Ag–AgBr/TiO₂/RGO nanocomposite: Synthesis, characterization, photocatalytic activity and aggregation evaluation

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A R T I C L E   I N F O

Article history:
Received 25 January 2016
Revised 25 March 2016
Accepted 5 April 2016
Available online 29 October 2016

Keywords:
Ag–AgBr/TiO₂
Reduced graphene oxide
Humic acid
Aggregation
Submerged membrane photoreactor (sMPR) system

A B S T R A C T

Ag–AgBr/TiO₂ supported on reduced graphene oxide (Ag–AgBr/TiO₂/RGO) with different mass ratios of graphene oxide (GO) to TiO₂ were synthesized via a facile solvothermal-photo reduction method. Compared to the single-, two- and three-component nanocomposites, the four-component nanocomposite, Ag–AgBr/TiO₂/RGO-1 with mass ratio of GO to TiO₂ at 1%, exhibited a much higher photocatalytic activity for the degradation of penicillin G (PG) under white light-emitting diode (LED-W) irradiation. The PG degradation efficiency increased with the increase of mass ratio of GO to TiO₂ from 0.2% to 1%, then it decreased with the increase of mass ratio of GO to TiO₂ from 1% to 5%. The zeta potentials of RGO-nanocomposites became more negative with the presence of humic acid (HA) due to the negatively charged HA adsorption, resulting in the shift of points of zero charge to lower values of pH. The aggregations of nanocomposites were more significant due to the bridging effect of HA. Furthermore, the aggregated particle sizes were larger for RGO-nanocomposites compared to other nanoparticles, due to the bindings of the carboxylic and phenolic functional groups in HA with the oxygen-containing functional groups in the RGO-nanocomposites. The microfiltration (MF) membrane was effective for the nanocomposites separation. In the continuous flow through submerged membrane photoreactor (sMPR) system, backwashing operation could efficiently reduce membrane fouling and recover TiO₂, and thus indirectly facilitate the PG removal.

Introduction

TiO₂ has been introduced as one of the most promising and suitable photocatalysts for degradation of organic pollutants. TiO₂-assisted heterogeneous photocatalysis has become a potentially cost-effective and environmentally-sustainable water and wastewater treatment alternative (Fox and Dulay, 1993; Klavarioti et al., 2009). However, the rapid recombination rate of photo-generated electron-hole pairs has greatly hampered the practical application of TiO₂. Recently, TiO₂-graphene and/or TiO₂-reduced graphene oxide (RGO) composites have received increasing attention (Bai and Shen, 2012; Machado and Serp, 2012). Since graphene, a single layer of sp²-bonded carbon atoms compacted into a two dimensional (2D) planar honeycomb lattice, has many exceptional properties (i.e. high theoretical specific surface area, superior mechanical and chemical stabilities, high thermal and electronic conductivities, etc.), (Geim, 2009), it is expected that TiO₂-graphene or TiO₂-RGO composites...
could exhibit high charge separation efficiency, leading to high photocatalytic activity. It is accepted that the robust bonding between TiO$_2$ and the graphene sheet is essential for the effective charge transfer and separation during photocatalysis. Zhang et al. (2009) and Fan et al. (2011) prepared composites with P25 nanoparticles supported on graphene or RGO via hydrothermal, UV-assisted photocatalytic reduction, and hydrazine reduction method. However, it is found that P25 nanoparticles were difficult to be anchored onto the graphene sheets evenly due to their aggregation property. Thereafter, the in-situ growth of TiO$_2$ on graphene sheets is an important approach to obtain the robust bonding between TiO$_2$ and the graphene sheet.

