Hybrid nanocomposites with enhanced visible light photocatalytic ability for next generation of clean energy systems

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Abstract

Heterogenous photocatalysis is widely used for waste-water treatment and degradation of pollutants and promises to advance the science of alternative materials with visible photo-excitation abilities. However, there are still fundamental material properties and processes that need to be understood in order to increase user-tailored catalytic systems' performance and efficiency, while ensuring their optimized reactivities and large-scale development and implementation.

Herein we developed graphene-based hybrid composites to be used as efficient nanocatalysts with increased ability to absorb visible light, that retain high corrosion-resistance properties when used in solution, and provide energy levels that match their reduction and oxidation half-reactions. Using both photo-deposition and photo-reduction methods, we first created platinum/tungsten trioxide conjugates with physico-chemical characteristics investigated by microscopical and spectroscopical analyses, and further decorated such conjugates onto graphene surfaces to create the hybrids. Our results demonstrate that the synthesized hybrids can degrade a model azo dye and further, show that graphene plays an important role in delaying electron transfer at its interface, with such effect being exploited for possible integration in the next generation of clean energy systems.

Keywords: graphene, hybrid, composite, delayed electron transfer

Introduction

Active research is currently focusing on identifying technologies capable to increase the energy efficiency while reducing the human footprint and its impact on the environment. Relying on converting solar resources such as photons-to-electricity[1, 2] or photons-to-heat-to-electricity,[3, 4] such technologies use user-tailored nanocatalytic systems and aim to improve energy generation.[5-7] However, there are still fundamental material' properties and processes that need to be understood in order to increase user-tailored catalytic systems' performance and efficiencies[8] while ensuring their optimized reactivities and large-scale integration.

Two main routes have been previously used to improve nanocatalyst's photocatalytic performance, i.e., increase of the electron-hole generation[9, 10] and delay of photo-induced charge recombination.[11, 12] Specifically, studies aiming to improve TiO₂ reactivity under visible light irradiation proposed introducing suitable heteroatoms onto its structure[13, 14] and/or narrowing its band-gap.[15] However, such heteroatoms inserts need special technologies processing (e.g., sputtering,[16] ion implantation,[17] thermal treatments,[18] and others), are high energy cost and largely inefficient when yield is desired, thus with limited large-scale consumer and industrial implementation. Further, photocatalysis efficiency of the heteroatoms modified semiconductor materials may not be significantly improved when compared to their starting counterpart.[19] Complementary, p-n junctions have been created in semiconductor nanomaterials such as molybdenum disulfide (MoS₂)/ nitrogen-doped reduced graphene oxide (n-rGO)[20] or nickel oxide (NiO)/ titanium dioxide (TiO₂)[21] to optimize photocatalytic activity,[22] while semiconductor nanoparticles-based surface heterostructures have been implemented to enhance separation of photogenerated carriers.[23-25] The resulting heterostructure interface was used to cage photoinduced electrons and consequently separate generated electron-hole pairs.[26] Additionally, n-n junctions heterostructures such as the ones found in structures of silver phosphate/ iron oxide (Ag₃PO₄/ Fe₂O₃),[27] silver vanadate/ zinc oxide (Ag₃VO₄/ ZnO),[28] or zinc oxide/ silver bromide/ iron oxide/ silver vanadate (ZnO/ AgBr/ Fe₃O₄/ Ag₃VO₄)[29] have recently been used to promote efficient separation of the charge carriers and generate high efficiency photocatalysis systems based on delayed electron-hole recombination effects. Further, it was also showed that the large surface area of graphene (GO) for instance,[30] its zero bandgap,[31] excellent electrical conductivity and ability to enhance electron transport,[32] its exceptional transparency,[33] and good chemical stability,[34] could lead to its integration as a promoter of photocatalytic reactions in heterostructures.[16]

