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Mohammad Mansoob Khan, Dr
Mohammad Ehtisham Khan
M. H. Cho, Prof

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Biogenic synthesis of a Ag–graphene nanocomposite with efficient photocatalytic degradation, electrical conductivity and photoelectrochemical performance†

Mohammad Ehtisham Khan, Mohammad Mansoob Khan* and Moo Hwan Cho*

This paper reports an environmentally benign, simple, cost efficient, one-step, surfactant free, and biogenic synthesis of a silver–graphene (Ag–graphene) nanocomposite using an electrochemically active biofilm (EAB). The EAB was used for the reduction of Ag⁺ to Ag⁰ onto the graphene sheets. The morphology, structure, composition, and optical properties and contact angle of the Ag–graphene were obtained using a range of techniques which confirmed the anchoring/presence of silver nanoparticles (AgNPs) onto the graphene sheets. The photocatalytic activity of Ag–graphene was evaluated by the degradation of methylene blue and Congo red dye in aqueous solution at an ambient temperature in the dark and under visible-light irradiation. The results showed that the photocatalytic activity of the Ag–graphene nanocomposite was enhanced significantly by the loading of AgNPs in the graphene sheets. Contact angle measurements confirm the hydrophilic nature of the Ag–graphene nanocomposite which is very helpful in photocatalysis. The electrical conductivity and photocurrent measurements of the Ag–graphene nanocomposite exhibited a much better performance than P–graphene. This study highlights the design of a novel facile synthetic route for a new photocatalyst using the SPR of Ag and graphene as a support. The as-synthesized Ag–graphene nanocomposite has potential applications in photocatalytic degradation, photoelectrodes and optoelectronic devices.

Graphene, a two dimensional (2D) carbon based material, is widely used as a catalyst support material in the photocatalytic field because of its high surface area, high electron mobility (200 000 cm² V⁻¹ s⁻¹) of charge carriers at room temperature, high thermal conductivity (∼5000 W m⁻¹ K⁻¹), high electrical conductivity (∼2.02 × 10² S cm⁻¹) and nanoscale thickness characteristics. Moreover, graphene nanosheets can act as a support centre in a composite photocatalyst owing to their large π-conjugation system and 2D planar structure. This allows interactions between the graphene sheets and organic contaminants. Graphene has attracted considerable interest in the recent years because of its outstanding electronic, mechanical and photocatalytic properties. The clever intercalation of metal nanoparticles into graphene sheets can effectively detach the graphene sheets and prevent the aggregation of graphene and noble metal nanoparticles, such as gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs), which have been introduced because of their extraordinary conductivity and excellent catalytic activities. Metal nanoparticle intercalation such as AgNPs offers the possibility to improve the aqueous dispersibility of graphene sheets, which means an improvement in hydrophilicity. Graphene sheets, which are single-atom-thick carbon materials with a high specific surface area and conductivity could be an ideal substrate for the anchoring...
of metal nanoparticles for high performance photodegradation and photoelectrochemical devices. Plasmonic nanomaterials, such as AgNPs, have very strong light absorption in the visible region, which is also called localized surface plasmon resonance.14 Graphene has very strong absorption over the solar spectrum, especially in the near IR region, and it is the most thermally conductive material known so far.15 The coupling between the optical properties of metallic nanoparticles with different shapes and graphene sheets affects their absorption cross sections, ultrafast optical responses and photocatalytic properties.16

To the best of the author’s knowledge, this is the first biogenic report on the synthesis of Ag–graphene nanocomposites using electrochemically active biofilms (EABs). In this synthesis, efforts have been made to combine the plasmonic effects of Ag with the electronic effects of graphene to achieve Ag–graphene nanocomposites with enhanced photocurrent and photocatalytic performance.16,17 EAB assisted synthesis reduces the use of harsh chemicals which had been previously used by other researchers and it will help to avoid another side product of pollution. This paper reports the effects of both the plasmonic effects of Ag and the electronic effect of graphene on the photocatalytic activity for the degradation of the methylene blue and Congo red, which are well known water pollutants. The efficient photodegradation of the pollutants in water was achieved in the presence of the prepared Ag–graphene nanocomposite as a photocatalyst. The Ag–graphene nanocomposite was also used as a photoelectrode to measure the improved photocurrent.17 This paper proposes a fast, facile, low cost, large-scale, and environment friendly preparation of Ag–graphene nanocomposite using an EAB as the reducing tool. This study opens the door for the biogenic fabrication of novel nanocomposites for the application in optoelectronic devices, photoelectrodes and efficient photodegradation of organic pollutants.

