<th>Coconut hardwood charcoal (Wt)</th>
<th>Specifications (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed carbon content</td>
<td>86</td>
</tr>
<tr>
<td>Ash content</td>
<td>3 (Max. on Dry Basis)</td>
</tr>
<tr>
<td>Moisture</td>
<td>5</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>3</td>
</tr>
<tr>
<td>Burning time</td>
<td>3.5 h</td>
</tr>
<tr>
<td>Shape</td>
<td>Irregular lengths (3-28cm)</td>
</tr>
</tbody>
</table>

### 2.2.2 Preparation of charcoal-supported silver phosphate composite (C\textsuperscript{AgP})

The powdered particles of the hardwood charcoal were acidified with HCl to remove the oxides of alkaline and alkaline-earth metals present in the charcoal and to enhance its surficial and textural properties prior to immobilization of AgP. Briefly, 1 g of charcoal powder was stirred in 100 mL of HCl (0.1 M) solution at 60°C for 1 h. The treated charcoal was recovered by centrifugation, washed with DI water and dried at 80°C for 24 h. Silver phosphate NPs was adsorbed to the surface of the treated charcoal by precipitation method to prepare charcoal-supported AgP (C/AgP) composites. Typically, 0.1 g of acidified charcoal was sonicated in deionized water (100 mL) for 3 h to give charcoal aqueous dispersions. Then 0.5 g of \( \text{AgNO}_3 \) in deionized water (50 mL) was added drop wise to the charcoal dispersions and the mixture was further sonicated for 3 h to ensure optimal charcoal-\( \text{Ag}^+ \) adsorption-desorption equilibrium. Under constant stirring, aqueous solution of \( \text{Na}_2\text{HPO}_4\cdot12\text{H}_2\text{O} \) (1 M, 50 mL) was slowly added into the charcoal-\( \text{Ag}^+ \) solution at the rate of 5 mL/min for 10 min. The resulting black-yellow precipitate of C/AgP composite was magnetically refluxed for another 5 h at 80°C. The product (C/AgP) was washed by centrifuge using deionized water and with absolute EtOH, and dried at 60°C for 12 h. For comparison, pristine silver phosphate (AgP) NPs were prepared by the same method reported for CAgP composite but without treated charcoal. The synthesized CAgP and AgP were kept in a dark container and stored.

### 2.3. Materials characterization
The solid reflectance spectra of charcoal, AgP and CAgP were recorded on a Shimadzu UV-VIS-NIR Spectrophotometer UV-3100 with a MPCF-3100 sample compartment with samples mounted between two quartz discs which fit into a sample holder coated with barium sulfate. The spectra were recorded over the wavelength range of 800-300 nm, and the scans were conducted at a medium speed using a 20 nm slit width. Fourier transform infra-red (FTIR) spectra were recorded on a Thermo Fisher Scientific FTIR spectrophotometer, using pressed KBr pellets. Transmission electron microscope (TEM) images of the samples were recorded using a JEOL JEM-2010 electron microscope operating at 200 KV. Surface morphologies of AgP and CAgP were analysed using a scanning electron microscope (SEM) equipped with energy dispersive analysis of X-ray equipment (EDAX) (XL 30 FEG ESEM). Raman spectroscopy Raman spectra for the samples were collected using a WITec alpha 300 RAS+ confocal micro-Raman spectrometer (Ulm, Germany) with 532 nm laser wavelength and a spectral acquisition time of 120 s was used to characterize the sample. To minimize the heating effects of the sample, a power of 3.41 mW was applied to the samples. X-ray photoelectron spectroscopy (XPS) analysis of the AFe was performed on a Kratos Axis Ultra X-ray Photoelectron Spectrometer equipped with a monochromatic Al Kα source (1486.6 eV). The hydrodynamic size distributions of AFe NPs, AFeAMX composite and AMX were measured using Malven Dynamic Light Scattering (DLS), Malven, UK. The XRD spectra of the samples were obtained with Bruker D8 ADVANCE diffractometer (Germany) using Cu Kα (1.5406 Å) radiation.

2.4 Photocatalytic formation of hydrogen peroxide (H₂O₂)

Photocatalytic hydrogen peroxide formation over pristine AgP and CAgP photocatalysts were investigated using O₂-saturated deionized water system under natural solar illumination. In a typical representative photocatalytic experiment, 20 mg of AgP or CAgP were dispersed into 50 mL of DI in 250 mL round bottom flask, and the suspension was sonicated for 1 h under dark to ensure complete dispersion of the catalyst in solution and establish adsorption-desorption equilibrium of the reacting mixture. Prior to solar illumination, the reaction mixture was bubbled with O₂ through a syringe needle, and the reaction vessel mounted on a retort stand at a 60° angle and directly irradiated for 5 h by natural sunlight of an average intensity of 615.42 W/m². Samples from the reacting mixture were regularly withdrawn at 1 h of solar irradiation, and filtered with syringe filter to separate the catalysts from the filtrates. The concentrations of hydrogen peroxide
in the filtrates were determined by colorimetrically using potassium titanium oxalate-sulfuric acid (PTO) reagents [16, 17].