Studies of TiO₂ integrated with graphene for instance demonstrated nanohybrids with increased light absorption capability, all relative to bare TiO₂ or TiO₂-carbon nanotubes-based composites with the same carbon content.[35] It was also reported that when graphene oxide was wrapped with Ag or Ag-based suspensions (e.g., AgX, with X=Br, Cl), high efficiency in removing organic pollutant methyl orange (an azo dye widely used in textiles and paper industries) under visible-light irradiation was achieved.[36] Further, when zinc oxide (ZnO) nanoparticles were loaded onto graphene sheets, the resulting heterostructures exhibited significant increases in their photocatalytic activities as well as in the degradation ability of rhodamine B dye in water, all under UV irradiation.[37] However, the large band gap of such nanomaterials as well as considerable recombination of photogenerated electron-hole pairs limits their photocatalytic efficiency and thus applicability. Further, their activity is largely restricted to UV light irradiation which accounts for only about 3–

5% of our solar spectrum[38] thus impeding their implementation. The next generation of efficient nanocatalysts will need to allow for an increased ability to absorb visible light and retain high corrosion-resistance properties when used in solution.

Among the visible active semiconductor nanoparticles, the optical[39] and electronic properties,[40] small band gap (2.4 eV-2.8 eV),[41, 42] high oxidation power in the valence band,[43] low production cost, reduced toxicity and increased stability[41, 42] make tungsten trioxide (WO_3) a potential candidate for catalytic-based applications[43-48] to be used for water treatment[47] or clean energy generation.[46, 49, 50] However, because of its low conduction band,[43] high and fast recombination of photo generated electron-hole pairs, pure WO_3 does not show high photocatalytic ability which limits its implementation. For this nanocatalysts to reach its potential in consumer applications, strategies that enhance its photocatalytic activity under visible light should potentially involve a variety of combinatorial techniques that allow for effective modifications approaches, and doping effects to lead to increased photon absorption efficiency and reactivity.

Herein we propose to synthesize the next generation of visible light absorbing heterostructures based on WO_3 and GO for efficient photodegradation of model compound, rhodamine B. Using liquid phase photoreduction,[44] we designed WO_3 -based nanoparticles/ GO heterostructure and evaluated their efficiency for stable photocatalysis. WO_3 was chosen as starting material based on its above properties and catalytic promises as well as its increased charge separation efficiency[51] and remote oxidation activity when under visible light irradiation.[52] GO was chosen as a template based on its two-dimensional crystalline structure that can ensure efficient electron transfer at nanointerfaces.[20] Rhodamine B[53, 54] was chosen as the model system to demonstrate high photodegradation efficiency because of its high stability under visible light irradiation and reduced biodegradability.[55] This is especially important in the context of heterogenous photocatalysis being widely used for wastewater treatment, with previous studies being based on either traditional Ti[56] or ZnO[57] catalysts, tantalates[58] or germanates.[59] Further, the focus on rhodamine B is also supported by previous studies that showed that the dye is an active carcinogen,[60] more difficult to remove than other dyes such as methyl orange or methylene blue.[61-64] Our research aims to unravel the fundamental mechanisms, properties and processes that allow for increased performance, reliability, competitiveness and implementation of WO_3 - GO heterostructures in robust architectures while preserving their performance, all under visible light.

Materials and Methods

Synthesis of Graphene Oxide

Graphene oxide (GO) was synthesized using the established Hummer method and natural graphite powders.[65, 66] In a typical experiment, 1 g graphite powder (Acros Organics), 0.5 g sodium nitrate (Acros Organics, 99%) and 25 mL concentrated sulphuric acid (96.4 %, Fisher Scientific) were mixed into a 250 mL flask placed in an ice bath. Subsequently, 3 g of potassium permanganate powder (Fisher Scientific) was slowly added and the mixture was continuously stirred and cooled with fresh ice for 2 h in a water bath maintained at a temperature below 20 °C. After time elapsed, the mixture was transferred to another water bath having a temperature of about 35 °C and stirred for an additional 0.5 h. Next, 46 mL of deionized (Di) water were added slowly to the mixture, and subsequently the flask was placed at 98 °C for 15 min. Lastly, 140 mL of Di water followed by 10 mL of 30 % hydrogen peroxide (H₂O₂) aqueous solution (Fisher Scientific) were added. The obtained solid product was isolated by centrifugation, washed several times with 5 % hydrogen chloride (HCl) solution (diluted from 37.3 %, Fisher Scientific), Di water and ultimately dried under the vacuum.[67]