Experimental section

Materials

Silver nitrate (AgNO3, 99%) and methylene blue (MB) were purchased from Sigma-Aldrich, whereas graphene was purchased from Iljin Nano Tech, Seoul, Korea (7–8 layer graphene sheets with a mean length of 500 nm). Congo red (CR), sodium acetate (CH3COONa) and sodium sulphate (Na2SO4) were obtained from Duksan Pure Chemicals Co. Ltd., South Korea. Ethyl cellulose and γ-terpinol (C10H18O) were obtained from KANTO Chemical Co., Japan. Carbon paper (without wet proof) was purchased from Fuel Cell Earth LLC, USA. All other chemicals used in this study were of analytical grade and were used as received. The solutions were prepared in de-ionized water, which was obtained using a PURE ROUP 30 water purification system.

The optical properties were examined using a UV-VIS-NIR diffuse absorbance spectrophotometer (VARIAN, Cary 5000, USA). The photoluminescence (PL, Kimon, 1 K, Japan) of the samples was recorded over the scanning range, 200–800 nm, at an excitation wavelength of 325 nm. X-ray diffraction (XRD, PANalytical, X’pert PRO-MPD, Netherlands) was carried out using Cu Kα radiation (λ = 0.15405 nm). The XRD peaks for the crystalline phases were well matched with those of the standard compounds reported in the JCPDS data file. Raman spectroscopy (Lab Ram HR800 UV Raman microscope; Horiba Jobin-Yvon, France) was performed to confirm the synthesis of the Ag–graphene nanocomposites. The microstructure was examined by field emission transmission electron microscopy (FE-TEM, Tecnai G2 F20, FEI, USA) operating at an accelerating voltage of 200 kV. Selected-area electron diffraction (SAED) was carried out by TEM. Elemental mapping of the sample containing the phases with different valences was obtained by TEM. Quantitative analysis was performed by energy dispersive spectrometry (EDS). X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XPS System, Thermo Fisher Scientific U.K.) was conducted using monochromated Al Kα X-rays (hv = 1486.6 eV, X-ray energy: 15 kV, 150 W and spot size: 500 μm, Take-off angle: 90 degree, Pass energy: 20 eV, BE resolution: 0.6 eV [calibrated by Ag 3d5/2]). XPS fitting was performed using “AVANTAGE” software according to a Shirley subtraction and the Gaussian–Lorentzian shape of the peaks was used for the deconvolution. The sensitivity factor used for Ag 3d5/2 was 30.5. PL and XPS were performed at the Korea Basic Science Institute, (KBSI) South Korea. The contact angles were measured using a video based contact angle device, OCA-20 (Dataphysics, Germany).

The photocurrent measurement, such as linear sweep voltammetry (LSV), was conducted using a 400 W lamp with an intensity of 31 mW cm–2 (3 M, λ > 400 nm, USA). The photocurrent experiment, such as LSV measurements, was performed using a potentiostat (Versa STAT 3, Princeton Research, USA) comprising of a standard three-electrode system. Ag/AgCl (3 M KCl), a Pt gauge and carbon paper coated with P-graphene and Ag–graphene nanocomposite were used as the reference, counter and working photoelectrodes, respectively. The experiment was performed in a 0.2 M Na2SO4 solution as the electrolyte at room temperature. The projection area of the photoelectrode was 1 cm2. The working electrodes for the photocurrent (LSV) were prepared as follows: 50 mg of each sample was mixed thoroughly by adding ethyl cellulose as a binder and γ-terpinol as a solvent for the paste. The paste was later coated on carbon paper using the doctor-blade method and used as a photoelectrode.