2.4.1. Colorimetric analysis of H$_2$O$_2$

The amount of H$_2$O$_2$ generated was determined colorimetrically using potassium titanium oxalate method [17]. A stock solution of titanium oxalate reagent containing mixture of K$_2$[TiO(C$_2$O$_4$)$_2$].2H$_2$O (0.02 M), and conc. H$_2$SO$_4$ (0.5 M) was prepared in 250 mL volumetric flask and used for further studies. The yield of H$_2$O$_2$ in the recovered filtrate was determined as follows: 2.5 mL each of the recovered filtrate and the titanium oxalate reagent was pipette into 10-mL flask and make up to the mark with deionized water. Blank solution of titanium reagent (2.5 mL) diluted to 10 mL mark was also prepared without the addition of the filtrate (peroxide). The absorbance of both blank and test samples were measured on the UV-Vis spectrophotometer at wavelength of ca. 400 nm, corresponding to the $\lambda_{max}$ of titanium (IV)-peroxide complex, Scheme 1. The molar concentration of H$_2$O$_2$ (in mol/L) was determined by subtracting the absorbance of the blank solution ($A_b$) from the absorbance of peroxide-containing filtrate ($A_p$) at wavelength of 400 nm using Eqn. 1:

$$[\text{H}_2\text{O}_2] = \frac{A_p - A_b}{x \epsilon_{400}} \cdot V_T$$

where $\epsilon_{400}$ is the molar absorptivity of titanium (IV)-peroxide complex (9351/mol$^{-1}$cm$^{-1}$); $A_b$ and $A_p$ are respectively the absorbance of the blank and peroxide solutions; $x$ is the volume of the peroxide solution (2.5 mL or 25 cm); $l$ is the path length (in cm) of the spectrophotometer cell, and $V_T$ is the total volume of the blank or peroxide solution (10 mL or 100 cm).

2.4.1.1. Standard calibration curve for hydrogen peroxide (H$_2$O$_2$) solution

A stock solution of the hydrogen peroxide (H$_2$O$_2$) solution was prepared by diluting 1 mL of commercial H$_2$O$_2$ (30% v/v) to 2000 mL using double distilled water. Further dilutions were made by adding 5 mL of acidified PTO reagents (0.02 M PTO and 0.05 M H$_2$SO$_4$) separately to 0.2, 0.4, 0.6, 0.8 and 1 mL from the standard H$_2$O$_2$ solution and diluted them to 10 mL separately in five different labelled conical flasks. The standard calibration curve was plotted between known concentrations (0.2 to 1 mL) of H$_2$O$_2$ solutions against their respective absorbance at a wavelength.
of 400 nm ($\lambda_{max}$ of PTO-H$_2$O$_2$ complex) on UV-Vis spectrophotometer. H$_2$O$_2$ concentration formed over the photocatalysts was extrapolated from the plotted standard calibration curve [18].

Scheme 1: Reaction between acidified potassium titanium oxide oxalate, PTO, and hydrogen peroxide to give titanium (IV)-peroxide complex.

Blank experiments were also carried out to determine the importance of solar irradiation, photocatalyst(s), and electron donor for hydrogen peroxide formation. The blank experiments were either conducted with only photocatalysts dispersed in O$_2$-saturated DI water but no electron donor (formic acid), or with formic acid (5%) in solution but no photocatalysts. Experiments in the presence of both photocatalysts and formic acid under dark reaction conditions were also conducted to demonstrate the importance of solar irradiation for the formation of hydrogen peroxide.

2.4.2 *In situ* active species capture experiment

Photocatalytic trapping experiments to investigate the role of active species and their mechanistic pathways during the formation of hydrogen peroxide over as-synthesized photocatalysts were carried out using silver nitrate (AgNO$_3$), benzoquinone (BQ), and isopropyl alcohol (iPA) as radical scavengers to mask the *in-situ* formation of electron, $\cdot$O$_2$, and hydroxyl radical ($\cdot$OH), respectively. The procedures for the experiments were similar to the method reported for the photocatalytic formation of hydrogen peroxide in the presence of AgP and CAgP, except that 1 mM of scavengers were separately added to the solution and the mixtures were irradiated for 6 h under sunlight.