It has been reported that plasmonic Ag–AgBr composites could exhibit high visible-light photocatalytic activity (Kuai et al., 2010; Wang et al., 2010). However, their visible-light photocatalytic activities could be restricted to some extent due to their micrometer-large particle sizes, which could induce the low surface areas and the high recombination rate of the photo-generated charge carriers. In order to efficiently harness solar energy for photocatalysis, Ag–AgBr/TiO$_2$ composites have attracted great attention in recent years (Hou et al., 2012; Hu et al., 2006; Tian et al., 2012; Wang et al., 2012). The nanojunctions between Ag–AgBr and TiO$_2$ could efficiently promote the separation of photoexcited electron-hole pairs. However, it is difficult to achieve the effectively hetero structured multi-semiconductor system due to the serious aggregation associated with the Ag–AgBr deposition onto P254 (Hu et al., 2006). To overcome this problem, Ag–AgBr could be controlled to deposit onto thorny anatase TiO$_2$ tubes (Tian et al., 2012). Nevertheless, it is generally complex and time-consuming. In addition, Ag/TiO$_2$ has also attracted attentions for the TiO$_2$ particles separation (Lim et al., 2011) where the UV–LED power source has the potential to alleviate the inherent problem associated with polymeric membrane deterioration when exposure to UV (Chin et al., 2006; Molinari et al., 2010) in the combined MPR system with the membrane module incorporated into the photoreactor. TiO$_2$ deposition on the membrane surface and/or inside its pores (Choo et al., 2008; Doll and Frimmel, 2005) would induce membrane fouling along with the loss of TiO$_2$ particles from the photoreactor for photo-activation, and thus lower the photocatalytic degradation efficiency of pollutants. Therefore, efforts should be made to prevent TiO$_2$ deposition, such as backwashing, air bubbling, membrane module vibration, and/or intermittent membrane cleaning, etc.

The main objective of this study was to synthesize a series of photocatalytic nanocomposites, Ag–AgBr/TiO$_2$ supported on reduced graphene oxide (Ag–AgBr/TiO$_2$/RGO) with different mass ratios of GO to TiO$_2$. They were characterized using X-ray diffraction (XRD), N$_2$ adsorption–desorption isotherm, Raman, thermo gravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), diffuse reflectance spectra (DRS) and photoluminescence (PL). Their photocatalytic activities were evaluated for the degradation of penicillin G (PG) under white light-emitting diode (LED-W) irradiations. The nanocomposite aggregations as a function of pH were investigated with and without the presence of humic acid (HA). A novel submerged membrane photoreactor (sMPR) system comprising a Vis-LED photoreactor and a submerged hollow fiber MF membrane module was developed. The performances of the sMPR system operated in the continuous flow-through mode with and without backwashing were investigated with regard to the PG degradation, TiO$_2$ separation and TMP change.

1. Experimental

1.1. Chemicals and materials

MilliQ water (Millipore Co. MilliQ) water with resistivity of 18.2 MΩ cm was used throughout the study unless otherwise stated. All chemicals were used as received without further purification. Natural graphite (SP1) was purchased from Bay Carbon Company (USA). Sodium nitrate (NaNO$_3$, 99%), potassium permanganate (KMnO$_4$, 99%), sulfuric acid (H$_2$SO$_4$, 98%), hydrogen peroxide (H$_2$O$_2$, 30%), hydrochloric acid (HCl, 37%), barium chloride (BaCl$_2$, 99%), potassium dihydrogen phosphate (KH$_2$PO$_4$, 98%), titanium butoxide (Ti(OC$_4$H$_9$)$_4$, 97%) and HA were procured from Aldrich. Absolute ethanol (99.9%), cetyltrimethyl ammonium bromide (CTAB, ≥98%), silver nitrate (AgNO$_3$, ≥98%), ammonia (25 wt.%), methanol (high performance liquid chromatography, HPLC grade), and penicillin G (PG) were procured from Merck.

