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Graphene based Nanoassembly for simultaneous Detection and Degradation of Harmful Organic Contaminants from Aqueous Solution

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Graphene based nanoassemblies that can simultaneously detect and degrade the harmful organic contaminants from water are important for conquering risk of hazardous chemicals. A unique semiconductor-metal-graphene nanosheet assembly design, have been successfully fabricated by a wet chemical method. Such nanoassembly arrangement is made up of ZnO-Ag core-shell nanostructures, integrates on the graphene nanosheets (GNS). High-resolution scanning transmission electron microscopy reveals ZnO-Ag core-shell nanostructures consist of (core ZnO nanosphere covered by Ag shell) are chemically decorated on the GNS surface. This ZnO-Ag-GNS nanoassembly is SERS active and hence able to sense organic contaminant such as acridine orange dye. The sunlight-driven photocatalytic activity of the ZnO-Ag-GNS nanoassembly design demonstrates the tremendous enhancement in the detection and degradation of organic contaminant. Results in the present study show that the enhancement in the photocatalytic activity that is attributed to the interfacial charge transfer effect in ZnO-Ag-GNS interfaces. This new design exhibits an efficient photocatalytic degradation of organic dye under sunlight irradiation. This could be a great potential for highly sensing, stable and reusable material for energy and environmental cleaning applications.

1. Introduction

Sensing and destroying of harmful organic contaminants in water bodies remains a major problem in the ecological system. The detection of toxic organic dye effluents released from various industries like tanneries, textiles, etc., containing nitroaromatic dyes used as a colouring agent and finds their way into rivers. These hazardous contaminants will destroy the ecosystem in the near future. The photocatalytic performances of semiconductor based nanoassemblies are helpful in the remediation of hazardous organic contaminants from water bodies.^{1a-c}

Under excitation with an energized photons need to separate electrons and holes in a semiconductor and allowing them to initiate degradation of organic dyes at the interface. ZnO, a wide band gap n-type semiconducting nanomaterial, is a widely studied system for photocatalytic applications.^{2a-b} For a photocatalytic reaction process, the reaction molecules receive electrons and holes from the surface sites for the further reduction reactions. In competition with the charge carriers (i.e., electrons and holes), most of them were

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recombined due to wide band gap energy and instability in the higher state, which is a crucial factor that limits the photocatalytic activity by low quantum efficiency.^{3a-c} In order to avoid the rapid recombination rate of electron-hole pair, a widely reported approach is to incorporate metal nanomaterials on a n-type semiconductor.⁴⁻⁸ The photogenerated electrons transfer to the metal nanomaterial across a junction and become trapped owing to the Schottky barrier whereas the holes generously spread to the semiconductor surface.

There are two factors that subjected to reducing the electron-hole pair recombination rate: (i) the appearance of defects during the formation of interface engineering in the hybrid nanostructures^{7a-c} and (ii) some electron rich cocatalysts with semiconducting metal oxides are incorporated to form a hetero-junction between the host semiconductor and the co-catalyst that generates a local electric field, which separates the electron-hole pairs completely.¹¹⁻¹² However, there are certain countable limitations are occur owing to the lack of bulk-to-surface sites in the created interfaces that reduce the exposed metal-semiconductor surfaces and thus makes it complicated for the reaction molecules to lift up the photo-induced charge carriers for reduction reactions on the surface.⁹⁻¹⁰

Subsequently, we decided to adopt a new materials design to conquer this undesirable condition. This new nanoassembly made by integrating a graphene nanosheet, which is a well identified two-dimensional material with excellent physiochemical properties and very high electron mobility, into