3. Results and discussions

3.1. Phase structure analysis

Figure 1 displays the phase structures of treated charcoal, pristine AgP and CAgP composite as elucidated using XRD technique. The characteristic X-ray diffraction patterns of treated charcoal
at $\theta = 24^\circ$, and $26.78^\circ$ are typical of graphite-type reflections and consistent with the peaks of carbon-based biomass[19, 20], while the distinct diffraction patterns of pristine AgP at $\theta = 20.8^\circ$, $(110)$, $29.6^\circ$, $(200)$, $33.2^\circ$, $(210)$, $36.5^\circ$, $(211)$, $42.8^\circ$, $(220)$, $47.6^\circ$, $(310)$, $52.6^\circ$, $(222)$, $54.8^\circ$, $(320)$, $57.1^\circ$, $(321)$ conform well with the standard diffraction planes of body centred cubic and crystalline Ag$_3$PO$_4$ with JCPDS card No. 71-1836, Figure 1. All the diffraction patterns in pure AgP are conspicuously visible in the diffractogram of the CAgP composites. The crystallinity and intensity of diffraction patterns of AgP in CAgP are however lower than the pure AgP, due to the change in the environment of AgP after composition with charcoal. The absence of diffraction peaks of charcoal in the XRD patterns of CAgP is due to the low weight percentage (wt%) of charcoal used for the preparation of the composite.
Fourier-transform infrared spectroscopy (FTIR) was used to validate the successful formation of the samples and also to confirm the presence of functional groups on their surfaces, Figure 2. The presence of vibrational peaks at 3000, 1654, and 1701 cm\(^{-1}\), attributed to OH stretching, OH bending, and C=O stretching vibrations, respectively, confirm the presence of oxygen functionalities on the surface of treated charcoal, Figure 1a. In the FTIR spectrum of pure AgP,
characteristic peaks at 563, 1025 and 1412 cm\(^{-1}\) are respectively attributed to the bending vibration of O=P-O, and stretching vibrations of P=O (in PO\(^3\)\(^{-}\)) and P–O–P (HPO\(^2\)\(^{-}\) ions) [21-23], suggesting successful AgP formation. The presence of adsorbed water molecules on the surface of AgP is confirmed by the stretching and bending vibrations of OH groups at 2771-3681 cm\(^{-1}\) and 1592 cm\(^{-1}\), respectively. The bending and stretching vibration bands of the phosphate and OH groups in the FTIR spectrum of pure AgP are also present in the spectrum of CAgP, with the exception that due to the presence of charcoal, these peaks are slightly shifted to either lower or higher wavenumbers, confirming physical interaction between AgP and the treated charcoal to form CAgP. Similar observations have been reported when Ag\(_3\)PO\(_4\) nanocrystals were immobilized on carbon nanostructures [21-23]. Due to the low content of charcoal used in the preparation of the composite, the vibrational bands of charcoal were masked by the strong and intense vibrational bands of AgP in the FTIR spectrum of CAgP.

![Figure 2. FTIR spectra of charcoal, bare AgP and CAgP composites.](https://ssrn.com/abstract=4091672)
of PO$_4^{3-}$ ions, respectively, Figure 3 [26]. The D band at 1380 cm$^{-1}$ and the G band at 1597 cm$^{-1}$ in the Raman spectrum of treated charcoal are attributed to the chaos of crystalline structures and deflection structures that are typical of carbonaceous materials [27, 28]. The presence of two prominent D and G vibrational bands associated with the charcoal at 1376 and 1605 cm$^{-1}$, respectively, as well as the intense symmetric vibrational band due to PO$_4^{3-}$ ions at 912 cm$^{-1}$, substantially confirm the coexistence of AgP and charcoal in the CAgP composite. The ratio of intensity of D band to G band, ($I_D/I_G$), was used to determine the degree of structural amorphization of the charcoal before and after composition. The calculated $I_D/I_G$ values of treated charcoal and CAgP are $\approx 0.86$, indicating that in the presence of AgP, the graphitic crystallite layers of the charcoal remained relatively intact and undistorted. The $I_D/I_G$ ratio of ~0.86 reported for charcoal and CAgP in this work are consistent with literature reports ranging from 0.86-1.20 [29]
The surface features of the prepared samples were revealed using a scanning electron microscope (SEM) in Figure 4. Figure 4a shows that the cascading layers (layers upon layers) of the graphitic structures of treated raw charcoal as viewed under SEM has rough surfaces and distorted shapes or sizes. The pristine AgP sample without charcoal had nanospherical morphologies with irregular sizes ranging from $0.4 \text{ – } 0.5 \mu m$, as revealed by the SEM image in Figure 4b. Because of the intra-particle interactions caused by their high surface energies in the nanoscale, the bare particles (of AgP NPs) appeared to aggregate and grow in size, Figure 4b. The AgP particles adhered to the surface of treated charcoal in the SEM image of CAgP composite, which is consistent with the graphitic layers of raw charcoal not being distorted during composition, Figure 4c. After being tethered to the surface of the charcoal to form CAgP, the shape of AgP particles remained fairly similar but the average sizes of the grains slightly reduced to $\approx 0.25 \text{ – } 0.4 \mu m$. Figure 4d shows that the major elemental compositions in CAgP composite are C, Ag, O, and P, and no other unwanted elements are detected, validating that CAgP was successfully formed and recovered in its pure form. The quantitative analysis from the EDX spectrum showed that the weigh% of C K, O K, P K, Ag L are 5.31, 18.85, 5.42 and 70.42%, respectively.
Figure 4: Scanning electron microscope images of (a) activated charcoal, (b) bare AgP (c) activated charcoal passivated AgP (CAgP), and (d) Energy-dispersive X-ray spectroscopy (EDX or EDS) analysis of CAgP.