1.2. Synthesis of nanocomposites

Detailed experimental procedure for synthesis of GO, and characteristics of the as-synthesized GO are shown in Electronic Supplementary Information. Ag–AgBr/TiO$_2$/RGO nanocomposites were synthesized using a facile solvothermal–photoreduction method (Wang et al., 2013b). Typically, an appropriate amount of GO was dissolved in 45 mL of absolute ethanol followed by ultra sonication for 2 hr. Then, 0.91 g of CTAB and 3.4 mL of titanium butoxide were added to obtain solution A. 0.16 g of AgNO$_3$ and 2.0 mL of ammonia were added to another 45 mL
of absolute ethanol to obtain solution B. Subsequently, solution A and solution B were mixed and ultrasonicated for 3 hr to obtain a homogeneous suspension. The suspension was then transferred into a 125-ml Teflon-sealed stainless steel autoclave, and solvothermally treated at 180°C for 6 hr to simultaneously achieve the crystallization of TiO2 and reduction of GO (He et al., 2011). The obtained suspension was further treated under LED-W (described in Section 1.4) irradiation for 2 hr with vigorous stirring. During the photo reduction process, AgBr would be decomposed to Ag nanoparticles and simultaneously the further photo reduction of GO would occur (Zhang et al., 2011). The product was separated by centrifugation, thoroughly washed with MQ water and dried at 60°C over night.

The as-synthesized nanocomposites are denoted as Ag–AgBr/TiO2/RGO-x (x = 0.2, 1, 5), where x is the mass ratio (%) of GO to TiO2. As reference, Ag–AgBr/TiO2, Ag/TiO2, TiO2, Ag–AgBr and Ag–AgBr/RGO-1 were also prepared using similar method with appropriate modifications.

1.3. Characterization

XRD patterns were obtained from a Bruker D8 ADVANCE X-ray Diffractometer with Cu Kα radiation (λ = 1.5418 Å) in a 2θ range of 5°–80°. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation with a Quanta chrome Autosorb-1 instrument at 77 K. TGA was performed on a thermogravimetric analyzer (Perkin–Elmer) with a heating rate of 10°C/min in an air flow. FTIR spectra of the nanocomposites and Raman spectra were obtained using a Perkin Elmer Lambda 35 UV–vis–DRS spectrophotometer equipped with an integrating sphere assembly with BaSO4 as the reflectance standard. Raman and PL spectra were measured at room temperature using a Renishaw Raman spectrometer with argon ion lasers at 633 nm and 325 nm as the excitation sources, respectively.

1.4. Photocatalytic activity test in the batch vis-LED photoreactor

The degradation of PG over the as-synthesized nanocomposites was investigated in a vis-LED photoreactor as described in our previous paper (Wang et al., 2013b, 2011b; Wang and Lim, 2010). Specifically, a tubular borosilicate glass photoreactor with a working volume of 200 mL was wrapped with a 2 m long vis-LED flexible strip (main emission wavelength λ = 450 nm, 30 unit/m, 7.5 W/m, SMD 5050) comprising 60 vis-LED units. In atypical experiment, 200 mL of suspension with photocatalyst dosage of 0.5 g/L and initial pollutant concentration of 10.0 mg/L in MQ water was stirred in the dark to reach adsorption/desorption equilibrium with in 1 hr. During photocatalysis, sample aliquots were collected at appropriate time intervals and filtering using 0.45 μm cellulose acetate syringe membrane filters for HPLC analysis. The detailed HPLC method for PG analysis could be found in our previous published works (Wang and Lim, 2012).

1.5. Nanocomposite aggregation evaluation

According to the Derjaguin, Landau, Vervey, and Overbeek (DLVO) theory, zeta potentials of the nanoparticles play an important role in the stability of their suspensions (i.e., nanoparticle aggregation) (Rodriguez et al., 2009; Thio et al., 2011). It is well known that the suspension pH has a substantial effect on the charges of the nanoparticles and the thickness of the electric double layer. In this study, zeta potentials and particle sizes for the as-synthesized nanocomposites as a function of pH were investigated. Typically, 100 mg of nanocomposites were dispersed in 200 mL of MQ water with varied pH, respectively. Then the suspensions were treated with ultra sonication for 1 hr to reach the aggregation equilibrium prior to the zeta potential and particle size measurements. Zeta potential was measured in triplicate using a Malvern Nano-ZS Zeta sizer, and derived from the electrophoretic mobility using Smoluchowski model. Particle size distribution of TiO2 in suspension was measured using a Malvern Mastersizer2000 equipped with a Hydro 2000SM sample dispersion unit.

