Boosting Photocatalytic Activity Using Vanadium Doped Titanium Oxide with Reduced Graphene Oxide (RGO)/Semiconductor Nanocomposites

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Abstract: Textile waste materials are increasing day by day with the depletion of water. This increasing concentration of ions, functional groups, and ammonia present in the water as a byproduct from the industries produce toxicity. This affects the human and aquatic life. The sustainability of the materials to rule out this toxicity can be done by Reduced Graphene Oxide synthesized by modified Hummer's method. The composite of V-doped TiO_2 and RGO was synthesized by hydrothermal method and V-doped TiO_2/RGO and perfluorocarbon synthesized by sonication. Methylene blue was used as an indicator to improve the pH of the wastewater under sunlight. The product was characterized by the powder X-ray Diffraction method. It has confirmed the synthesis of the product. The ultraviolet/visible spectroscopy was employed to study the absorbance decreases with time which is the confirmation of degradation of methylene blue with time and it was clearly observed that photocatalytic activity of the product for the degradation of methylene blue which is an organic dye and hazardous to the environment. The findings obtained can be utilize for the industrial waste-water treatment with metallic ions.

Keywords: Photocatalytic degradation, methylene blue, vanadium doped TiO_2, perfluorocarbon, reduced graphene oxide

1. Introduction

Industrialization and globalization improve the life and in parallel threating the environment as the organic pollutants removed from the industrial waste are harmful to the soil as well as habitat around. Organic dyes contribute major amount to the water bodies and their major contributions are from the leather, textile, food, and printing industries. As most of these organic dyes are not harmful to the humans but their concentration in water affect the aquatic life which may indirectly causing problems [1]. When transferred to body these dyes produce certain disorders in the body. The problems associated with carcinogenic, mutagenic, genotoxic and heart issue arise. There are some practical methods of removing these dyes like adsorption, physical desorption, chemical and microbiological methods to remove the dyes or to convert them into secondary pollutants [2-4].

Titanium (Ti) and Vanadium (V) are wonder transition elements with prominent characteristics having high melting temperature, low density, and lightweight. The metals with their alloys are sustainable for energy, aerospace, industry, food, and biological processing applications. The world is growing rapidly with energy demands [5]. Carbon-free fuels

are common as they don't produce contaminated waste products that contribute to the environment [6]. Renewable energy methods are considered the alternate source of energy for mankind. For this metal oxides with reduced graphene oxides (RGO) or graphene oxide (GO) can be utilized for the photocatalytic generation of energy [7-9]. The catalysts provide jerks during the phot activity to convert methane to fuels. The most efficient method for the preparation of graphene oxide is Hummer's method [10].

The monoatomic layered carbon (graphene) material is characterized by single-atom thickness, smooth honeycomb structure, and tight bonding. The discovery of graphene has had a major impact on research, and its impact has been reflected in papers around the world, and research continues today. Fullerenes (0D), nanotubes (1D), and laminated graphite (3D) are all forms of graphene [11,12]. The easiest way to obtain graphene sheets or layers is lamination (by mechanical exfoliation). Carbon has two well-known crystals, diamond, and graphite, which are massive and exhibit properties such as unique symmetry and mechanical strength [13,14]. These two forms of carbon are used in a variety of applications that are reflected in their bonding. In graphene, the 2px and 2py electrons are arranged in the 2s orbital, resulting in a carbon-carbon bond. These orbitals provide rise to stationary local σ bonds [15-18]. Graphene has a zero bandgap between the conduction and valence bands and is a semimetal, so it has very high electrical conductivity [19,20].

In this work, we aimed to study the photocatalytic generation of carbon fuel by catalysts Ti/V as it allows with RGO and GO. Preparation of RGO by modifying it from the hummer's method. It will help in producing RGO from simple GO. The amount of graphene oxide increases in the matrix will increase the amount of RGO that has been seen, and it enhances the activity of the reaction initially and then decreases regularly. The decrease in electrical conductivity is due to the change in the hybridization state of the carbon from sp2 to sp3 as the electronic orbitals are partially filled changes to filled by adding more amount of Ti/V as a catalyst experiencing photoactive behavior. This is due to the contributions of p-orbital electrons from *2px, 2py, 2pz* shells.

2. Experimental Procedure

Perfluoro-octane C_8F_{18} (purity>98.9 %, Sigma-Aldrich), Sodium nitrate $NaNO_3$ (purity>98 %, Sigma-Aldrich), Vanadium pentoxide V_2O_5 (purity>99.9 %, Merck), Titanium chloride $TiCl_4$ (purity>98 %, Sigma-Aldrich), Sodium hydroxide NaOH (purity>98 %, Sigma-Aldrich), Hydrogen peroxide H_2O_2 (purity>98 %, Merck), Graphite powder C (purity>98 %, Sigma-Aldrich), Sulfuric acid H_2SO_4 (purity>98 %, Sigma-Aldrich), Methylene blue $C_{16}H_{18}ClN_3S$ (purity>98 %, Merck), Hydrochloric acid HCl (purity>98 %, Sigma-Aldrich) brought from China were taken in stoichiometric amount. The powders were mixed and stirred using the magnetic stirrer for 30 minutes. The pH of the solution was maintained. The sonication of solution on ultrasonic sonicate XL-2020 model for the formation of composite and was centrifuged (model YJ 03-043-4000) for 10-15 minutes to remove the impurities. The reaction temperature was obtained around 300-400 °C in an oven having model DINCN 60525-IP-20.