For the DC electrical conductivity measurements, a pellet of P-graphene and the Ag–graphene nanocomposite was prepared using a hydraulic pressure instrument at a 40 kN pressure for 10 min. The DC electrical conductivity (σ) was measured using a 4-in-line probe electrical conductivity measuring instrument in a PID controlled oven (Scientific Equipment’s, Roorkee, India). The photocatalytic degradation performance was monitored by measuring the absorption of organic pollutants by UV-vis spectrophotometry (OPTIZEN 2120UV).

Development and growth of an electrochemically active biofilm

The development of EAB on carbon paper was achieved using the approach reported elsewhere.16 In particular, 0.2 g of sodium acetate was added as a substrate to 200 mL of a mineral salt medium. This was followed by the addition of 10 mL of
an aerobic sludge (Biogas plant in Paju, Republic of South Korea) and sparging with \( \text{N}_2 \) gas for 5 min to create strictly anaerobic conditions. Finally, carbon paper (2.5 cm × 4.5 cm) was dipped in it and the bottle was sealed compactly. All media, including the bacterial inoculum were changed every two days under strict anaerobic conditions. The process was repeated over a two week period. The EAB developed on the carbon paper were confirmed using a microbile fuel cell by obtaining the appropriate voltage.\(^{19}\) The living EABs were employed for the synthesis of the Ag–graphene nanocomposite for further studies.

**Biogenic synthesis of the Ag–graphene nanocomposite using electrochemically active biofilm**

In a typical synthesis process, 0.25 g of the graphene sheets were added to 200 mL of \( \text{H}_2\text{O} \) and stirred for 30 min for the exfoliation of graphene sheets and an aqueous 6 mM \( \text{AgNO}_3 \) solution was added. The mixture of \( \text{AgNO}_3 \) and graphene sheets was stirred for 15 min to allow the adsorption of \( \text{Ag}^+ \) ions onto the graphene surface. After the adsorption of \( \text{Ag}^+ \) ions onto the graphene surface, 0.2 g of sodium acetate was added as an electron generator and the EAB was hung in the reaction bottle. The reaction bottle was kept for 12 h with continuous stirring. The EAB produced electrons under anaerobic conditions were used for the reduction of \( \text{Ag}^+ \) ions onto the graphene surface, leading to the formation of the Ag–graphene nanocomposite. The solution was then centrifuged to isolate the Ag–graphene nanocomposite powder and dried in an oven at 60 °C for 24 h. The isolated Ag–graphene nanocomposite sample was stored in a desiccator until needed.

**Photocatalytic degradation performance of Ag–graphene nanocomposite under visible light irradiation**

The photocatalytic degradation performance of the as-prepared Ag–graphene nanocomposite was studied by the photodegradation of MB and CR under visible light irradiation using a 400 W lamp (\( \lambda > 400 \text{ nm} \)). 2.0 mg of each photocatalyst was added to 200 mL of a MB and CR aqueous solution (10 mg L\(^{-1} \)). Each solution was sonicated for 5 min in the dark. The solutions were later stirred in the dark for 30 min to reach the adsorption and desorption equilibrium of the specific substrate on the Ag–graphene nanocomposite. The reaction mixture was irradiated at a working distance of 25 cm. The degradation of dyes as a function of the irradiation time was measured by UV-vis spectrophotometry (OPTIZEN 2120UV). The experiments were observed for 6 and 5 h in the case of MB and CR degradation, respectively. The rate of dye degradation was monitored by taking 2 mL of the samples from each set at every 1 h, centrifuging them to remove the catalyst and recording the UV-vis spectrum in each case. The level of MB and CR photodegradation was calculated from the decrease in the absorbance of the respective degraded solutions.

**Photocurrent measurement of the Ag–graphene nanocomposite as a photoanode**

The photocurrent response of P–graphene and as-prepared Ag–graphene nanocomposite was examined using a photocurrent measurement experiment, such as LSV, which was carried out under ambient conditions in the dark and under visible light irradiation in a 50 mL, 0.2 M \( \text{Na}_2\text{SO}_4 \) aqueous solution at room temperature. LSV was first performed in the dark and then under visible light illumination (\( \lambda > 400 \text{ nm} \)) at a scan rate of 50 mV s\(^{-1} \) over the potential range, −0.6 to 0.6 V.