HA is ubiquitous in nearly all the natural waters and municipal wastewaters. It is postulated that HA has a profound effect on the charge balance of the nanocomposites, and thus on their aggregation. In this study, the effect of HA on the zeta potentials and particle sizes of the as-synthesized nanocomposites as a function of pH were investigated. HA was dissolved in MQ water (pH 11 adjusted by 1 mol/L NaOH solution), filtered through a 0.45 μm cellulose acetate syringe membrane filter, and then stored in dark at 4°C as stock solution. Different amounts of HA stock solutions were added to the nanocomposites suspensions to make different HA concentrations expressed in terms of total organic carbon (TOC) concentration (mg C/L) measured using a Shimadzu ASI-V TOC Analyzer.

1.6. Performance of the sMPR system

The sMPR system consisted of a vis-LED photoreactor and a MF membrane module (Fig. 1). It was a modification of the sMPR system previously investigated in our group which didn’t include backwashing operation (Wang et al., 2013a). The membrane module fabricated with commercial hollow fiber polyvinylidene fluoride (PVDF) MF membrane (total effective membrane area of 22.61 cm2, mean pore size of 0.1 μm, inner and outer diameter of 0.6 and 1.2 mm, respectively, provided by Memstar Technology Ltd. (Singapore)) was submerged in the photoreactor. The transmembrane pressure (TMP) and permeate flux were auto-recorded at predetermined time intervals by a data logging system. In the case of operation with backwashing, the solenoid valve in the permeate line was closed, while the solenoid valve and Masterflex peristaltic pump in the backwashing line were open to draw permeate water from the permeate side to the feed side. The sMPR system was operated at a constant flux of 220 L/(m2·hr) (Hydraulic
Retention Time (HRT) = 120 min) in a continuous flow-through mode. Fresh PG solution (10.0 mg/L) was continuously fed into the photoreactor to maintain a constant working volume (1 L) of the photoreactor. Sample aliquots of permeate water were collected at predetermined time intervals for HPLC analysis. In order to investigate the effectiveness of TiO2 separation by the MF membrane, the turbidity of permeate water was measured in triplicate using a HACH 2100 N turbidimeter.

2. Results and discussion

2.1. Characteristics of the as-synthesized nanocomposites

2.1.1. Structure and textural properties

Diffraction peaks at ca. 25.2°, 37.8°, 48.2°, 53.6°, 55.0°, 62.7°, 68.9°, 70.3° and 75.1° could be attributed to the anatase phase (JCPDS No. 21-1272) for all the as-synthesized TiO2-nanocomposites (Fig. 2), while no rutile phase was observed. No diffraction peaks for the graphene component were observed in the RGO-nanocomposites, possibly due to the peak overlap with the anatase phase at 25.2°. Three diffraction peaks at ca. 44.4°, 64.5° and 77.4° could be indexed to Ag0 (JCPDS No. 65-2871) in Ag/TiO2. For the Ag–AgBr/TiO2 and Ag–AgBr/TiO2/ RGO nanocomposites, diffraction peaks at ca. 26.7°, 31.0°, 55.0°, and 73.4° could be indexed to AgBr (JCPDS No. 06-0438), diffraction peaks at ca. 77.4° could be assigned to Ag0, while diffraction peaks at ca. 44.4° and 64.5° could be attributed to both Ag0 and AgBr. It suggested that Ag0 and AgBr co-existed in the Ag–AgBr/TiO2 and Ag–AgBr/TiO2/RGO nanocomposites. Diffraction peaks indexed to Ag0 and AgBr were also observed in both Ag–AgBr and Ag–AgBr/RGO. The crystallite sizes of anatase TiO2 and AgBr and the specific surface areas of the nanocomposites were summarized in Table 1. The crystallite sizes of anatase TiO2 increased due to the dispersion of Ag–AgBr on the TiO2 particles and the incorporation of RGO. The incorporation of TiO2 and RGO enhanced the growth of AgBr.