The transmission electron microscope (TEM) was also used to investigate the nanostructures and morphologies of the prepared samples after sonication in abs. ethanol. TEM micrograph of treated raw charcoal appeared as roughened layers of thin-sheets stacked on top of one another, Figure 5a. Figure 5b shows that the uncoated particles of AgP clearly interacted with other neighbouring particles in solution, resulting in highly aggregated particles [30]. By contrast, surface of the charcoal became coarse after grains of AgP was tethered to it, indicating that the CAgP composite
was successfully formed, Figure 5c. The addition of charcoal as a solid substrate reduced the grain particle sizes of AgP, as well as reducing aggregation and improving the overall stability of the composite compared to pure AgP. The performance of the composite under light illumination will be improved due to the increased stability and reduced nanoparticle agglomeration.

![Figure 5: Transmission electron microscope (TEM) micrographs of (a) activated charcoal, (b) bare AgP, (c) CAgP and (d) enlarged image of CAgP under investigation from Figure 5c.](image)

To elucidate the size distribution (hydrodynamic) of the synthesized samples, dynamic light scattering (DLS) measurements were performed at 50 μg/mL for each sample in a mixture of methanol:water (1:10 v/v) [31]. According to the DLS data, raw charcoal has a size distribution ranging from 120 – 960 nm. At a maximum intensity of ≈ 35 percent, the size distribution of pure AgP peaked at 530 nm, while the particle size of the CAgP composite shifted slightly to 459 nm, with maximum intensity peaking at 30%, Figure 6.
Figure 6: Dynamic light scattering (DLS) measurements of activated charcoal, bare AgP and CAgP composite.

The UV-Vis diffuse reflectance spectra of the photocatalysts (bare AgP and CAgP composite) and treated raw charcoal were used to investigate their energy band gap structures and light (UV or visible) absorption potentials, Figure 7. The UV absorption spectrum of treated charcoal shows intense absorption peak within the UV region at 260 nm which is due to the $\pi-\pi^*$ electronic transition of $sp^2$ graphitic carbon [32, 33], and no obvious absorption peak was observed in the visible region. Both AgP and CAgP show wide and strong absorption bands covering the entire UV and visible regions. In the UV-Vis absorption spectra of bare AgP and CAgP composite, the onset (wavelength) absorption band edges are 525 and 551 nm, respectively. The energy band gap of AgP at onset wavelength of 525 nm is 2.36 eV, while the energy band gap of CAgP extrapolated at absorption edge of 551 nm is 2.25 eV, Using Eq. 2.

$$E_g (eV) = 1240/\lambda$$

Where $E_g$ is energy band gap (eV); and $\lambda$ is onset (wavelength) absorption measured in nm.
Figure 7: UV-Vis diffuse reflectance spectra of activated charcoal, bare AgP and CAgP composite.

The chemical constituents of CAgP composite and their atomic valence states was examined using X-ray photoelectron spectroscopy (XPS). From Figure 8, the overview of XPS analysis of CAgP composite shows that the wide survey has signals of P2p, C1s, Ag3d, O1s, Ag3p3, and Ag3p1 at binding energy of 133.4, 284.3, 367.1-373.4, 527, 573.4, and 604.1 eV, respectively. The signals and the respective binding energy positions are consistent and in good agreements with literature reports on XPS analysis of Ag$_3$PO$_4$, Figure 8 [34, 35]. The C1s signal in the XPS spectrum of CAgP was attributed to the raw charcoal used as a substrate for the immobilization of Ag$_3$PO$_4$, indicating that both charcoal and Ag$_3$PO$_4$ co-existed in the CAgP composite, Figure 9. The XPS spectrum of C1s signal was deconvoluted into three different peaks positioned at 284.5, 285.5, 287.1 eV, which are attributed to carbon atoms in sp$^3$ hybridized C-C, epoxy groups of C-O and carbonyl groups of C=O bonding states, respectively, Figure 9 [36,37]. The high resolution XPS spectrum of O 1s shows an intense peak and a smaller peak with binding energy peaks at 531.1 and 529.2 eV, respectively. The former peak at higher binding energy is associated with the oxygen in P–O–Ag bond, while the later peak at a lower binding energy was assigned to non-bridging oxygen atoms of P=O bond in Ag$_3$PO$_4$ [38]. The high resolution XPS spectrum of P 2p was resolved into a single binding energy peak at $\approx$ 133.5 eV, which corresponds to the +5 oxidation state.
The core level Ag3d signal, which was resolved into two binding energy peaks at 367 eV and 373 eV are assigned to 3d$_{5/2}$ and Ag 3d$_{3/2}$, respectively. The two resolved binding energy peaks have spin-orbit separation of $\approx 6.0$ eV, confirming that the valence state of Ag in CAgP is +1 [40].

**Figure 8:** Representative XPS wide-scan survey spectrum taken from the surface of activated charcoal-AgP composite.
Figure 9: Deconvoluted XPS peaks of C 1s, O 1s, P 2p and Ag 3d for CAgP composite.