**DC electrical conductivity measurement of the Ag–graphene nanocomposite**

The DC electrical conductivity (\( \sigma \)) of the as prepared materials, as a pellet of P–graphene and the Ag–graphene nanocomposite, was measured using a 4-in-line probe electrical conductivity measuring instrument in a PID controlled oven and were calculated using the following equation:

\[
\sigma = \left[ \left( \frac{2S(w)}{\ln 2} \right) \right] / \left( 2\pi S(V/I) \right)
\]

where, \( I, V, w, \) and \( S \) are the current (A), voltage (V), thickness of the pellet (cm), and probe spacing (cm), respectively, and \( \sigma \) is the DC electrical conductivity in S cm\(^{-1} \).

**Stability and reusability test of the Ag–graphene nanocomposite**

The stability test of the Ag–graphene nanocomposites is the prime concern. This study examined the stability of the Ag–graphene nanocomposite by sonicating a suspension of the Ag–graphene nanocomposite in water for one hour. The centrifuged solution was then analyzed for the leached AgNPs using a UV-visible spectrophotometer. The UV-visible spectra showed no AgNP absorbance peak (Fig. S1, ESI†).

The reusability test of the Ag–graphene nanocomposite was later tested three times with the same catalyst in the dye solutions. After reusing three times, 95% of the photocatalytic activity was retained, revealing the good reusability of the as-prepared nanocomposite as a photocatalyst. This showed that the Ag–graphene nanocomposite had not been deactivated significantly (Fig. S2, ESI†).

**Results and discussion**

**Biogenic synthesis and the proposed mechanism for the Ag–graphene nanocomposite**

The Ag–graphene nanocomposite was prepared using a novel biogenic approach, which is environment-friendly. EAB was used as an environment friendly, sustainable and reductant-free method, which can be appropriate for this objective.\(^\text{13,18}\) Fig. 1 shows the formation of the Ag–graphene nanocomposite by sonicating a suspension of the Ag–graphene nanocomposite in water for one hour. The centrifuged solution was then analyzed for the leached AgNPs using a UV-visible spectrophotometer. The UV-visible spectra showed no AgNP absorbance peak (Fig. S1, ESI†).

\[
\text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} + \text{EABs} \rightarrow 8e^- + 9\text{H}^+ + 2\text{HCO}_3^-
\]

The advantage of this protocol is that it does not involve any external energy input or harsh chemicals, which makes this synthesis quite useful and efficient for nanocomposite synthesis.
Recently, syntheses of similar nanocomposites using EABs were reported.\textsuperscript{13,18–20} This is the first report of the biogenic synthesis of the Ag–graphene nanocomposite using EABs. This study highlights the design of a new synthetic route and the preparation of a new photocatalyst using the SPR of Ag and the electronic behaviour of graphene. Graphene acts not only as a support for the AgNPs, but also allows the storage of electrons produced by the EABs within the arrangement of carbon atoms. These stored electrons increase dramatically the reduction of silver ions at the surface of the graphene sheets.

**Optical properties of the P–graphene and Ag–graphene nanocomposite**

The optical diffuse absorbance spectra of the as prepared Ag–graphene nanocomposite and P–graphene were measured at room temperature over the wavelength range of 200–800 nm. Fig. 2(a) shows the UV-vis absorption spectra of the Ag–graphene nanocomposite; the characteristic absorption peak of graphene was observed at 230 nm. The presence of AgNPs in the graphene sheets was confirmed by the absorption peak in the range of 410–430 nm. This specific range shows the surface plasmon effect of AgNPs. This was confirmed by the absorption peak in the range of 410–430 nm. The presence of AgNPs in the graphene sheets leads to the SPR characteristics.

