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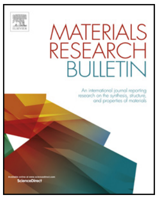

TiO_2·rGO nanocomposite as a photo catalyst for the reduction of Cr^{6+}

Dusadee Khamboonrueang[a,c], Sasithorn Srirattanapibul[a], I-Ming Tang[b], Sirikanjana Thongmee[a,*]

[a] Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
[b] Computational Applied Science for Smart Innovation Cluster (CLASSIC), Faculty of Science, King Mongkut's University of Technology Thonburi, Bangkok 10149, Thailand
[c] Faculty of Science and technology, Rajabhat Nakhon Sawan University, Nakhon Sawan 60000, Thailand

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ABSTRACT

Titania decorated reduced graphene oxide (TiO_2·x%rGO (x = 0, 1, 05, 10, 15, 20 and 25) nanocomposites (NC's) were fabricated using a hydrothermal process. Scanning electron microscope (SEM) images show that the rGO surfaces were covered with TiO_2 nanoparticles whose average sizes increased as x is increased. X Ray Diffraction (XRD) of all the NP's exhibits the diffractions peaks of the anatase phase of the TiO_2. The Fourier-Transform Infrared (FT-IR) spectra of these NC's indicate an increase in the Ti-O-C interfacial chemical bond vibration signals as x increases. A decrease in the energy of the band (energy) gap as the amount of rGO is increased is determined from the UV–vis light absorption spectra. The use of these TiO_2·x%rGO NC's to reduce toxic Cr^{6+} ions to nontoxic Cr^{3+} ions is studied. The photo-catalytic reduction of the toxic Cr^{6+} is seen in general to increase as x is increased.

1. Introduction

Water pollution, which arises from modern industrialization and from the rapid increase in the urbanization of the human population, is an ongoing problem across the world. In the past decade, water pollution has received much attention from researchers and the government. Part of this interest is due to the absolute need to alleviate the danger to human life by water pollution and some is due to the financial liability of the companies to the damages caused by the pollution. An example of this is the chromium 6+ contamination of the ground water by Pacific Gas & Electric (PG&E) in the 90′s [1]. The legal case against PG&E was settled for $333 million dollars in 1996. The cost of the damage done by the pollution by Hooker Chemical Co. in the Love Cannel tragedy [2] case was borne by the US government. In 2016, a CNN report [3] said that Cr(6+) is still in the US drinking water. This is an example of how difficult it is to remove pollutants from ground water.

In the 1960′s, photocatalysis technology began to be used for treatment of waste water. TiO_2 has been used as a photocatalyst for various applications such as degradation of organic pollutants [4,5] and air purification [6]. However, TiO_2 has its photo catalytic activity in the UV region and the earth's solar spectrum contains only around 5% UV radiation. It has limited activity in the visible range of the solar spectrum. Lastly, the recombination rate of the electron hole pair is high in TiO_2. Many of the photoelectrons generated would not be available for the photocatalysis process. Many of these drawbacks would not be present if the TiO_2 were attached to reduce graphene oxide (rGO). Two review papers on the use of these TiO_2-rGO nanocomposites (NC's) for waste water treatment have appeared recently [7,8]. Ahmadk-haniha, Izadpanah and Rastkari [9] reported that the TiO_2·rGO NC's facilitate the photo degradation of gaseous toluene. Tan et al., [10] reported that the TiO_2-rGO NC's can act as a photocatalyst for the conversion of carbon dioxide into hydrocarbon fuels. Chen, Zou, Li and Zheng [11] reported that TiO_2·rGO NC's can act as an advanced catalyst for the hydrogen evolution reaction. Zhao, Zhao, Chen and Wang [12] and Liu et al. [13], reported that the TiO_2-rGO NC's could convert Cr^{6+} into Cr^{3+}, thus removing the highly toxic Cr^{6+}. Cr^{6+} is 600 times more toxic than is Cr^{3+}. Chen et al., [14] looked at the improved photo degradation of Rhodamine B by their TiO_2·rGO NC.