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fabricated n-type semiconductor (ZnO) – metal (Ag) core-shell nanostructure. Interestingly, Ag nanoparticles showing Localized Surface Plasmon resonance effect (LSPR) improves Raman scattering of organic contaminants and thus facilitates the sensing through surface enhanced Raman spectroscopy (SERS).¹¹⁻¹³ As the graphene nanosheet is in close contact with the metal nanomaterial in this assembly, it is anticipated that the electrons gathered on the conduction band of semiconductor can transfer to the graphene nanosheets through a metal-graphene pathway and entirely taken up by oxidized molecules and simultaneously the holes reside on the semiconductor for reduction reactions.¹⁴⁻²⁰ The adaptability of this new nanoassembly is superior than other recent reported literatures, because of its capability of both sensing and rapid photodegradation of organic contaminants in aqueous medium.^{21a-e} The significance of the each component in the ZnO-Ag-GNS nanoassembly is portrayed in fig 1.

In this work, we demonstrate a unique semiconductormetal-graphene nanoassembly design, which can perfectly overcomes the above mentioned limitations and thus enhances the photocatalytic activity by LSPR and interfacial charge transfer effects. The versatility of using this unique nanoassembly can simultaneously detect and degrade the organic contaminants dispersed in the aqueous solution under natural sunlight irradiation.



Fig.1 (a) GNS and Ag Nps works to enable detection of organic contaminants in the aqueous solution and (b) Photoinduced charge carriers from the semiconductor can transfer to the graphene nanosheets through a metal-graphene pathway and entirely diffused the target molecules.

2. Experimental Section

2.1 Materials

All the chemicals used in this work were analytical grade and were used without any further purification. Graphite (325 mesh, Alfa Aesar), potassium permanganate (Sigma-Aldrich), hydrogen peroxide (30 wt%, Sigma-Aldrich), sulfuric acid (Rankem Chemicals), hydrochloric acid (Rankem Chemicals), zinc acetate dihydrate (Fischer Chemicals), oxalic acid (Fischer Chemicals), silver nitrate (SRL Ltd.), ethanol (Hayman limited), and acridine orange dye (Fischer Chemicals).

2.2 Synthesis of ZnO nanomaterials

In a typical experiment, 1.0 M of zinc acetate $[Zn(CH_3COO)_2.2H_2O]$ was dissolved in double-distilled water

(200 mL) at ~5 °C and stirred for 30 minutes. 1.5 M of Oxalic acid ($H_2C_2O_4.2H_2O$) dissolved in double-distilled water (200 mL) at ~5 °C was slowly added to the cold solution of Zinc acetate. The mixture was further stirred for 2 hours at low temperature till the solution gradually turned into white precipitate. The precipitate was then filtered and washed with ethanol and allowed to dry at 80 °C for 2 hours and that end up in Zinc oxalate formation. Zinc oxalate was further calcined at 400 °C for 2 hours to obtain pure ZnO nanomaterial.

2.3 Preparation of ZnO-Ag core-shell nanostructures

Experimentally, a facile wet chemical approach has been developed to fabricate the ZnO-Ag core-shell nanostructures with different Ag shell thickness. In detailed experimental procedure, a given amount of silver nitrate (1 mM, 4 mM and 7mM) and 100 mg of zinc oxide were dispersed in 100 mL of ethanol under vigorous magnetic stirring. Subsequently, the suspension was aged at room temperature for 2 hours and finally, it was dried isothermally at 80°C for 12 hours and then the residue was transferred into the furnace at various temperatures for 2 hours to crystallize the materials. The thickness of the Ag shell could be varied by changing the concentration of silver nitrate precursor as 1 mM, 4 mM and 7 mM and named as ZnO-Ag – 1, ZnO-Ag – 2 and ZnO-Ag – 3 respectively.

2.4 Synthesis of ZnO-Ag-GNS Nanoassembly

The synthesis procedure for ZnO-Ag-GNS nanoassembly was schematically explained in the fig. 2. The as-synthesized GNS (100 mg) was dispersed in double distilled water (100 mL) using ultrasonicator to form a colloidal suspension. The GNS solution was added to a higher silver nitrate concentration of ZnO-Ag core-shell (ZnO-Ag – 3) suspension (100 mg of material is dispersed in 100 mL double distilled water). The obtained precipitate was stirred vigorously and separated by centrifugation at 4000 rpm. The resulting product was washed with ethanol and dried in a vacuum oven at 100°C for 24 hours to get a ZnO-Ag-GNS nanoassembly.