Synthesis of Conjugates and Hybrid Materials

To create tungsten trioxide (WO₃) conjugate, a photodeposition method was used. Briefly, 500 mg of WO₃ nanoparticles (99 %, Sky Spring Nanomaterials Inc) were dispersed in 50 mL Di water by ultrasonication. Subsequently, 10 mg GO were added to the solution, with the mixture being stirred overnight at room temperature and then filtered and washed with 1 M HCl solution containing 1 % H₂O₂ in Di water to remove impurities.[68] The wet powder was subsequently suspended in a solution containing 95 mL Di water and 5 mL methanol (99%, Fisher Scientific) and irradiated using a 500 W lamp for a 2 h period to produce reduced WO₃-GO hybrids, subsequently denoted as WO₃/r-GO.

In order to create platinized WO₃ and platinized WO₃/r-GO (Pt/WO₃ and Pt/WO₃/r-GO respectively) hybrids, a photocatalytic deposition/ reduction approach of Pt onto WO₃/r-GO was performed. Briefly, the method was achieved under visible light by using a 500 W lamp and chloroplatinic acid (MP Biomedicals, LLC) in methanol solution (5 mL methanol, 99 % in 95 mL Di water). The weight of Pt was chosen relative to lead to 2 wt %.[69]

Samples Characterization

The morphologies of the samples were evaluated using a Hitachi S-4700 Field Emission Scanning Electron Microscope (SEM) and a JEM-2100F Transmission Electron Microscope (TEM) respectively. For SEM characterization, samples (1 mg/mL in Di water) were dried under vacuum on silica wafers and imaged using a field emission gun operating at 10 kV.

Energy dispersive X-ray analysis (EDX) was used for quantitative elemental analysis. The experiments were performed on a Hitachi S-4700 Field Emission Scanning Electron Microscope (USA) with a S-4700 detector combining secondary (SE) and backscattered (BSE) electron detection (all in a single unit), operating at 20 kV. Results are presented as a map of element distribution.

Analysis of particle size distribution was performed using a dynamic light scattering instrument (DLS, DelsaTM Nano Particle Analyzer Beckman Coulter, Germany). The DLS measurement used Stokes-Einstein equation to yield the radius or the diameter of the samples. Briefly, suspensions of WO₃ and Pt/WO₃ were

prepared in Di water at a concentration of 100 $\mu\text{g/mL}$ and the mean particle diameter was calculated by analyzing the intensity, volume, and number distribution data collected for each one of the samples.

Raman spectroscopy (Renishaw InVia Raman Spectrometer, CL532-100, 100 mW) allowed determination of the physical and chemical characteristics of the samples. Briefly, powders were deposited on glass slides (Fisher, 25 x 75 x 1 mm) and irradiated through a 20X microscope objective using an Argon ion (Ar^+) laser beam with a spot size of $<0.01 \text{ mm}^2$ and operating at 514.5 nm. Scan were performed in the 100 to 3200 cm^{-1} ranges and low laser energy (i.e., $< 0.5 \text{ mV}$) with short exposure times (10 s) were used to prevent unexpected heating effects of the samples.

A digilab FTS 7000 Fourier transmission infrared spectroscope (FTIR) with an attenuated total reflectance (ATR) unit and a diamond crystal was employed to investigate the chemical characteristics of the samples. For this, 200 mg of the individual sample were pressed into barium sulfate paste (Shimadzu Corporation) to form a solid pellet subsequently used under FTIR conditions. Spectra ranging from 750 to 4000 cm^{-1} were collected using a Shimadzu 2550.

Ultraviolet (UV)–visible (VIZ) spectra were recorded using in the diffuse reflectance mode a Shimadzu 2550 UV–visible spectrometer equipped with an integrating sphere (UV 2401/2, Shimadzu).