Photocatalytic generation of H$_2$O$_2$ over synthesized photocatalysts

The photocatalytic performances of AgP and CAgP were investigated for the formation of H$_2$O$_2$ in an O$_2$-saturated DI water under visible light illumination. Figure 10a shows the amount of H$_2$O$_2$ produced over AgP and CAgP composite as a function of time, ranging from 0–60 min in the dark to 1 to 6 h under visible light irradiations. To further rationalize the importance of the catalysts for the formation of peroxide, some control experiments were also carried out in the absence of the photocatalysts: by direct irradiation of the reaction mixture with 1 mM hole scavenger (FA) or
without addition of FA. The formation of peroxide was negligible under these control conditions, i.e., in the absence of photocatalysts, indicating that both FA and/or solar irradiation had no activity to produce hydrogen peroxide in the absence of catalysts, Figure 10a. Furthermore, catalytic control experiments conducted in the dark and in the presence of catalysts revealed negligible peroxide formation, which is an indication that the synthesized catalysts required the use of light illumination to generate charge carriers to produce peroxide in the solution. When O$_2$-saturated water was irradiated in the presence of AgP and CAgP catalysts, the yields of hydrogen peroxide increased nearly linearly over time up to 5 h, then plateaued at a constant level until 6 h. As a result, after 6 h of light irradiation, the formation of hydrogen peroxide over the catalysts peaked, indicating that a steady-state has been achieved in which the rate of H$_2$O$_2$ formation equals the rate of its decomposition, Figure 10a [41]. The yields of peroxide when AgP and CAgP were added to O$_2$/H$_2$O/FA system were higher than the amounts of peroxide formed in O$_2$/H$_2$O system, Figure 10b. In Table 1, concentrations of AgP and CAgP in O$_2$/water solution without FA are 154 and 185$\mu$M, respectively. These values are significantly higher than the values reported for peroxide produced over bare CdS (27 $\mu$M) and CdS-G2 (128 $\mu$M) after 12 h of solar irradiation [15]. The results clearly show that in the absence of scavengers or special chemical compounds, significant amounts of hydrogen peroxide were produced over AgP and CAgP, demonstrating that both catalysts have the required thermodynamic feasibility to drive the formation of H$_2$O$_2$ and are thus suitable for the purpose of producing H$_2$O$_2$. In contrast, when O$_2$/water-containing FA solution was irradiated in the presence of AgP and CAgP, H$_2$O$_2$ concentrations of 222 and 371$\mu$M were formed, suggesting that the photocatalytic performances of catalysts/H$_2$O/FA system significantly differs from catalysts/H$_2$O system, with CAgP/H$_2$O/FA system showing the highest photocatalytic activity for H$_2$O$_2$ generation. This supports that the use of hole scavenger or electron donor is very crucial for generation of H$_2$O$_2$ via photocatalysis [2, 10]. After 6 hours of light irradiation, the yields of peroxide produced in the CAgP/H$_2$O/FA system are up to 1.67, 2.00 and 2.06 times higher than the yields of peroxide produced in the AgP/H$_2$O/FA, AgP/H$_2$O and CAgP/H$_2$O systems, respectively, Table 1.

HCOOH + $h^+ \xrightarrow{\text{CAgP/\text{hv}}} \text{CO}_2 + 2H^+ + e^-_{cb}$  

O$_2$ + e$^- \xrightarrow{\text{CAgP/\text{hv}}} \text{O}_2^-$
\[ \cdot \text{O}_2^- + H^+ \stackrel{\text{CAgP/}hv}{\rightarrow} \cdot \text{HO}_2 \]

\[ \cdot \text{HO}_2 + e^- \stackrel{\text{CAgP/}hv}{\rightarrow} \text{HO}_2^- \]

\[ \text{HO}_2^- + H^+ \stackrel{\text{CAgP/}hv}{\rightarrow} \text{H}_2\text{O}_2 \]

\[ \text{O}_2 + 2H^+ (\text{HCOOH}) + 2e^- \stackrel{\text{CAgP/}hv}{\rightarrow} \text{H}_2\text{O}_2 \]

\[ \text{O}_2 + 2H^+ (\text{H}_2\text{O}) + 2e^- \stackrel{\text{CAgP/}hv}{\rightarrow} \text{H}_2\text{O}_2 \]

The use of FA prevented the formation of holes in the VB of CAgP and simultaneously improved the ejection and transition of electrons from the VB to the CB of CAgP to facilitate the photocatalyzed \( \text{H}_2\text{O}_2 \) formation via two-electron reduction of dissolved molecular oxygen, Eqns. 3-7 [2, 15, 42-44]. In the first step, FA is decomposed by the visible light to form CO\(_2\) and proton (H\(^+\)). The photo-excited electrons reacted with dissolved O\(_2\) on the CAgP surface to form superoxide radicals (\( \cdot \text{O}_2^- \)), Eqn. 4. The photogenerated protons (H\(^+\)) from FA decomposition reacted with O\(_2\) to form hydroperoxy radical (\( \cdot \text{HO}_2 \)), Eqn. 5, which was further reduced spontaneously by the electrons to form hydroperoxylanions (\( \text{HO}_2^- \)), Eqn. 6. In the final product, hydrogen peroxide was generated through reaction between hydroperoxyl anion and photogenerated proton H\(^+\), Eqn. 7. Thus, the overall formation of \( \text{H}_2\text{O}_2 \) in CAgP/O\(_2\)/\( \text{H}_2\text{O}/\text{FA} \) which was attributed to the decomposition of FA in solution and reduction of O\(_2\) by photoexcited electrons, is represented in Eqn. 8. In contrast, plausible mechanism for CAgP photocatalyzed \( \text{H}_2\text{O}_2 \) formation in the absence of FA (CAgP/O\(_2\)/\( \text{H}_2\text{O} \)), which was attributed to water oxidation and reduction of O\(_2\) by electrons, is represented in Eqn. 9[15]. Generally, the increased photocatalytic activity of CAgP over AgP can also be attributed to the strong interaction between AgP and the hydrophilic carbon used as a solid substrate. Even though the hydrophilic charcoal provides a good support for AgP (as in CAgP), it also serves as electron mediator by absorbing excess electrons from the conduction band via oxygen functionalities on its surface [12]. In solution, bare AgP has an aggregation tendency, which reduces its light sensitivity, and resulting in less photocatalytic activity to generate \( \text{H}_2\text{O}_2\) \textit{in situ}. Based on the high photocatalytic activity of
CAgP/FA system for H$_2$O$_2$ formation, further studies in terms of photocatalyst and hole scavenger dosages were conducted to optimize its catalytic activity.