2.5 Characterization

X-ray diffraction (XRD) data were collected with a PANalytical X-Ray diffractometer using Cu K α (λ = 1.54 Å) radiation. The

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samples were scanned in the 2θ range of 10° to 80° . All of the peaks were assigned and compared with data from Joint Committee on Powder Diffraction Standards (JCPDS) database. XPS measurements were obtained using ESCA+, Omicron probe spectrometer Nanotechnology **FSCA** with monochromatized Al Ka X-rays (energy: 1486.6 eV). The X-ray power applied was 300 W. The pass energy was 50 eV for survey scans and 20 eV for specific regions. Sample solution was spotted on a molybdenum sample plate and dried in vacuum. Spectra in the required binding energy range were collected, and an average spectrum was taken. Each spectrum was confirmed after scanning eight times for confirmation (except survey scan, which was scanned only once). While taking the spectra, the scan steps per second was fixed for all of the narrow scans. Beam-induced damage of the sample was reduced by adjusting the X-ray flux. The base pressure of the instrument was 5.0 \times 10 $^{\rm 10}$ mB. The binding energy was calibrated with respect to the adventitious C 1s feature at 284.6 eV. Most of the spectra were deconvoluted to their component peaks, using the software CASA-XPS. Highresolution scanning transmission electron microscopy (HRSTEM) of the samples was carried out using a FEI Tecnai G2 S-twin instrument with a UHR pole piece. HRSTEM samples were prepared by drop-casting two or three drops of sampledispersed ethanol solution to carbon-coated copper grids and allowed to dry at room temperature overnight. The photoluminescence (PL) spectrum was recorded by Perkin Elmer MPF-44B equipment under (325 nm) excitation.

2.6 Photocatalytic activity

The Photocatalytic activity of ZnO-Ag-GNS nanoassembly was evaluated by the degradation of Acridine orange (AO) under solar light. In a typical process, 150 mL of (3.0X10⁻⁵ M, 3.5X10⁻⁵ M and 4.0 X10⁻⁵ M) concentrations of AO dye solution and 50 mg of ZnO-Ag-GNS nanostructures was stirred for about 1 hour. Before exposure to illumination, the suspensions were stirred in the dark for 30 minutes to ensure the establishment of adsorption/desorption equilibrium of AO on the sample surfaces. Consequently, the suspension was irradiated with direct sunlight and this was carried out for all the experiments under similar conditions on sunny days in Chennai city (geographical location 13.04° N and 80.17° E on the southerneast coast of India), between 12:00 p.m. and 3:00 p.m. (outside temperature, 29°C to 31°C). The measured illuminance power of the direct sunlight at the given interval of time was around 110000 lux to 120000 lux obtained by using Digital illuminance meter (TES Electrical Electronic Corp. Taiwan). At a given time interval of irradiation, 5 mL of the suspension was withdrawn and subsequently centrifuged at a rate of 3000 rpm for 5 minutes. UV-Vis absorption spectra of the supernatant were then measured using a UV-visible spectrophotometer.

3. Results and discussion

3.1 Structural analysis

The crystalline structures, phase purity and textural features of the as-synthesized nanostructures were studied by XRD analysis. The XRD patterns of the pure ZnO, ZnO-Ag core-shells and ZnO-Ag-GNS stack design were shown in fig. 3. All of the samples were crystalline in nature and of hexagonal wurtzite phase ZnO (JCPDS No. 36-1451). However, the ZnO-Ag coreshells exhibited additional Ag diffraction peaks located in the fig. 3, which could be indexed to the metallic silver with facecentered cubic system (JCPDS No. 01-1167), signifying that the Ag nanomaterials were covered on the ZnO surface. Increase in the Ag concentration, the Ag peak intensity also increases accordingly.²²⁻²³ The XRD patterns of the ZnO-Ag-GNS stack show a broad peak at 25.7 and 41.16 degrees, corresponding to the (002) and (100) reflections. It is evident that the graphene oxide is significantly reduced to graphene nanomaterials.^{24a-c} Very low guantity of ZnO-Ag-3 core-shell nanostructure were integrates onto the GNS surfaces that can be evidently compared and analyzed with individual nanomaterials. However, the existence of metallic Ag in ZnO-Ag-GNS can be obviously elucidated by XPS analysis, as discussed in the next section.