PHI Versaprobe 5000 Scanning X-Ray Photoelectron Spectrometer (XPS, Physical Electronics) was used to examine the electronic state of the sample (i.e., for the presence of Pt, C, W, O elements respectively). The C1s peak at 284.6 eV was used as reference and to calibrate the binding energy of the different elements identified in the spectrum.[70]

Photocatalytic Degradation Tests

Synthesized samples (WO_3 , Pt/WO_3 , $\text{WO}_3/\text{r-GO}$, or $\text{Pt/WO}_3/\text{r-GO}$ respectively) were dispersed in 20 mL rhodamine B solution (10 $\mu\text{g/mL}$, Fisher Scientific) for a final concentration of 2 mg/mL. The mixture was stirred continuously for 0.5 h and subsequently exposed to a visible light lamp (500 W), at room temperature for 360 min, while under shaking. At each given time interval (10, 30, 60, 180, or 360 min respectively), 1 mL of the rhodamine B solution containing nanoparticles was isolated and centrifuged at 5000 rpm for 1 min, then 500 μL supernatant was isolated and monitored using an Evolution 300 UV-Vis spectrophotometer that allowed for absorption changes at 554 nm to be recorded.[71] A blank group (Di water mixed with nanoparticles however not irradiated) was used as control for each time point.

Rhodamine B degradation efficiency was expressed as C/Co , where C was the concentration of rhodamine B at different time intervals and Co was its starting concentration; the lower C/Co , the higher the degradation efficiency, where the concentration of rhodamine B was obtained by converting the absorption data using the Beer–Lambert law.[72]

Kinetic Parameters Calculation

Knowing that the photodegradation of rhodamine B follows roughly a pseudo first order reaction,[73] the kinetic of photodegradation reaction was evaluated using the following equation:

$$\ln (C/\text{Co}) = -kt,$$

where t was the reaction time and k is the reaction rate, as calculated from the slope of different $\ln (C/\text{Co})$ versus t curves.

Statistical Analyses

The photocatalytic degradation tests were repeated 6 times and the analyses are presented as mean $\pm$ standard deviation. The average size of nanoparticles is also presented as mean $\pm$ standard deviation with at least 15 individual nanoparticles being evaluated in TEM to obtain particle average size.

Results and Discussion

We used photodeposition of platinum (Pt) onto tungsten trioxide (WO_3) nanoparticles to generate (PtWO_3) conjugates. Previous research has showed that PtWO_3 has enhanced photoreaction ability mainly due to its improved multi-electron O_2 reduction,[74] with the presence of Pt promoting photo-irradiated electrons to react efficiently with O_2 before being trapped onto the WO_3 surface (Scheme 1).

The topography and morphology of the conjugates was first evaluated using Scanning Electron Microscope (SEM) and high-resolution Transmission Electron Microscopy (HR-TEM) and compared to that of the starting materials. SEM analyses identified porous structures and nanoparticles of spherical geometries (Figure S1), while TEM allowed for both size and crystalline lattice spacing determination. Specifically, evaluation of the WO_3 revealed size distributions between 20 to 100 nm (average of 61 ± 34 nm) and crystalline lattice spacing of about 0.38 nm corresponding to the (020) plane (Figure 1a).[75] Analyses also showed that the PtWO_3 conjugates were different than their starting WO_3 counterparts and were formed either from small (ranging from 5 to 20 nm) or large (20 to 100 nm) conglomerates (Figure 1b). HR-TEM identified the (111) lattice plane of Pt and its interplanar spacing of 0.23 nm (Figure 1c), as well as revealed the non-uniform distribution of the Pt at the interface with the WO_3 nanoparticle template. Such distribution was presumably associated with Pt's inclination to deposit and interact at the small facets or edges, the ones mostly corresponding to the (020) crystalline structure of the template, with previous research indicating that photodeposition of Pt is induced by direct adsorption of ions and the surface charge respectively.[45]