The luminescence properties were examined to further clarify the optical properties of the Ag–graphene nanocomposite and its potential applications as a photonic material. Fig. 2(b) presents the photoluminescence (PL) spectra of P–graphene and Ag–graphene. The emission of the Ag–graphene nanocomposite occurs in the 450 nm region because of the electronic behaviour of graphene. In the case of Ag–graphene nanocomposite, the intensity of the emission peak was increased significantly (Fig. 2(b)). This is also an indication of the AgNP interactions with graphene sheets.\textsuperscript{22} This suggests an additional pathway for the increase in charge carriers because of the interactions between the AgNPs and graphene sheets. The PL also shows higher charge transfer ability, which could be responsible for improved photocatalytic activity.\textsuperscript{13,23}

**Structural analysis of the P–graphene and Ag–graphene nanocomposite**

The crystalline nature of the Ag nanostructures in the Ag–graphene nanocomposite was confirmed by XRD. Fig. 3(a) shows XRD patterns of the Ag–graphene nanocomposite with all the major diffraction peaks, which were obtained at 26.5° (002), and 54.7° 2θ (100), confirming the presence of the crystal face of graphene, whereas the XRD peaks at 38.1° (111), 44.4° (200), 64.8° (220), and 77.6° 2θ (311) were assigned to AgNPs (face-centered cubic, JCPDS File no. 89-3722).\textsuperscript{24} The peak at 38.15° 2θ is the characteristic peak for the Ag metal, which confirms the deposition of Ag on the graphene sheets. No XRD peaks for any other impurities were detected, highlighting the purity of the products. This confirmed the presence/anchoring of AgNPs to the graphene sheets and the overall synthesis of the Ag–graphene nanocomposite.

The mean crystallite size of the Ag–graphene nanocomposite was calculated using the Scherer’s formula, \( D = \frac{\kappa \lambda}{\beta \cos \theta} \), where \( \kappa \) is the shape factor and has a typical value of \( \sim 0.9 \), \( \lambda \) is the wavelength (Cu K\(_1\) = 0.15405 nm), \( \beta \) is the full width at half maximum of the most intense peak (in radians), and \( \theta \) is the main peak of P–graphene at 26.53° 2θ for which the calculated crystallite size of the most intense peak was 22.3 nm. In contrast, the main peak of the Ag–graphene nanocomposite was observed at 2θ of 26.53° and the calculated crystallite size of the most intense peak was 24.16 nm. This shows that the crystallite size is increasing, which is due to the anchoring/presence of AgNPs in the graphene sheets. This further confirmed the successful synthesis of the Ag–graphene nanocomposite.

Raman spectroscopy provides valuable information on the electronic and structural properties of graphene. Fig. 3(b) shows the Raman spectra of P–graphene before and after the AgNPs are anchored on its surface. The characteristic peaks of the D and G bands at approximately 1350 cm\(^{-1}\) and 1590 cm\(^{-1}\) were observed.
The D band provides information on the breathing mode of the \( k \)-point, and the G band is related to the tangential stretching mode of the \( E_{2g} \) phonon of sp\(^2\) carbon atoms.\(^{25}\) The intensities of these two bands were enhanced dramatically after the anchoring of AgNPs to the surface of the graphene sheets, which further proves the successful presence of AgNPs to the graphene sheets. In the case of the 2D band, after the reduction of AgNPs using EAB, a broad 2D band at 2729 cm\(^{-1}\) for the Ag–graphene nanocomposite was observed. This confirms the intercalation/decoration of AgNPs in the graphene sheets, which revealed the presence of few layer graphene sheets in the as-prepared Ag–graphene nanocomposite.\(^{25, 26}\)