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Fig. 3 XRD patterns of the pure ZnO, different shell thickness of ZnO-Ag-1, ZnO-Ag-2, ZnO-Ag-3 and ZnO-Ag-GNS hybrid nanostructures

3.2 Chemical state analysis

To obtain further essential information on surface structure, chemical analysis and oxidation states of ions of the asprepared nanostructures, XPS analysis was performed on the ZnO-Ag-GNS hybrid nanostructures. Figure 4 (a) exhibits the survey spectrum, which indicates that the sample contains Zn, O, Ag and C elements and evidently confirms that no other elements were indentified. The peaks located at 1020.4 eV and 1043.4 eV correspond to Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively, representing the existence of Zn²⁺ state (in fig. 4 b).²⁵ Figure 4 (c) shows the Ag 3d XPS spectra with two broad band's at 367.3 eV and 373.3 eV binding energies, which are ascribed to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively. No other peak corresponding to Ag₂O or AgO was observed in the XPS

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20_

Sd: 15

Ag 3d 3/2

369

Binding Energy (eV)

C 1s regions of ZnO-Ag-GNS hybrid nanostructures.

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Sd) 12

Fig. 4 (a) XPS survey spectra and (b) high resolution spectra of Zn 2p, (c) Ag 3d, and (d)



286 285 284 283 28

Binding Energy (eV)

3.3 Electron microscopic studies

The electron microscopic images of the as-synthesized nanomaterials ZnO, ZnO-Ag-1, ZnO-Ag-2, ZnO-Ag-3 core-shell nanostructures and ZnO-Ag-GNS hybrid nanostructures, are given in Figs. 5 and 6. The surface morphology of the ZnO nanomaterial exhibits uniform spherical structure of diameter ranging from 20 nm to 25 nm that is exhibited in fig. 5 (a). To fabricate core-shell nanostructures with different shell thickness, by increasing the silver nitrate concentration (1 mM, 4 mM and 7 mM) and coated onto the ZnO under stimulated reaction medium (in figures 5 b, c & d). The thickness of the outer shell is in the range of ~3 nm to 4 nm for (ZnO-Ag-1), ~4 nm to 6 nm for (ZnO-Ag-2) and ~6 nm to 8 nm for (ZnO-Ag-3) respectively. The respective insets clearly show the surfaces of the ZnO were completely coated with metallic Ag nanoshell of different thickness, which were obtained by increasing the concentration of silver nitrate precursor, which are in good agreement with the XRD results.

Figure 6 evidently shows the formation of GNS with ultrathin wrinkled silk wave like structure. This is apparent that the GNS definitely acts as a two-dimensional support for the incorporation and growth of homogeneous core-shell nanostructures. After integrated with larger shell thickness of ZnO-Ag core-shell nanostructure, the GNS was completely decorated by crystalline ZnO-Ag core-shell nanostructures.



Fig. 5 Electron micrographs of (a) ZnO, (b) 1 mM Ag concentration of ZnO-Ag-1, (c) 4 mM concentration of ZnO-Ag-2 and (d) 7 mM concentration of ZnO-Ag-3 core-shell nanostructures, respective insets shows its higher magnification.



Fig. 6 Electron micrographs of (a) GNS and (b) ZnO-Ag-GNS hybrid nanostructures, respective insets shows its higher magnification images.