Energy Dispersive X-ray Spectroscopy (EDX) also confirmed the non-uniform distribution of the elements and their random concentrations within the samples (Figure S2). Lastly, dynamic light scattering (DLS) analyses showed that the size of the nanoparticles was not significantly changed by the deposition of Pt when compared to the pristine counter samples (Figure S3, Table S1). However, the calculated nanoparticles average size in DLS was larger than the one observed in TEM, and was presumably due to the degree of agglomeration as resulted from the dispersion of the nanoparticles in water.[76]

Secondly, hybrid materials based on reduced graphene (r-GO) and WO_3 or PtWO_3 conjugates respectively, were obtained by photodeposition under visible light as previously described.[77] Raman spectroscopy confirmed the generation of the r-GO-based hybrid materials; specifically, peaks around 810 cm^{-1} and 710 cm^{-1} which were attributed to the stretching of the O–W–O bonds, as well as peaks at 328 cm^{-1} and 270 cm^{-1} which were related to the bending vibration of the W–O–W bonds were noted.[78] Peaks below 200 cm^{-1} were also observed and were generally associated with the vibrations in the lattice modes of the WO_3 -based nanoparticles, while the D peak around 1350 cm^{-1} was related to the disorder induced in the carbon (C) structure by the photoreduction of the r-GO surface. Complementary, the G peak around 1600 cm^{-1} was associated with sp^2 C vibration.[79] The relative intensity (I) of D to G peaks (an indicator of the disorder degree in the C-based hybrids[76]) was 0.96 and 0.97 for the $\text{WO}_3/\text{r-GO}$ and $\text{PtWO}_3/\text{r-GO}$ respectively, all relative to the r-GO (0.83) used as control. The increase in I_D/I_G ratio indicated the higher degree of disorder upon formation of the hybrid, as well as suggested decreased regular sp^2 C structure upon the photoreduction of GO.[80]

Attenuated Total Reflectance (ATR) Fourier Transform Infrared spectroscopy (FTIR) allowed direct analyses of the hybrid chemical signatures, through Fick's

second law. Specifically, in Figure 2b the peak around 649 cm^{-1} was attributed to W-O-W stretching mode and was shifted towards lower wavelength for the r-GO-based hybrid materials when compared to their counterparts. Analyses also showed that the principal vibration peaks around 728 cm^{-1} , which were related to the O-W-O stretching mode,[81] seemed to disappear for the r-GO related samples ($\text{WO}_3/\text{r-GO}$ and $\text{PtWO}_3/\text{r-GO}$ respectively) possibly indicating that a strong interaction was formed between r-GO and the WO_3 interfaces; such interactions could have changed sample's surface chemistry. The peak around 1053 cm^{-1} was attributed to the carboxylate group formed onto the functionalized r-GO surface, while the new small peak at around 1565 cm^{-1} was indexed to the C=C skeletal vibration model in the r-GO structures.[82] The additional peak at 3430 cm^{-1} in the r-GO-based hybrid was presumably due to O-H vibration and may be possibly associated with the photoreduction procedure used during the hybrids formation.[83] Analyses also revealed that the peaks related to the r-GO structure were relatively weaker when compared to the other peaks, thus confirming previous results recorded for r-GO sheets in hybrid nanocomposites with low amount of graphene.[84]

After ultraviolet-visible spectrophotometry (UV-VIS) analyses in the 380-800 nm scans, a redshift (shift towards higher wavelengths) was observed for all the samples (WO_3 , PtWO_3 , $\text{WO}_3/\text{r-GO}$, $\text{PtWO}_3/\text{r-GO}$ respectively) being tested (Figure 2c). The shift for the $\text{PtWO}_3/\text{r-GO}$ hybrids was attributed to the chemical bonding between WO_3 and the specific sites of C onto r-GO's.[85] Furthermore, the optical absorption edges of the WO_3 , PtWO_3 , $\text{WO}_3/\text{r-GO}$, or $\text{PtWO}_3/\text{r-GO}$ showed cut offs at 469, 470, 471, and 473 nm respectively. Such cut offs corresponded to optical band gaps of 2.64, 2.64, 2.63, and 2.62 eV respectively as calculated using:

$$E\text{ eV} = h * c / \text{wave length (nm)} = 1240 / \text{wave length (nm)},$$

where h is Planck's constant and c is the speed of light.[86]