In this paper, we would like to report of our study of TiO_2·rGO NC's in which the amounts of rGO in the NC's are changed. We increased the amount of rGO in the NC from 0% to 1% to 5% to 10% to 15% to 20% and finally to 25%. The NC fabricated by Liu et al., [13] contained 0%, 2%, 5% and 10% rGO. Neither Zhao et al. [12], nor Chen et al. [14], varied the amount of rGO in their NC's. We are interested here in the chemical removal of Cr^{6+}. This removal is accomplished by the chemical reaction

$$Cr(6+) + 3e^- \rightarrow Cr(3+),$$

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[*] Corresponding author.
E-mail address: fscisjn@ku.ac.th (S. Thongmee).

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where e^- could be the photo excited electron produced when the NP's such as TiO_2 (or ZnO) absorbs light of energy $h\nu$. The conversion occurs at an active site on the surface of the NP. The minimum energy of the radiation needed if the NP is a semiconductor is the value of the energy gap E_g. There are several ways to engineer the values of the semiconductor gap. Tan et al., [10] reported that the energy band gap of TiO_2 was reduced from 3.2 eV to 2.90 eV when decorated onto the rGO. Chen et al., [14] showed that the energy gap in their fixed amount of rGO could be engineered by changing the hydrothermal synthesizing temperature. In this study, we found that the band gap could be engineered, i.e., systematical decreased, by changing the amount of rGO in the NC. We have kept the temperature constant. The interfacial chemical bonds between the NP TiO_2 and the rGO, the C—O—Ti bonds in the present system, also provides a pathway for the transfer of the photoexcited electrons to the surface of the rGO, making for additional active sites on the rGO sheets available for the conversion of Cr^{6+} to Cr^{3+}.

In Section 2, we present detail information on the fabrication of our TiO_2·rGO NC's with different amounts of rGO surfaces onto which the TiO_2 NR will be decorated and of the measurements which will be done. In Section III., the results of the X-Ray Diffraction (XRD) studies, images of the Scanning Electron Microscopy (SEM), the UV–vis absorption spectra, the FT-IR spectra and the results of the measurements of the Cr^{6+} conversion to Cr^{3+}) are presented. In the Section IV, the significance of the results to the overall conversion is given.

2. Experimental details

2.1. Fabrication details

Synthesis of Graphene Oxide (GO): GO was prepared by modified Hummers and Offeman method. Firstly, a mixture between 360 ml of H_2SO_4 and 40 ml of H_2PO_4 was placed in an ice bath and stirred 15 min. After that, 3 g of graphite powder and 1.25 g of $NaNO_3$ were added. The temperature of the mixture was held below 5 °C. The mixture was stirred in ice-bath for 60 min. Afterward, the mixture was removed from ice-bath and stirred continuously at room temperature for 5 days. After the fifth day, 400 ml of DI water was added to adjust then were added to the mixture and stirred 30 min. Next step, 18 g of KMnO was slowly mixed in. temperature to 98 °C. The mixture was stirred continuously for 60 min. at which time H_2O_2 was added to stop the reaction. The mixture was now centrifuged to remove the graphene oxide powders which were washed with 5% HCl followed by dilution with DI. Finally the GO powders were dried at 60 °C for 16 h.

Synthesis of TiO_2-x%rGO NC's: TiO_2-x%rGO NC was prepared by solvol thermal method based on Rajamathi's work [15] with modification. Briefly, 4 g GO was dissolved in a solution of 60 ml ethanol mixture using by ultrasonic treatment for 6 h. 400 mg AR grade Titanium (IV) dioxide (99% Sigma-Aldrich) was added to a GO solution with difference mass ratios of rGO (1, 5,10,15,20 and 25 wt%, respectively). To obtain a homogeneous suspension, the mixtures were stirred continuous stirring for 1 h. Afterwards the suspensions were transferred to a Teflon-lined autoclave which was maintained at 180 °C for 8 h. During this step, the GO will be reduced to rGO. The suspended products were removed by filtration. They were then rinse in by DI water several times and dried at 60 °C for 12 h. The sample produced by this way will be denoted as TiO_2-x%rGO with x = 0, 1, 5, 10, 15, 20, 25 (Table 1).