Five peaks at ca. 147, 196, 399, 519 and 638 cm$^{-1}$ were observed in the Raman spectra of all the TiO2-nanocomposites (Fig. 3), which could be ascribed to anataseTiO2 (Zhang et al., 2008). Two more peaks were observed in the RGO-nanocomposites, namely peaks at ca. 1338 cm$^{-1}$ (D band) and 1608 cm$^{-1}$ (G band) with a D/G intensity ratio of ~1.1 which was slightly higher than that of GO (~1.0). This suggested that the increase in the number

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<th>Table 1 – Physicochemical properties of the as-synthesized composites.</th>
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SSA: Specific surface area.
of defects and the decrease in the average size of sp² domains during the dispersion of Ag–AgBr and TiO₂ nanoparticles on the graphene sheets and the reduction of GO (Song et al., 2012; Wen et al., 2011). There is insignificant difference in the Raman spectra among the RGO-nanocomposites.

TEM images show that irregular nanoparticles were well-decorated on or intercalate into the RGO sheets with micrometer-long wrinkles in Ag–AgBr/TiO₂ and the formation of defects and the decrease in the average size of sp² domains during the dispersion of Ag–AgBr and TiO₂ nanoparticles on the graphene sheets and the reduction of GO (Song et al., 2012; Wen et al., 2011). There is insignificant difference in the Raman spectra among the RGO-nanocomposites.

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2.1.2. XPS analysis
The peak at 284.8 eV in the Cls XPS spectra could be attributed to the adventitious elemental carbon and/or the sp² or sp³ carbon species from GO and/or organic precursor (mainly C–C and C=O) (Fig. 4a) (Wang et al., 2011a, 2011b; Wen et al., 2011). The peaks centered at ca. 286 and 288 eV could be assigned to the oxygenated carbon species (i.e., C–O, O–C and O = C–O) (Wen et al., 2011), of which the peak intensities in the RGO-nanocomposites were much lower than those in GO. This indicated the effective reduction of GO via the solvothermal-photoreduction treatment. Two peaks at ca. 373.8 and 367.7 eV could be attributed to Ag⁺ in AgBr or in the Ag 3d XPS spectra (Fig. 4b) (Hou et al., 2012; Wang et al., 2012), while the peaks for metallic Ag were insignificant due to its low content. It suggested that Ag species were mainly present as Ag⁺ in the Ag–AgBr/TiO₂ and Ag–AgBr/TiO₂/RGO nanocomposites. The peak at ca. 68.1 eV could be assigned to Br⁻ in AgBr (Fig. 4c) (Wang et al., 2012). Two peaks at 464.5 eV and 458.5 eV could be assigned to Ti 2p₁/₂ and Ti 2p₃/₂, respectively (Fig. 4d) (Wang et al., 2011a, 2011b). The Ti 2p core levels for the Ag–AgBr/TiO₂/RGO nanocomposites shifted towards lower binding energies possibly due to the incorporation of RGO.

2.1.3. Optical properties
All the as-synthesized nanocomposites exhibited higher visible-light absorption compared to P25 (Fig. 6). Due to the presence of oxygen vacancies on the surface of TiO₂, TiO₂ showed slightly stronger visible-light absorption and red shift of absorption edge than P25 (Shi et al., 2006). Noticeable red shift of absorption edge and visible-light absorption ability were observed in Ag–AgBr/TiO₂ due to the surface plasmon resonance (SPR) effect of Ag nanoparticles (Wang et al., 2010; Zhang et al., 2011) and the visible-light response of AgBr (Kuai et al., 2010). Compared to Ag–AgBr/TiO₂, Ag/TiO₂ showed much stronger absorption ability in the visible-light region due to the SPR effect of Ag nanoparticles present on their surface (Wang et al., 2010; Zhang et al., 2011). According to the results of XRD and XPS analysis, Ag species mainly existed as Ag⁺ in Ag–AgBr/TiO₂. Therefore, Ag nanoparticles might be the main reason for the high visible-light absorption ability. More remarkable visible-light absorption was obtained in the RGO-nanocomposites with the increase of mass ratio of GO to TiO₂.