**Figure 10:** (a) Photocatalytic formation of H$_2$O$_2$ over bare AgP and CAgP under different experimental conditions, (b) formation of H$_2$O$_2$ over AgP and CAgP photocatalysts after 6 h light irradiation using either O$_2$/H$_2$O or O$_2$/H$_2$O/FA systems, and (c) formation of H$_2$O$_2$ over CAgP composite as a function of catalyst loading in O$_2$/H$_2$O/FA system.
Table 2: Concentration of H$_2$O$_2$ (in mM) over AgP and CAgP photocatalysts after 6 h light irradiation using either O$_2$/H$_2$O or O$_2$/H$_2$O/FA systems.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>AgP/FA (mM)</th>
<th>CAgP/FA (mM)</th>
<th>AgP/H$_2$O (mM)</th>
<th>CAgP/H$_2$O (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.108</td>
<td>0.105</td>
<td>0.151</td>
<td>0.138</td>
</tr>
<tr>
<td>2</td>
<td>0.179</td>
<td>0.217</td>
<td>0.151</td>
<td>0.143</td>
</tr>
<tr>
<td>3</td>
<td>0.188</td>
<td>0.261</td>
<td>0.161</td>
<td>0.141</td>
</tr>
<tr>
<td>4</td>
<td>0.198</td>
<td>0.317</td>
<td>0.170</td>
<td>0.154</td>
</tr>
<tr>
<td>5</td>
<td>0.212</td>
<td>0.360</td>
<td>0.176</td>
<td>0.156</td>
</tr>
<tr>
<td>6</td>
<td>0.222</td>
<td>0.371</td>
<td>0.185</td>
<td>0.154</td>
</tr>
</tbody>
</table>

To determine the effect of catalyst dosage, the photocatalytic formation of H$_2$O$_2$ was demonstrated with various doses of CAgP in the presence of 0.5 mM formic acid (FA). Figure 11 depicts the catalyst-dependent profile of H$_2$O$_2$ formation under solar irradiation when CAgP dosage was varied from 5 to 90 mg. The catalytic efficiency of CAgP for H$_2$O$_2$ formation increased from 0.441 mM at 5 mg and reach its optimal value at 0.569 mM with 10 mg catalyst dosage, implying that increasing catalyst dosage also leads to an increase in catalytic active and adsorption sites on CAgP, providing more sites for e\textsuperscript{−}/h\textsuperscript{+} pair separation and facilitating transfer of photo-excited electrons from CB to oxygen molecules or protons to produce H$_2$O$_2$ [2]. As the catalyst dose was increased beyond the optimal 10 mg, the concentration of peroxide steadily decreased, reaching 0.179 mM at 70 mg, then remained fairly constant to 0.172 mM at 90 mg. The solution becomes increasingly turbid as the catalyst loadings in the reaction mixture increase, and more powders (CAgP) in solution coalesce into larger particles to induce aggregation, which reduces the amount of solar light penetrating into the reaction mixture, resulting in lower photocatalytic activity at higher catalytic doses.