**Transmission electron microscopy**

Fig. 4(a) presents a representative TEM image of the Ag–graphene nanocomposite formed. The surface of the graphene sheets was decorated with AgNPs. Most of the synthesized AgNPs were almost spherical in shape and dispersed uniformly over the graphene sheets with almost no aggregation, which displays a good interfacial interaction between the AgNPs and graphene sheets. No free AgNPs were observed outside the graphene sheets. The transparent and few layer graphene sheets can be observed in the background. Fig. 4(b) shows a HR-TEM image, which clearly indicates the interface between the AgNPs and graphene sheets, further proving the good interfacial interaction between the AgNPs and graphene sheets. It shows that the average particle size is in the 10–30 nm range, which is previously mentioned in the literature for the better quenching behaviour. In other words the quenching behaviour could be explained by interfacial charge transfer from graphene to AgNPs. The catalytic efficiency of the metal nanoparticle for an electron transfer is closely related to the size-dependent redox properties.\(^{22}\) Fig. 4(c) shows the lattice fringes of AgNPs and graphene sheets for the confirmation of the interaction between AgNPs and graphene sheets. Fig. 4(d) shows the SAED patterns, which revealed the polycrystalline nature of the Ag–G nanocomposite. Fig. 4(e) shows the size distribution histogram of the AgNPs which clearly shows the mean particle diameter, which is \( \approx 8–12 \) nm. This can be attributed to an increase in the active surface area of the AgNPs with decreasing size of the catalyst. Fig. 4(f) shows the line intensity profile obtained from TEM software analyses, indicating the plane distance of AgNPs which is 0.24 nm. Fig. S3 (ESI\(^{\dagger}\)) shows the results of EDS analysis of the Ag–graphene nanocomposite, which showed that the AgNPs had been successfully anchored to the surface of the graphene sheets. This was observed in various regions of the Ag–graphene nanocomposite.

**XPS exploration of P–graphene and Ag–graphene nanocomposite**

XPS analysis of P–graphene and the as-prepared Ag–graphene nanocomposite was performed to determine the surface composition. Fig. 5(a) shows the high resolution spectra of C 1s at a characteristic binding energy (B.E.) of 284.4 eV for P–graphene, whereas for the Ag–graphene nanocomposite, the C 1s shifted to 284.6 eV B.E., which confirms the successful formation and anchoring of AgNPs onto the graphene sheets.\(^{23}\) The inset in Fig. 5(a) shows the survey scan spectra of the Ag–graphene nanocomposite, in which the peak associated with C 1s became predominant and a peak of Ag 3d\(^{5/2}\) appeared, which provides evidence for the successful anchoring/formation of AgNPs at the graphene sheets after being treated with the EAB. In addition, there were no peaks for other elements in the XP spectrum except for C and Ag, which indicated the high purity of the as-prepared nanocomposite.\(^{23, 27}\) Fig. 5(b) shows the high resolution XP spectra of the Ag 3d peaks for the Ag–graphene nanocomposite. To further examine the chemical state of the AgNPs, there were two peaks at the Ag (3d\(^{5/2}\)) and Ag (3d\(^{3/2}\)) core levels centered at binding energies of 367.4 eV and 373.5 eV.
The binding energies of these photoelectron peaks are characteristic of metallic Ag, which is indicative of Ag\(^0\) on the surface of the graphene sheets and also confirms the oxidation state of Ag\(^+\). Overall, the EAB has effectively reduced Ag\(^+\) ions to Ag\(^0\) on the surface of graphene sheets. XPS revealed a strong interaction between the graphene sheets and AgNPs in the Ag–graphene nanocomposite.

**Contact angle measurement of P–graphene and Ag–graphene nanocomposite**

The contact angle is an important parameter to study the surface hydrophobic and hydrophilic characteristics of any photocatalyst. The liquid sessile drop method was used to determine the contact angle of the photocatalyst. An image of a water drop formed on the photocatalyst as a substrate was recorded by a video camera with an initial waiting period of 10 s to stabilize the water drop on the surface of the P–graphene and the as-prepared Ag–graphene nanocomposite as a substrate. An image analysis system was used to measure the contact angle \(\theta\) from the shape of the water drop. Li et al. reported that the metal nanoparticle intercalation can improve the aqueous dispersibility of graphene. Here, static contact angle analysis, as shown in Fig. 6(a) and (b), was performed on the shape of the water drop formed to examine the impact on the hydrophilic/hydrophobic features of the P–graphene and Ag–graphene nanocomposite. P–graphene exhibited a hydrophobic nature. Fig. 6(a) shows the contact angles of the left 79.1° and right 79.3°, which reflects its hydrophobic nature, whereas for the Ag–graphene nanocomposite, Fig. 6(b) shows relatively hydrophilic nature with contact angles of left 57.9° and right 56.6°. Fig. 6(b) suggests that the hydrophilic characteristic can indeed be obtained by modifying the surface of graphene sheets with AgNPs due to the hydrophilic property of the Ag–graphene nanocomposite, which plays a crucial role in photocatalysis and optoelectronic devices.