2.1.4. Photoluminescence
Ag/TiO₂ possessed lower PL intensity than the pure TiO₂ (Fig. 7). This could be attributed to that the Schottky barrier formed at the Ag–TiO₂ interface could act as electron store to promote the electron-hole separation efficiently (Chen et al., 2007; Linsebigler et al., 1995; Liu et al., 2004). A more efficient electron-hole separation was observed in Ag–AgBr/TiO₂ which might be induced by the electron transfer in the AgBr → Ag → TiO₂ nano junctions (Wang et al., 2012). Compared to Ag–AgBr/TiO₂, much lower electron-hole recombination rates were achieved in the Ag–AgBr/TiO₂/RGO nanocomposites, resulting from the further transfer of electrons to the surface of RGO followed by an interfacial transfer along the n–π graphitic carbon network (Lightcap et al., 2010; Xiang et al., 2011). However, the excessive RGO in the nanocomposites could act as the recombination centers to enhance the recombination of the photo-generated electrons and holes, leading to the increase of PL intensity. The lowest PL intensity corresponding to the lowest recombination rate of electron-hole pairs was obtained in Ag–AgBr/TiO₂/RGO-1.

2.2. Photocatalytic activity evaluation in the batch vis-LED photoreactor
Fig. 8 shows that the PG concentration decreased by 12% after 2 hr of LED-W irradiation via photolysis (without photocatalyst). Based on the apparent rate constant (k_{app}) value calculated by pseudo-first-order kinetics model (Herrmann, 2005) the photocatalytic activities of the TiO₂nanocomposites followed the order of significance: Ag–AgBr/TiO₂/RGO-1 (k_{app} = 31.6 × 10⁻³ min⁻¹) > Ag–AgBr/TiO₂/RGO-0.2 (k_{app} = 30.2 × 10⁻³ min⁻¹) > Ag–AgBr/TiO₂/RGO-5 (k_{app} = 21.8 × 10⁻³ min⁻¹) > Ag–AgBr/TiO₂ (19.6 × 10⁻³ min⁻¹) > Ag/TiO₂ (10.1 × 10⁻³ min⁻¹) > Ag/ TiO₂ (6.08 × 10⁻³ min⁻¹) > Ag–AgBr (5.52 × 10⁻³ min⁻¹) > TiO₂ (2.84 × 10⁻³ min⁻¹). TiO₂ exhibited slightly higher visible-light
photocatalytic activity compared to P25 due to its stronger visible-light absorption and red shift of absorption edge. Compared to the single-component nanocomposites (P25 and TiO$_2$), the PG degradation was further enhanced by the two-component (Ag–AgBr and Ag/TiO$_2$) and three-component (Ag–AgBr/TiO$_2$/RGO-1 and Ag–AgBr/TiO$_2$/RGO-5). A more efficient PG degradation was achieved with the four-component nanocomposites (Ag–AgBr/TiO$_2$/RGO-1 > Ag–AgBr/TiO$_2$/RGO-0.2 > Ag–AgBr/TiO$_2$/RGO-5). It might be attributed to the excessive RGO serving as the recombination centers could enhance the recombination of the photo-generated electrons and holes. On the other hand, the excessive RGO could absorb the visible light, thus reduce the visible-light photons available to generate electron-hole pairs. In this study, Ag–AgBr/TiO$_2$/RGO-1 possessed the highest visible-light photocatalytic activity for PG degradation.

It is concluded that each component in the Ag–AgBr/TiO$_2$/RGO-1 nanocomposite could contribute to its visible-light photocatalytic activity: (1) the SPR effect of Ag nanoparticles (Moskovits, 2011; Rycenga et al., 2011); (2) the enhanced utilization of visible light assisted by AgBr which could be excited by the
light with a wavelength at ca. 477 nm (Hou et al., 2012); (3) the efficient transfer of charge carriers due to the well-dispersed nanojunctions between Ag–AgBr and TiO$_2$ (Tian et al., 2012); (4) the long-range transfer of electrons to the surface of RGO followed by an interfacial transfer along the π–π graphitic carbon network (Lightcap et al., 2010; Zhang et al., 2014b); and (5) vectorial electron transfers of AgBr → Ag → TiO$_2$ → RGO and/or AgBr → Ag → RGO resulting in the efficient separation of photo-generated holes and electrons.