Next we investigate the effect of formic acid (FA) on the catalytic formation of H$_2$O$_2$ in an O$_2$-saturated water system and in the presence of CAgP catalyst. Formic acid (FA) is an electron-
donating compound and also has high hydrogen content of about 4.4 wt.% which are often released in solution upon its decomposition under solar irradiation [45]. The evolved hydrogen molecules from HCOOH decomposition can react with *O2 to form H2O2, Eqn. 8, hence it is proposed here as a source of H2 to improve the overall formation of H2O2. The concentrations of FA were varied from 0.5 to 2.5 mM and the solutions were irradiated with sunlight for 6 h. From Table 2 and Figure 12, it was found that the amount of H2O2 formed increases steadily as the irradiation time increases from 1 to 6 h for each FA concentration. However, after 6 h irradiation time, the amount of H2O2 formed slightly decreased from 0.352 to 0.341 mM, corresponding to an increase in FA concentration from 0.5 to 1.5 mM, followed by a sharp decline in the peroxide formation to 0.279 mM at 2.5 mM of FA. The results indicate that at FA concentrations below 1.5 mM, hydrogen (H2) produced (during FA decomposition) reacted with O2 to produce a significant amount of hydrogen peroxide, up to 0.352 mM, Eqn. 8. The excess FA in the solution at concentration above 1.5 mM may compete with the catalyst for visible light absorption, lowering light absorption efficiency of CAgP, and reducing the rate of hydrogen evolution [46]. Thus, photocatalytic formation of H2O2 is inhibited at higher FA concentrations [46]. It's worth noting that the equivalent amount of H2O2 produced after 6 h of solar irradiation with 2.5 mM FA was achieved in 3 h when 0.5 mM FA was used. As a result, FA concentration of 0.5 mM was selected as the optimal value for hydrogen evolution, and to facilitate photo-induced hole trapping in order to improve the photocatalytic performance of CAgP for hydrogen peroxide formation.
Table 3: Amount of H\(_2\)O\(_2\) produced over CAgP composite as a function of FA ranging from 0.5 to 2.5 mM for 6 h of light irradiation in O\(_2\)/H\(_2\)O/FA system.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>0.5 (mM)</th>
<th>1.0 (mM)</th>
<th>1.5 (mM)</th>
<th>2.0 (mM)</th>
<th>2.5 (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.221</td>
<td>0.217</td>
<td>0.214</td>
<td>0.184</td>
<td>0.174</td>
</tr>
<tr>
<td>2</td>
<td>0.232</td>
<td>0.228</td>
<td>0.224</td>
<td>0.193</td>
<td>0.183</td>
</tr>
<tr>
<td>3</td>
<td>0.267</td>
<td>0.262</td>
<td>0.258</td>
<td>0.222</td>
<td>0.210</td>
</tr>
<tr>
<td>4</td>
<td>0.298</td>
<td>0.293</td>
<td>0.288</td>
<td>0.248</td>
<td>0.234</td>
</tr>
<tr>
<td>5</td>
<td>0.328</td>
<td>0.322</td>
<td>0.317</td>
<td>0.273</td>
<td>0.258</td>
</tr>
<tr>
<td>6</td>
<td>0.352</td>
<td>0.347</td>
<td>0.341</td>
<td>0.294</td>
<td>0.277</td>
</tr>
</tbody>
</table>

Figure 12: Photocatalytic formation of H\(_2\)O\(_2\) over CAgP composite as a function of formic acid (FA) after 6 h of light irradiation in O\(_2\)/H\(_2\)O/FA system. [Conditions: catalyst dosage 30 mg, contact time 6 h, FA concentration: 0.5 to 2.5 mM, and temperature: 25 ± 2 °C].

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Trapping experiments and reaction mechanism

Having validated that CAgP or AgP catalysed formation of H$_2$O$_2$ are both possible in an airsaturated aqueous solution, we carried out further controlled trapping experiments to determine the effects of benzoquinone (BQ), AgNO$_3$, and isopropyl alcohol (iPA) which were used as superoxide, electron and hydroxyl radical scavengers, respectively, for the formation of H$_2$O$_2$. For the purpose of uniformity and clarity, previous experiments with CAgP/H$_2$O/FA were repeated and the results were compared to CAgP/H$_2$O/BQ, CAgP/H$_2$O/AgNO$_3$ and CAgP/H$_2$O/iPA systems. Figure 13 shows that the amount of H$_2$O$_2$ produced by CAgP/H$_2$O/AgNO$_3$ system was slightly higher than the amount reported for the CAgP/H$_2$O/FA system. The finding is intriguing and suggests that H$_2$O$_2$ can be formed not only by the e$^-$ reduction of O$_2$ to form H$_2$O$_2$, but also by holes in the VB of the catalyst [47]. Thus, the formation of H$_2$O$_2$ in the absence of electrons can be hypothesized to occur via the oxidation of H$_2$O by holes to generate hydroxyl radicals (*)OH, Eqns. 10&11, which is then followed by the combination of two *HO to produce H$_2$O$_2$, Eqn. 12[10,47]. When the *O$_2^-$ and *HO radicals were trapped with 1 mM BQ and iPA, the amount of H$_2$O$_2$ formed in the solution was significantly suppressed and reduced to nearly 50% equivalent of the amount formed in the presence of FA and AgNO$_3$ at the same concentrations and volume. This suggests that the primary active species responsible for the generation of H$_2$O$_2$ are *O$_2^-$ and *HO, which were formed via electrons and holes in the CAgP catalyst, respectively.

$$\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^- \quad \text{Eqn. 10} \\
\text{OH}^- & \rightarrow + \cdot\text{OH} \quad \text{Eqn. 11} \\
2\cdot\text{OH} & \rightarrow \text{H}_2\text{O}_2 \quad \text{Eqn. 12}
\end{align*}$$

The mechanisms of the photocatalytic reactions is proposed and validated based on the positions of conduction band (CBE) and valence band edges (VBE) of CAgP under visible light irradiation. The potentials of CBE and VBE were determined using empirical Mulliken electronegativity equations, Eqns. 13 and 14 [48]:

$$VBE = \chi - E^e + 0.5E_g$$

13
where $\chi$, is the absolute electronegativity of semiconductor, Ag$_3$PO$_4$ ($\chi$ value of Ag$_3$PO$_4$ is 6.16 eV vs. NHE [49]), $E^e$ is the energy of free electrons and about \( \sim 4.5 \) eV vs. NHE, $E_g$ is the energy band gap of semiconductors (AgP = 2.36 eV and CAgP = 2.25 eV CAgP, as calculated from Eqn. 2).