X-ray Photoelectron Spectroscopy (XPS) revealed peaks located at 71.2 and 74.5 eV in the PtWO_3 and $\text{PtWO}_3/\text{r-GO}$ samples, which were attributed to the Pt (0) ($4f\ 7/2$) and Pt (0) ($4f\ 5/2$) respectively,[87] thus confirming Pt loading onto the r-GO template (Figure 3a).[85] Complementary, characteristic peaks around 284.6 and 287.0 eV were observed for the r-GO-based hybrids and were attributed to C1s of the C-C and the C-O respectively (Figure 3b),[48] further confirming the decoration of the nanoparticles. Analyses also showed that the W atoms were in the formal valence band +6,[78] with the observed binding energy peaks at around 35.8 and 37.8 eV being associated with spin-orbit splitting of the W $4f\ 7/2$ and W $4f\ 5/2$ respectively (Figure 3c).[88] Lastly, in the O core level XPS spectrum (Figure 3d), the 530.8 eV peak corresponding to the O1s[89] showed no changes in all the samples being investigated, thus indicating that Pt coating and r-GO modification, while changing the surface chemical/physical properties of the hybrids did not affect their crystalline structure.

To evaluate the photocatalytic performance of the user-synthesized nanoparticles or resulting hybrids, we monitored the degradation of rhodamine B under visible light irradiation and at room temperature (Figure 4a). In control, the changes in the C/C_0 of rhodamine B in aqueous solution and in the absence of any sample respectively were also monitored, with C and C_0 representing the concentration of rhodamine B at times t and 0 respectively. Typical results showed photocatalytic activities for all the sample, with the degradation of rhodamine B being sample dependent. Specifically, after 6 h

of visible light irradiation, the C/Co percentage of rhodamine B without addition of nanoparticles was about 83% of its initial concentration before visible light irradiation. However, addition of WO₃ to the rhodamine B solution induced about 69% decomposition after 6 h visible light irradiation, when compared to the initial rhodamine B solution without addition of nanoparticles. Furthermore, addition of Pt-coated or r-GO modified hybrid materials (PtWO₃, WO₃/r-GO, or PtWO₃/r-GO) led to a more significant enhancement in the photodegradation ability, with the rhodamine B solution being completely decomposed in the presence of the PtWO₃/r-GO hybrids after only 3 h.

The increased photocatalytic ability of the Pt-based samples is presumably due to the Pt serving as electron accepting species to promote the formation of superoxide radical anions or retard electron-hole recombination at the WO₃-based interfaces.[90] Further, the increased catalytic ability of the r-GO-based hybrids when compared with pure WO₃ is presumably due to the chemical coupling between WO₃ nanoparticles and specific sites of C onto r-GO's, which could thus enhance the hybrid's ability for organic dye degradation by increasing dye's adsorptivity at the hybrid interface[91] and improving photogenerated charge carrier lifetime, or by boosting a two-electron reduction of O₂ to H₂O₂ in solution.[92] The enhanced photocatalytic ability of the r-GO-based hybrids could also derive from the strong coupling between the r-GO-decorated surfaces, which can promote interfacial electron transfers to effectively reduce electron-hole pair recombination rates[93] and thus increase the amount of radical components with strong oxidation capability (for instance hydroxyl radicals; Scheme S1) and lifetime of charge carriers upon their formation.[94]