**Applications of Ag–graphene nanocomposite**

**Photoelectrochemical measurement of P–graphene and Ag–graphene nanocomposite**

The photoelectrochemical measurement of the nanomaterials can be determined by the light-harvesting capacity of nanomaterials. Complementary information regarding the photocurrent response of the Ag–graphene nanocomposite was obtained from the LSV measurements. LSV was performed over the potential range, \(-0.6\) to \(0.6\) V, in the dark and under visible light irradiation to examine the visible light response of P–graphene and Ag–graphene nanocomposite for the photocurrent measurements. Fig. 7 shows that the photocurrent of the Ag–graphene nanocomposite increased progressively compared to P–graphene, which suggests that the anchoring of AgNPs to the graphene sheets can effectively improve the photoconversion efficiency and light harvesting ability of graphene. Generally, an increase in photocurrent suggests that the sample has strong ability to generate and transfer the photogenerated charge carriers under visible light irradiation. The increased photocurrent under visible light irradiation also shows an increase in the transport rate of the photoinduced carriers. This highlights the better interaction and anchoring of AgNPs onto the graphene sheets, which suggests that the separation efficiency of photo-induced electrons was improved by the SPR effect of AgNPs and the electronic behaviour of graphene sheets. This synergistic behaviour enhances the performance of the Ag–graphene nanocomposite under visible light irradiation.

**DC electrical conductivity measurement of P–graphene and Ag–graphene nanocomposite**

Various factors influence the electrical conductivity and the percolation threshold of the composites such as the concentration of filler, the aggregation of filler, processing methods, modification and the aspect ratio of graphene sheets, inter-sheet junction, distribution in the matrix, wrinkles, folds and intercalation of metal NPs.

The electrical conductivity of P–graphene and Ag–graphene was measured using a four-probe detector. The electrical properties of graphene can be tuned by the decoration of metal NPs, such as, AgNPs. Silver has an electrical conductivity (6.30 × 10\(^5\) S cm\(^{-1}\)) three times order of magnitude larger than that of even highly conductive graphene \((\sim 2.02 \times 10^5 \text{ S cm}^{-1})\). The measured DC electrical conductivity of the P–graphene and Ag–graphene nanocomposite was 1.89 and 2.29 S cm\(^{-1}\), respectively, and as shown in Fig. 8, it was found that the conductivity

![Fig. 6](image1.png) Static contact angle of (a) P–graphene, and, (b) the as-prepared Ag–graphene nanocomposite.

![Fig. 7](image2.png) Photocurrent measurements by the LSV for the P–graphene and Ag–graphene nanocomposite in the dark and under visible light irradiation.
of the Ag–graphene nanocomposite was improved greatly via the uniform decoration of AgNPs. This shows the combined effect of the π–π interaction between the graphene sheets and AgNPs. This further suggests that the decoration of graphene sheets using metal NPs is as an alternative route to improve the electrical conductivity of graphene. In addition, as an excellent electrical conductor, silver has been widely used as the electrode material to ensure good electrical contact and graphene as a support. The decoration of AgNPs is expected to reduce the contact resistance between the graphene sheets. This greatly facilitates the flow of charge carriers across the contact regions, thus enhancing the electrical conduction behaviour of the resultant composite.

Estimation of the photocatalytic degradation of organic dyes using the Ag–graphene nanocomposite

The photocatalytic activity of the Ag–graphene nanocomposite was evaluated by degrading MB and CR as model pollutants under visible light irradiation. Fig. 9(a) and (b) shows the photocatalytic degradation kinetics of MB and CR as a function of the irradiation time. Here, C is the absorption of the MB and CR solutions at each time interval of irradiation, and C₀ is the absorption of the initial concentration (time 0). In the presence of the Ag–graphene nanocomposite as a photocatalyst, the MB and CR degradation was enhanced remarkably. The absorbance intensity decreased gradually with increasing reaction time, which was an indication of the photodegradation of MB and CR. Approximately 65% of MB and 90% of CR was degraded after 6 and 5 h, respectively, under visible light irradiation in the presence of the Ag–graphene nanocomposite as a photocatalyst. This suggests that the small size of the AgNPs anchored at the surface of the graphene sheets enhanced the photocatalytic activity of graphene for effective pollutant degradation under visible light irradiation. Compared to earlier studies, the Ag–graphene nanocomposite induced the much better visible-light-induced photocatalytic degradation of organic pollutants. The AgNPs are well known for their super-antibacterial activities. Therefore, purified water will be free of salt and impurities and most bacteria and microorganisms.¹³,³⁷,³⁸