3.4 Detection of Organic contaminant

SERS is a versatile technique for the detection of organic molecules in the aqueous solution; it employs the interaction between the organic molecule (target) and the LSPR of Ag NPs, to intensify the Raman signal of the organic molecule. Moreover, the GNS in ZnO-Ag-GNS nanoassembly can improve SERS signals due to quenching in the fluorescence effect along with its Raman-enhancing properties.²⁷ Herein, we investigated the capability of this ZnO-Ag-GNS nanoassembly to perform as chemical sensors by employing acridine orange as the target molecule. ZnO-Ag-GNS nanoassembly was disperses in aqueous solution of various concentrations of AO and SERS studies were carried out by using 532 nm laser excitation source. Figure 7 shows SERS spectrum of ZnO, ZnO-Ag core-shells (7mM concentration of Ag shell material) and ZnO-Ag-GNS nanoassembly are in contact with 1mL of 3.0 X 10⁻⁵ M concentration of AO in aqueous solutions. Control experiment was carried out with AO in aqueous solution and with ZnO nanorods show no detectable Raman signal. However, ZnO-Ag-GNS nanoassembly under the same conditions delivers significant enhancement of the Raman Published on 17 March 2016. Downloaded by Mahidol University on 17/03/2016 11:38:53

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signal of AO as Ag shell layer close in contact with GNS serve as SERS active sites. The prominent bands in the region between 500 cm⁻¹ - 700 cm⁻¹ were assigned to out of plane ring and CH deformation modes. The weak band around 1171 cm⁻¹ mainly arises due to the CH deformation and CN stretching vibration. Additionally, the bands between 1350 cm⁻¹ - 1650 cm⁻¹ corresponding to the C=C and C=N stretching vibrations are also seen.²⁸



Fig. 7 SERS spectra of 3.0X10⁻⁵ M concentration of AO in the presence of ZnO, ZnO-Ag core-shells and ZnO-Ag-GNS nanoassembly. All the samples were kept in 1 mL of 3.0X10⁻⁵ M concentration of AO in aqueous solution and allowed to immobilize for 30 min prior to SERS experiment.



Fig.8 SERS spectra of AO in the presence of ZnO-Ag-GNS handassembly at AC concentrations of 3.0X10⁻⁵ M, 3.5 X10⁻⁵ M and 4.0 X10⁻⁵ M in aqueous solution.

ZnO-Ag-GNS nanoassembly sensor consent the flexibility of detecting wide range of organic molecules since GNS is interfaced with Ag shell layer, that can detect a low level of organic molecules from aqueous solution. Thus, the material construction of ZnO-Ag-GNS nanoassembly provides a flexible route for detection of a wide range of organic molecules at lower concentrations. For comparison, the SERS response of ZnO-Ag-GNS nanoassembly by varying AO concentration is shown in Fig. 8. GNS not only gives a 2-D platform for the fabrication of a chemical sensor but also adsorbs the organic molecules with higher chemical concentrations. Furthermore, the organic molecules interact with GNS through van der Waals forces, which assist in the concentration of organic molecules onto the surface of the GNS. These interactions provide fasten to attract and immobilize the organic molecules (pollutants) at the material interface and simultaneously degrades the pollutants under the exposure of natural sunlight.²⁹⁻³⁰ However, the degradation mechanism of organic pollutants using this material can be obviously elucidated by photocatalytic experiments, as discussed in the following sections.