Previous results support our studies and show that carrier motility, the ability to photogenerate electron-hole pairs, as well as the efficiency of recombination could affect nanoparticle photocatalytic performance.[86] For instance, Xu et al., generated GO-based hybrid containing ZnO nanoparticles and showed significant enhancement of their photocatalytic performance as resulted from the increased migration efficiency of photo-generated electrons and the inhibition of charge carriers recombination at interfaces.[24] Similar results were obtained by Meng et al., which combined *p*-type MoS₂ nanoplatelets with *n*-type nitrogen-doped r-GO (*n*-r-GO) to generate *p*-MoS₂/*n*-r-GO heterostructures with significantly enhanced photocatalytic activity in water. Authors also showed that such heterostructures had improved charge generation and suppressed charge recombination at their junction.[20] Similarly, Sang et al., fabricated TiO₂/r-GO nanosheets via *in situ* photochemical reduction and showed that the hybrid interfaces could drain the excited electrons from the TiO₂ to increase charge-carrier separation and enhance hybrid's photocatalytic performance.[95] Lastly, surface plasmon resonance (SPR) was proposed to extend visible light response and increase the absorption capacity and light-absorption efficiency of such materials.[96] In particular, studies showed improvement of quantum yield, extension of the visible light response, and enhancement of both the absorption capacity and localized electric field at nanointerfaces.[97, 98]

Linearized reaction kinetic data for rhodamine B are shown in Figure 4b. Analyses showed that the photocatalytic degradation obeyed first order kinetics with the calculated values of reaction rate for WO₃, PtWO₃, WO₃/r-GO, and PtWO₃/r-GO being 3.17x10⁻³ min⁻¹, 4.64 x10⁻³ min⁻¹, 7.22x10⁻³ min⁻¹, and 2.19x10⁻² min⁻¹ respectively. It was also observed that the PtWO₃/r-GO hybrids had a significant increase in their photocatalytic activities when compared to the other samples being tested.

Our results are comparable with the ones obtained upon photodegradation of

rhodamine B by macroporous TiO₂ particles (i.e., reaction rate close to $3.0 \times 10^{-2} \text{ min}^{-1}$), which are known to exhibit enhanced photodegradation ability when compared to dense TiO₂ (reaction rate close to $1.0 \times 10^{-2} \text{ min}^{-1}$). [99] Such results are presumably due to the increased surface area of these nanoparticles when compared to their bare counterparts. Further, in our study, the degradation reaction rate observed for the PtWO₃/r-GO under visible light was around 14 times higher than the one observed in the presence of TiO₂ under UV ($0.6 \times 10^{-3} \text{ min}^{-1}$) or VIS ($1.6 \times 10^{-3} \text{ min}^{-1}$) irradiation. [100] This demonstrated that the synthesized PtWO₃/r-GO hybrids could compete in a more efficient manner with the currently available enhanced TiO₂ porous semiconductor materials for photoreaction and removal of rhodamine B, all under visible light. The higher efficiency is presumably due to combination of semiconductor nanoparticles and r-GO interfaces which could reduce electron-hole pair recombination rates, as well as increase the lifetime of charge carriers to promote generation a stronger oxidation capabilities and thus organic dye degradation. While our rates of degradation are currently lower than the ones observed upon the evaluation of TiO₂/GO hybrid materials exposed to UV (i.e., 0.2 min^{-1} [93, 95]), they are still very encouraging since they are obtained all under normal visible radiation and at lower intensity.

We believe that our results could be extended to include degradation of other dyes, namely methyl orange and methylene blue normally present as soluble molecules or ions in contaminated waters. [61, 101] Such dyes are known to have lower adsorption capacities than rhodamine B, as shown by the analysis of Aanadurai et al., [61] thus their photodegradation by our user-tailored systems should be more efficient. Such hypothesis is supported also by previous studies that have showed that the reaction rate constant for rhodamine B is around $.0058 \text{ min}^{-1}$ on a hyper-crosslinked polymeric adsorbent in aqueous solution, which is almost the double compared to $.0028 \text{ min}^{-1}$ for methyl orange. [61, 62, 102] Although a direct comparison between these studies [61-64] is rather difficult because of the differences in the working conditions and sample preparation, it is evident that optimum user-tailored properties and sample characteristics will largely influence the ability to photodegrade any of the proposed tested dye.