The $VBE$ and $CBE$ of AgP, and CAgP are 2.84/0.48 eV and 2.79/0.54 eV, respectively, Figure 14. For the photocatalytic reactions to be thermodynamically feasible, the redox potential of donors must be less positive than the potentials of $VBE$, and the redox potential of the acceptor must be less negative than the magnitude of potential edge of CB [50]. Water oxidation by photo-induced holes is thermodynamically feasible, as the redox potential of $\text{OH}^-/\text{OH}$ at +1.99 V vs. NHE is less positive than the potential of $VBE$ of CAgP at +2.79 eV vs. NHE, Figure 15 [50]. Similarly, the photo-excited electrons could drive the reduction of $O_2$ to form $H_2O_2$ because the CBE of CAgP at (+ 0.54 eV vs. NHE) is more negative than the potential of $O_2/H_2O_2$ at 0.68 vs. NHE, Figure 15. As a result, the reactions in Eqns. 8 and 12 are valid for the formation of $H_2O_2$. 

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Figure 13: Effects of different scavengers on the photocatalytic formation of H$_2$O$_2$ over as-prepared CAgP composite. Inset: Amount of H$_2$O$_2$ produced over CAgP in the presence and absence of scavengers after 6 h of irradiation.

Figure 14: Energy band structures of charcoal, bare AgP, and CAgP composite.

Figure 15: Schematic mechanism of H$_2$O$_2$ formation over as-synthesized CAgP (as representative) through photocatalytic reaction in aerated water.

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Recovery and stability runs

Recovery, stability, and reusability are key features required in photoredox applications to ensure that the photocatalysts maintain their activities after prolonged exposure to light. Photostability performances of bare AgP and CAgP photocatalyzed H₂O₂ formation were evaluated by performing five recycle experiments under the same experimental conditions reported for O₂-saturated DI water, Figure 16. The photocatalytic performance of bare AgP was seen to gradually decrease in mass and activity from 100% to ~33% after the fifth recycle test, due to a number of factors, including uncontrollable aggregation of particles in solution, increased photo-corrosion and photo-decomposition of Ag₃PO₄ to Ag⁰ and PO₃⁻⁴, Eqn. 15 [12]. Similar reports on the photo-excited electron induced deactivation/dissolution of silver-based photocatalysts have been reported in the literature [12]. The stability of the CAgP composite, on the other hand, remained relatively stable until the fourth cycle test, when its catalytic activity dropped slightly below 90%, implying that the passivation of CAgP surface with activated charcoal reduced the rate of Ag₃PO₄ decomposition under solar illumination. Thus, CAgP has improved and remarkable photostability.

Ag₃PO₄ + 3e⁻ → 3Ag⁰ + PO₃⁻⁴
Figure 16: Plot of photocatalytic H$_2$O$_2$ formation efficiency (%) against number of cycles for photocatalytic stability evaluation of AgP and CAgP composite.

**Conclusion**

A cost-effective approach has been reported for the preparation of bare AgP and CAgP and their photocatalytic performances for hydrogen peroxide (H$_2$O$_2$) formation in O$_2$-saturated water was elucidated under natural solar illumination. The bare AgP was prepared by chemical precipitation method using disodium hydrogen phosphate (Na$_2$HPO$_4$) as a precipitating agent. CAgP was prepared in the same way as bare AgP, except that raw charcoal was first acidified in an aq. HCl solution and electrostatically interacted with Ag$^+$ before it was precipitated as Ag$_3$PO$_4$ on the surface of activated charcoal using Na$_2$HPO$_4$. The as-synthesized bare AgP and CAgP composite were characterized using techniques such as XRD, FT-IR, Raman, TEM, SEM, EDX, and XPS. The CAgP composite demonstrated remarkable photocatalyzed H$_2$O$_2$ production compared to bare AgP nanoparticles, due to the presence of activated charcoal, which serves as a solid support for Ag$_3$PO$_4$ and reduces the chance of photodecomposition of Ag$_3$PO$_4$ under solar irradiation. Additionally, the activated carbon improved electron mobility and charge carrier separation via oxygen groups on its surface. In the presence of FA (O$_2$/H$_2$O/FA system) as a hole scavenger, H$_2$O$_2$ formation over CAgP was thermodynamically facilitated by $2e^-$ reduction of dissolved molecular oxygen; while the second pathway involved water oxidation by photo-induced holes and combination of the two photogenerated *HO to form H$_2$O$_2$ in the presence of AgNO$_3$(O$_2$/H$_2$O/AgNO$_3$ system) as an electron scavenger. Thus, through $2e^-$ reduction of dissolved O$_2$ and water oxidation, CAgP satisfy two-channel pathways for H$_2$O$_2$ formation.

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Original draft writing: Owolabi M. Bankole

Supervision; validation, visualization: Owolabi M. Bankole, and Segun E. Olaseni.
REFERENCES