2.3. Nanocomposite aggregation

Fig. 9a shows that the points of zero charge of P25 and TiO$_2$ were ~6.5 and ~6.1, respectively, which coincide to previously reported results (Kosmulski, 2011). It is postulated that the nanocomposites were positively charged at pH lower than the points of zero charge due to the adsorption of H$^+$ ions, while negatively charged at pH higher than the points of zero charge due to the adsorption of OH$^-$ ions (Rodriguez et al., 2009). Compared to P25 and TiO$_2$, the point of zero charge of Ag–AgBr/TiO$_2$ was slightly lower (~5.8) due to the modification using Ag–AgBr. For the RGO-nanocomposites, the points of zero charge decreased from ~5.5 to ~4.6 with the increase of mass ratio of GO to TiO$_2$ from 0.2% to 5%. This could be attributed to the oxygen-containing functional groups in the RGO-nanocomposites. As shown in Fig. 9a, synthesized GO was negatively charged in pH from 2 to 10. Fig. 10a presents that P25, the as-synthesized TiO$_2$, Ag–AgBr/TiO$_2$ and RGO-nanocomposites were most unstable and easily aggregated at the points of zero charge, while they were most stable at pH far away from their points of zero charge. This could be explained by the DLVO theory (Rodriguez et al., 2009). The absolute value of the zeta potential is lower at pH near to the point of zero charge, which could lead to a lower repulsive electrical double layer interaction and thus a trend for the nanocomposites aggregation. On the contrary, with a higher absolute value of the zeta potential at pH far away from the point of zero charge, the nanocomposites could not tend to aggregate so easily due to the higher repulsive electrical double layer interaction.

HA was negatively charged at pH from 2 to 10 (Fig. 9a), which could be attributed to the carboxylic and phenolic functional groups (Dickson et al., 2012). It is believed that HA could affect the zeta potential and stability of the nanocomposites. Compared to the case without HA in suspension, the zeta potentials of P25, the as-synthesized TiO$_2$, Ag–AgBr/TiO$_2$ and RGO-nanocomposites became more negative with the presence of HA (Fig. 9b, c, d), which could be due to the negatively charged HA adsorption to neutralize the positive charges (Thio et al., 2011). This resulted in the shift of points of zero charge to lower values of pH. In addition, the shift was more significant with the increase of HA concentration.

With the presence of HA of 1 mg C/L, the points of zero charge for P25, the as-synthesized TiO$_2$, Ag–AgBr/TiO$_2$ and RGO-nanocomposites slightly shifted to lower pH (Fig. 9b) compared to the case without the presence of HA (Fig. 9a).
The aggregations of nanocomposites were more significant (Fig. 10b), due to the bridging effect of HA (Wang et al., 2013a). Furthermore, the aggregated particle sizes were larger for RGO-nanocomposites compared to other nanoparticles. This could be attributed to the bindings of the carboxylic and phenolic functional groups in HA with the oxygen-containing functional groups in the RGO-nanocomposites.

With the presence of HA of 4 mg C/L, the points of zero charge for P25, TiO2 and Ag–AgBr/TiO2 were at around pH 3–4, while they were at around pH 2–3 for the as-synthesized RGO-nanocomposites (Fig. 9c). The aggregations of nanocomposites were more remarkable at pH near to their points of zero charge (Fig. 10c), which could be explained by the DLVO theory.

With a further increase of HA to 10 mg C/L, all the nanocomposites were negatively charged at pH from 2 to 10, and there was no point of zero charge (Fig. 9d). This indicated that the nanocomposites were significantly covered by HA (Zhou and Keller, 2010). It is found that the aggregated particle sizes were larger at lower pH than those at higher pH (Fig. 10d), which could be due to the lower repulsive electrical double layer interaction caused by the lower absolute value of the zeta potential at lower pH.