3.5 Photocatalytic degradation of AO dye under direct sunlight irradiation

The photocatalytic activity of the as-prepared ZnO, ZnO-Ag core-shell, and ZnO-Ag-GNS hybrid nanostructures were studied by monitoring the degradation of mutagenic organic pollutant (AO) under direct sunlight irradiation. The change in the absorption spectra of AO aqueous solutions showed the changes of its concentration. The initial concentration (C_0), the residual concentration (C), and the degradation rate (D%), is illustrated by the mathematical expression as follows:

$$D\% = (C_0 - C/C_0) \times 100\%$$
(1)

Figure 9 showed the AO degradation plot versus time for ZnO, ZnO-Ag-1, ZnO-Ag-2, ZnO-Ag-3 core-shells, and ZnO-Ag-GNS nanoassembly photocatalysts, respectively. C/C_0 spectra indicate that the 3.0×10^{-5} M concentration of AO dye was decomposed of about 48% for pure ZnO nanomaterial within 70 minutes, 51% for ZnO-Ag-1 core-shell within 100 minutes, 57% for ZnO-Ag-2 core-shell within 70 minutes, 89% for ZnO-Ag-3 core-shell within 70 minutes and 99% for ZnO-Ag-GNS hybrid nanostructures within 20 minutes (fig. 10 c&d) under direct sunlight irradiation. ZnO-Ag-GNS nanoassembly showed higher photocatalytic efficiency than that of the pure and core-shell nanomaterials. This result attributed that GNS enhances the photocatalytic performance of ZnO-Ag core-shell nanomaterial under direct sunlight irradiation.

Figures 10 (a) and (b) illustrate that the photocatalytic degradation process of AO over ZnO-Ag-GNS nanoassembly photocatalyst under sunlight irradiation was effectual. More importantly, by increasing the AO dye concentrations like $3.0 \times 10-5$ M, $3.5 \times 10-5$ M, and $4.0 \times 10-5$ M, and it was indicated that the ZnO-Ag-GNS nanoassembly photocatalyst could easily degrade the AO dye within 20 minutes of irradiation under direct sunlight and can be separated and reused by centrifugation. The stability of the nanoassembly photocatalysts was examined by three consecutive experimental cycles, which are very essential for the photocatalyst to be applied in environmental technology.

After three cycles of experiment, the ZnO-Ag-GNS photocatalyst still provides high photodegradation rate under direct sunlight irradiation. It shows that the ZnO-Ag core-shells were decorated onto GNS by electrostatic interaction which offers higher stability to the photocatalysts for multipurpose remediation process. Hence, it could be significantly promote

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their practical application to remove various harmful mutagenic organic pollutants from wastewater under direct sunlight irradiation.



Fig. 9 Time-dependent photocatalytic degradation of AO (a) dye under sunlight irradiation, ZnO (b), ZnO-Ag-1 (c), ZnO-Ag-2 (d), ZnO-Ag-3 (e) core-shells and ZnO-Ag-GNS hybrid nanostructures (f).



Fig. 10 Concentration dependent AO dye degradation under sunlight irradiation (a), stability and reusability studies (b) and C/C₀ & degradation percentage of AO in the presence of as-prepared nanostructures (c&d).

3.6 Mechanism of enhanced photocatalytic activity under sunlight

From the above studies, the proposed mechanism of the efficient photocatalytic performance towards the degradation of organic pollutant under sunlight could be credited mainly due to LSPR effect and interfacial charge transfer process in this unique ZnO-Ag-GNS nanoassembly. We anticipate that the electrons gathered on the conduction band of semiconductor can transfer to the graphene nanosheets through a metal-graphene pathway and entirely taken up by oxidized molecules in the mean time, whereas the holes reside on the semiconductor for reduction reactions.^{10, 26, 31}

$ZnO-Ag + hv \rightarrow e^{-}(Ag) + h^{+}(VB, ZnO)$	(2)
$GNS + e^{-}(Ag) \rightarrow e^{-}(GNS) + ZnO$	(3)
$GNS + e^{-}(AO) \rightarrow e^{-}(GNS) + AO$	(4)
$H_2O + h^+ (VB, ZnO) \rightarrow \bullet OH + H^+$	(5)
AO (ad) + \bullet OH \rightarrow CO ₂ + H ₂ O	(6)



ZnO-Ag-GNS Nanoassembly

Fig. 11 Schematic illustration of a plausible mechanism involved in the charge transfer process from the different energy levels of the ZnO-Ag-GNS for the photodegradation of acridine orange dye.