A standard absorption/Cr^{6+} concentration curve was constructed by mixing 100 mg of CrO_s crystals in 1 L of pure water. This mixture was further diluted to give solutions having 0.5, 1, 2, …, 10, 15, 20, 25 and 30 mg CrO_3/L H_2O. The absorption of UVA radiation used in this study by each of the diluted Cr^{6+} mixtures was measured with the UV–vis light spectrometer. The information was then plotted to get a Cr^{6+}concentration/absorption plot. This plot was used to convert the absorption data into the Cr^{6+} concentration needed to achieve the absorption being measured.

Table 1
Composition of TiO_2·x% rGO Nanocomposites.

TiO_2·x% rGO	Surface density TiO_2 per area of rGO (gms/cm^2)
TiO_2·1% rGO	$2.188662401 \times 10^{-5}$
TiO_2·5% rGO	$0.416888076 \times 10^{-5}$
TiO_2·10% rGO	$0.197176793 \times 10^{-5}$
TiO_2·15% rGO	$0.124003535 \times 10^{-5}$
TiO_2·20% rGO	$0.087546496 \times 10^{-5}$
TiO_2·25% rGO	$0.065676291 \times 10^{-5}$

2.2. Measurement details

After fabricating the various TiO_2•x%rGO NC's, their crystal structure was determined using an X-Ray Diffractometer (XRD) (Model: D8 Advance, Germany). The morphology was imaged with Scanning Electron Microscope (SEM) (Model: Quanta 450, Netherlands). The sizes of the NC's in each reverse contract SEM image were determined using the program (Image J). The Fourier Transform-Infrared Spectra (FTIR) spectrums were recorded (TENSOR 27, Brunker, Germany). The UV–vis absorption spectrums were recorded with UV–vis Spectrometer (Model: Perkin Elmer Lambda 650, Waltham, USA). The UV–vis Spectrometer was also used for the photo-catalytic measurement.

2.3. Photocatalytic experiment

To determine the photocatalytic reduction of Cr(6+), 0.100 g. of each TiO_2•x%rGO (x = 0, 1, 5, 10, 15, 20 and 25%) NC powder was mixed with 100 ml of the prepared Cr(6+) solution. The pH of each solution was adjusted to 5.6 – 6.7. Each of the mixtures was mixed in the dark for 60 min. to establish adsorption/desorption equilibrium. Each of the mixed solutions was then exposed to the light emitted from UVA (Black light) 36 W Model: Toshiba FL40T8BL/18, 2 Tubes lamp. 2 ml of each mixture were drawn at different times after the beginning of the light exposure. The intensities of the transmitted radiations in the frequency range 859–1176 THz for each TiO_2•x%rGO was then measured using the UV–vis spectra spectrometer. The intensities of the absorptions peaks centered at 255 nm and 349 nm were taken to reflect the concentration of the Cr^{6+} ions remaining in the solution. The decrease in the intensities indicates the degree of the photoreduction of Cr^{6+} by the TiO_2 decorated rGO NC's.

3. Results

3.1. Physical properties

3.1.1. SEM images

The surface morphology of one of the NC's is shown in Fig. 1. In Fig. 1a, we see small growth on a smooth surface. The small growths are the TiO_2 NP's the while the smooth surfaces are the rGO sheets. Fig. 1b shows the same NC's, but now the background is the rGO sheet. The TiO_2 NP's are now seen as black spots of different sizes. The SEM images of the other TiO_2·x% rGO NC's are similar. Of particular interests are the reverse images (ones in which the rGO is seen as white surfaces and the TiO_2 NP's as dark spots since they can be scanned to determine the average sizes of the NP's on the different rGO sheets.

3.1.2. XRD patterns

Since reduced grapheme oxide (rGO) is a single layer system, the XRD pattern of rGO would not be expected to exhibit any reflection peaks. The peaks (See Fig. 2) observed in the XRD patterns of the TiO_2 decorated rGO NC's are the peaks of anatase phase of titanium, meaning that the TiO_2 nanoparticles attached to the surfaces of the rGO are anatase and not rutile. Since the particles are composites and not