Our study showed that the photodegradation ability of hybrids depends on their heterostructure and their physico-chemical properties, with the optimum photocatalytic interface and its characteristics being influenced by the morphological, topographical, and chemical signatures of the individual sample being templated. As such, our analyses may hint that the fundamental mechanisms that drive photocatalysis at such user-formed heterointerfaces relate to the available area for reaction and the electron-hole pair recombination rate. Thus, our study provides insight into the development of the next generation of visible light absorbing efficient photocatalysts to be used for consumer applications. In particular, one could control Pt decoration as well as Pt distribution to ensure uniform coating of the GO templates to thus increase energy transfer and carrier mobility at such interfaces for high efficiency, long lifetime energy generation to be used in the next generation of energy storage and conversion devices (i.e., solar cell, fuel cell electrode).

Conclusion

We synthesized WO₃-based nanoparticles (WO₃ and PtWO₃) and r-GO-based hybrid materials using photoactivation and photoreduction methods. The WO₃ nanoparticles dispersed onto the r-GO templates formed hybrid materials as confirmed by a combination of analytical analyses. The existence of r-GO with zero

bandgap improved hybrid material's ability to separate carriers and to delay electron/hole pair recombination thus leading to enhanced photocatalytic activity when degradation of rhodamine B, a cationic dye used as model system, was considered. Our facile synthesis approach provides a facile methodology for the preparation of semiconductor/graphene-based hybrid functional materials with enhanced photocatalytic efficiency to be used for water treatment and clean energy generation.

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Figures Caption

Figure 1: High Resolution Transmission Electron Microscopy (HR-TEM) images of (a) WO_3 ; (b) Pt/WO_3 ; and (c) $\text{WO}_3/\text{r-GO}$ samples. Samples analyses allowed for size distribution and crystalline lattice spacing of about 0.38 nm corresponding to the (020) plane in the WO_3 identification (Figure 2a). Analyses also showed that the morphology of the PtWO_3 conjugates was different than that of their starting WO_3 counterparts (Figure 2b). The (111) lattice plane of Pt and its interplanar spacing of 0.23 nm was identified in Figure 2c.

Figure 2: Physico-chemical signatures of the nanoparticles and nanoparticles-based hybrids. (a) Raman spectrum of WO_3 , Pt/WO_3 , $\text{WO}_3/\text{r-GO}$ and $\text{Pt}/\text{WO}_3/\text{r-GO}$ samples respectively onfirmed the generation of the r-GO-based hybrid materials, with the insert figure showing the characteristic peaks of GO. (b) Attenuated Total Reflectance (ATR) Fourier Transform Infrared spectroscopy (FTIR) allowed direct analyses of the chemical signatures of WO_3 , Pt/WO_3 , $\text{WO}_3/\text{r-GO}$ and $\text{Pt}/\text{WO}_3/\text{r-GO}$ nanoparticles and derived hybrids respectively. (c) UV-Vis spectrum of WO_3 , Pt/WO_3 , $\text{WO}_3/\text{r-GO}$ and $\text{Pt}/\text{WO}_3/\text{r-GO}$ nanoparticles and hybrids respectively. A redshift (shift towards higher wavelengths) was observed for all the nanoparticles and hybrids being tested.

Figure 3: X-ray Photoelectron Spectroscopy (XPS) spectrum of Pt, C, W, O element status in the different samples being investigated. Complementary, characteristic peaks were observed for the r-GO-based hybrids further confirming the templating of the WO_3 and Pt/WO_3 onto the r-GO surfaces. While Pt coating and r-GO modification changed the surface chemical/physical properties of the hybrids, did not affect their crystalline structure.

Figure 4: (a) Photocatalytic activities of WO_3 , Pt/WO_3 , $\text{WO}_3/\text{r-GO}$ and $\text{Pt}/\text{WO}_3/\text{r-GO}$ nanoparticles and resulting hybrids respectively under visible light irradiation. (b) Kinetic analyses of WO_3 , Pt/WO_3 , $\text{WO}_3/\text{r-GO}$ and $\text{Pt}/\text{WO}_3/\text{r-GO}$ samples under visible light irradiation when considering rhodamine B degradation.

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