Mechanism of the enhanced photocatalysis for the photodegradation performance of MB and CR

In the photocatalysis process, under visible light irradiation, oxygen species, such as the superoxide radical (O₂⁻), hydroxyl radical (·OH) and hydrogen peroxide (H₂O₂), are formed in situ and these reactive oxygen species (ROS) initiate the photodegradation activity. These radicals are produced by the photocatalytic reduction of oxygen and oxidation of water.³⁷–³⁹

Fig. 10 presents the electron transfer mechanistic outline of the photoinduced charge separation, migration and photodegradation process under visible light irradiation.⁴⁰ In the presence of visible light the dye* could act as a sensitizer and excited electrons were injected to the graphene (electron acceptor) surface to become dye*⁻, followed by self-degradation or decomposition by the adsorbed O₂.⁴¹–⁴³ The injected electrons on the graphene surface could subsequently move to AgNPs, which specially separated the dye*⁻ and electrons, thus retarding the recombination process. In addition, the graphene with ultrahigh charge carrier mobility at room temperature, thus, can significantly enhance the charge transfer and separation of photogenerated electrons. This makes graphene an electron acceptor and electron transport “highway” in the composite photocatalytic system.⁴¹ The decline in electron accumulation on the graphene surface evidently enhanced the continuous electron transfer from dye*⁻ to graphene. In addition, the irradiation could induce the formation of free radicals (·OH) in solution,⁴⁴ which oxidize the dye more easily. Furthermore, as AgNPs is an electron mediator

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**Fig. 8** DC electrical conductivity measurement of the P–graphene and Ag–graphene nanocomposite.

**Fig. 9** C/C₀ versus time (h) plot for the photodegradation/decolourization of (a) MB, and (b) CR using the P–graphene and Ag–graphene nanocomposite under visible light irradiation.

**Fig. 10** Proposed mechanism of photosensitized degradation of dyes over the Ag–graphene nanocomposite under visible light irradiation.
for charge separation, the surface adsorbed O$_2$ could trap the electrons from AgNPs to form various ROS, thus greatly enhancing the performance of photodegradation. In general, the dye was firstly excited to dye*, followed by an electron transfer from the dye* to graphene. Then, the electron further moved to the AgNPs and was trapped by O$_2$ to produce various ROS.

The higher photocatalytic activity of the Ag–graphene nanocomposite could be attributed to the (i) high adsorption ability of the dye, (ii) strong π–π interaction with the dye chromophoric groups, (iii) efficient photosensitized electron injection, and (iv) slow electron recombination rate. The above mentioned features make the Ag–graphene nanocomposite a good photocatalyst for the photodegradation of organic pollutants.

Conclusions

This paper proposed a fast, facile, low cost, large-scale, and environmentally friendly preparation of the Ag–graphene nanocomposite using EAB as a reducing tool. This opens the door to the fabrication of novel nanocomposites for the efficient photodegradation of organic dyes and improved photocurrent studies. The main goal of this work was to synthesize and test a nanocomposite with a small concentration of AgNPs decorated on the graphene sheet, which would enhance the visible light harvesting, leading to an increase in the rate of degradation of organic dyes and photocurrent. The photodegradation and photocurrent measurements indicated an increase in the charge carrier mobility which is associated with increase in the light harvesting ability of the Ag–graphene nanocomposite. Contact angle measurement confirms the hydrophilic nature of the Ag–graphene nanocomposite which further supports the enhancement in photocatalysis. The Ag–graphene nanocomposite exhibited higher photocatalytic activity, photocurrent and DC electrical conductivity compared to P–graphene, which may have applications in the fabrication of commercial and industrial photocatalytic devices, environmental conservation, purification processes, photoelectrodes and optoelectronic devices.

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References