In the ZnO-Ag-GNS nanoassembly, the photogenerated electrons in the ZnO can be moved to the conduction band and separate the holes in the valance band by fascinating solar spectrum due to the suitable narrow band gap of ZnO-Ag coreshell structure. These photogenerated electrons can be transferred to GNS and metallic Ag nanomaterials. On the other hand, photogenerated electrons cannot flow directly from AO to ZnO-Ag core-shell nanostructures (in fig. 11), since there was a mismatch in their energy levels. A photo-excited electron from AO flows into CB of ZnO core in the ZnO-Ag core-shell nanostructures via GNS, where the photogenerated electrons react with oxygen molecules in the aqueous solution producing oxygen peroxide radicals. The positively charged holes breaks the hydroxide ion derived from aqueous solution to form hydroxyl radicals.³²⁻³⁵ These oxygen peroxide radicals and hydroxyl radicals generated from ZnO-Ag-GNS nanoassembly can mineralize and oxidative decomposition of acridine orange dye to CO₂, H₂O, and other by-products. Surprisingly, GNS has excellent electron mobility due to its two dimensional honey comb structure, the interfacial charge transport of photogenerated carriers could be achieved, and an effective charge separation is consequently proficient. Therefore, the photodegradation is enhanced by excellent interfacial charge transport in ZnO-Ag-GNS nanoassembly. Moreover, the

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influence of interface engineering could enhance the photocatalytic activity of ZnO-Ag-GNS hybrid nanostructures. **3.6 Photoluminescence studies**

The charge separation property and recombination rate of photogenerated electrons-holes can be identified bv photoluminescence spectroscopic studies. The photogenerated electrons in the excited state can endure recombination with the holes, and results in irradiative release of energy in the form of fluorescence. Based upon the fluorescence emission characteristics of ZnO, ZnO-Ag and ZnO-Ag-GNS can be measuring monitored by the room temperature photoluminescence spectra (in fig. 12). It is manifest that the peak at 385 nm shows strong UV band and the weak green emission peak at 535 nm have been observed for pure ZnO nanomaterials due to its free excitonic emission near the band edge and local defect states respectively. The PL spectra of the ZnO-Ag core-shell nanostructure compared with the pure ZnO nanomaterials, the intensity of the ZnO peaks decreases and shifted significantly due to the presence of Ag layer.³⁶⁻³⁷ It is obvious that there is a heterojunction between the semiconductors that certainly reduces the defect during coreshell formation process. Decrease in the PL emission intensity indicates the better charge separation efficiency. Furthermore, the emission intensity of the ZnO-Ag-GNS nanostructure peak decreased significantly, implying that the recombination rate of photogenerated charge carriers was effectively suppressed.⁹ As a result, GNS is an excellent candidate for enhance the photocatalytic activity in terms of prolonging the electron-hole pair lifetime, which drastically reduced the recombination rate of electron-hole pair and accelerates the interfacial charge transfer process.



Fig. 12 Room temperature PL spectra of ZnO, ZnO-Ag core-shell and ZnO-Ag-GNS hybrid nanostructures

4. Conclusions

In summary, the simultaneous detection and degradation of organic contaminant by using a unique designed ZnO-Ag-GNS nanoassembly is demonstrated. Such nanoassembly combining the ability to target organic molecules with SERS active and photocatalytic activity provides a robust platform for multipurpose sensing and destroying applications. Moreover, this nanoassembly structure facilitates efficient charge transfer process and the separation of electron-hole. In consequence, the separation of electron-hole pairs is a significant process for all the applications concerning semiconductor materials. It seems that, this strategy may also be applicable to synthesis various hybrid nanostructures and also it recovers all the limitations and solutions in the photocatalytic field. We envisage that it will create a new development in designing hybrid nanomaterials for simultaneous sensing and photocatalytic environmental cleaning applications.

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Graphical Abstract