2.4. Nanocomposite separation and PG removal in the sMPR system

The particle size distributions of Ag–AgBr/TiO2/RGO-1 in suspensions were determined in triplicate, and the average result is presented in Fig. 11. It shows that the particle size of Ag–AgBr/TiO2/RGO-1 in suspension after 1 hr of mixing was slightly smaller than that after 10 hr of mixing, both of which were larger than the mean pore size of MF membrane. TiO2 particles with the size smaller than the pore size of membrane might have a chance to pass through the membrane. Nevertheless, the larger TiO2 particles could form a
porous cake layer ("secondary dynamic membrane") on the membrane surface during MF process, which would be effective for the further rejection of the smaller particles. Furthermore, the turbidity of permeate water was measured in order to investigate the effectiveness of TiO$_2$ separation by the MF membrane. The initial turbidity of Ag–AgBr/TiO$_2$/RGO-1 suspension in the photoreactor was 2370 NTU. However, the turbidity of permeate water was consistently <0.2 NTU. It indicated that the MF membrane can be successfully applied for the separation of TiO$_2$ for reuse.

TMP changes were monitored to evaluate membrane fouling originated from Ag–AgBr/TiO$_2$/RGO-1 separation throughout the experimental period. It can be observed from Fig. 12a that the TMP increased in the first 3 hr in the sMPR system without backwashing, which could be attributed to the TiO$_2$ cake layer deposition on the membrane surface. After that, the steady state TMP was observed, implying that the cake build-up became limited due to a finite inventory of particles most likely

![Fig. 10](image_url) Mean particle size of the as-synthesized nanocomposites as a function of pH with different HA concentrations in solutions. (a) 0 mg C/L, (b) 1 mg C/L, (c) 4 mg C/L, (d) 10 mg C/L. HA: humic acid.

![Fig. 11](image_url) Particle size distribution of Ag–AgBr/TiO$_2$/RGO-1 in suspension after different mixing times.
to deposit. In order to prevent TiO$_2$ deposition on the membrane surface, the membrane was backwashed every 10 min for a duration of 10 sec with backwashing pressure of 40 kPa. It was found that a rather stable TMP was observed in the sMPR system with backwashing throughout the experimental period. It indicated that the backwashing operation could efficiently reduce membrane fouling and recover TiO$_2$.

The PG photocatalytic degradation was investigated using Ag–AgBr/TiO$_2$/RGO-1 as photocatalyst in the sMPR system without and with backwashing, respectively (Fig. 12b). The PG removal rate and efficiency were smaller for the case without backwashing than the case with backwashing. This was possibly attributed to the continuous deposition of TiO$_2$ particles on the membrane surface over time without backwashing, resulting in the decreased photocatalyst concentration in the irradiated suspension. Therefore, backwashing could indirectly facilitate the PG removal through dislodging the TiO$_2$ particles from the membrane surface back to the photoreactor.

3. Conclusions

A series of photocatalytic nanocomposites, Ag–AgBr/TiO$_2$/RGO, were synthesized via a facile solvothermal-photo-reduction method. Ag–AgBr/TiO$_2$/RGO-1 with mass ratio of GO to TiO$_2$ at 1% exhibited the highest photocatalytic activity. The negatively charged HA adsorption on the RGO-nanocomposites could neutralize the positive charges, resulting in the shift of points of zero charge to lower values of pH. The bridging effect of HA induced significant aggregations of nanocomposites. MF membrane was effective for the nanocomposites separation. Backwashing operation could efficiently reduce TiO$_2$ deposition on the membrane surface, and thus indirectly facilitate the PG removal. This work shows that Ag–AgBr/TiO$_2$/RGO-1 in the hybrid MPR system has the scientific merit and practical significance for treating antibiotics-polluted water using indoor light or sunlight. Nevertheless, the pretreatment of feedwater has to be addressed when considering a large-scale application of sMPR.

Acknowledgments

This work was supported by Nanyang Environment & Water Research Institute (NEWRI). The author is grateful to Dr. Xianbin Liu for the technical assistance in the XRD, Raman, PL and XPS analysis, and Dr. Yuxin Tang for the technical assistance in the TEM analysis. The author is also grateful for Dr. Teik-Thye Lim for providing constructive suggestions during the manuscript preparation and vetting through its final version.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.04.032.

REFERENCES