2.1 Synthesis of Graphene Oxide (GO)

Hummer synthesis was used to prepare graphene oxide. Taking 92mL of H_2SO_4 in ab beaker that was placed in the ice bath. Add 2g of graphite powder, and 2 grams of sodium nitrate to the ice-cooled sulfuric acid. Add 6 grams of $KMnO_4$ gradually while stirring. The temperature was maintained at 100°C. The beaker was removed from the ice bath while stirring the mixture for thirty minutes. When the temperature was increased to around 120°C the solution mixture was transferred to the oil bath. This temperature was maintained for 15 minutes by slowly adding 92 ml of distilled water. The reaction was stopped by adding 280 ml of distilled water followed by 17 ml of 30% hydrogen peroxide. The resulting mixture was washed with 5% HCl and the resulting powder was dried in an oven.
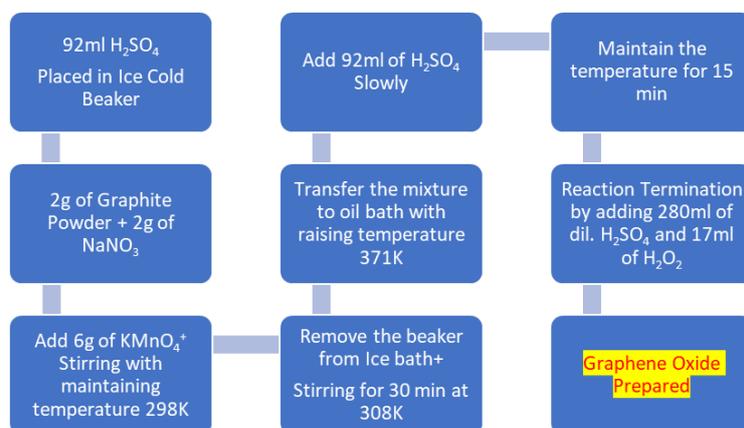
Fig. 1 - Synthesis of graphene oxide by Hummer's method

2.2 Synthesis of V-doped TiO₂ Nanoparticles

Hydrothermal synthesis method was used for the preparation of V-doped TiO_2. Addition 1 ml of $TiCl_4$ into 10 ml of water to dissolve it properly. 0.22g of V_2O_5. The solution was collected into a Teflon-line autoclave. It was heated at 200 °C for 2 hours. The cooling and washing were done at room temperature with water, respectively. The pH of the solution was maintained around 7. The sample was dried at 80 °C in the oven. The particles obtained were annealed/sintered at 500°C.
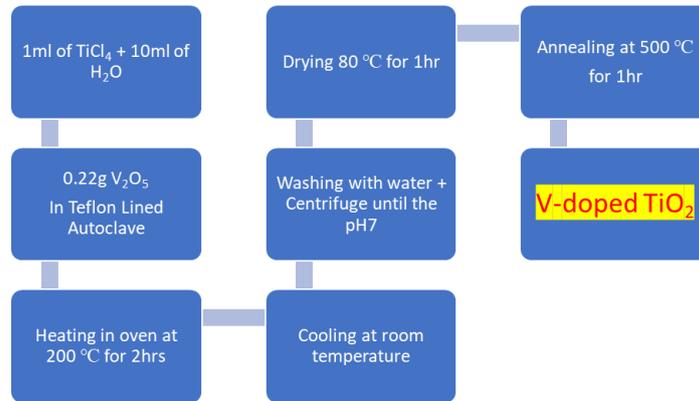
Fig. 2 - Synthesis of vanadium doped TiO₂

2.3 Synthesis of V-doped TiO₂/RGO Nanocomposite

The weighted 1g of V-doped TiO_2 was put in water. The sonication process was done for the proper mixing of the particles to make a suspension. The suspension was stirred for 10-20 mins. The addition of NaOH 2.5g in the solution for the dispersion. In another beaker 0.20 g of graphene oxide was taken and sonication was done for 10 mins. The suspension containing V-doped TiO_2 nano particles was added to graphene oxide suspension. It was put in the Teflon autoclave with stainless steel shell. The assembly was placed at 120 °C overnight. The crystals were washed with HCl and dried at 80 °C overnight.
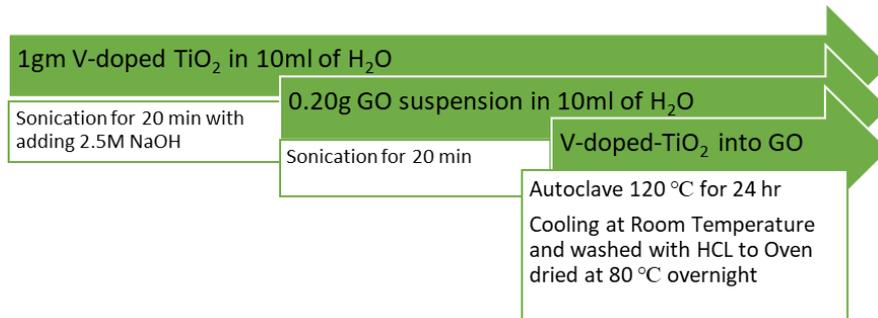
Fig. 3 - Synthesis of vanadium doped TiO₂/RGO

2.4 Synthesis of V-doped TiO₂/RGO/PFCs (Perfluoro-Octane) Nanocomposite

0.7 g V- doped TiO_2/RGO sample and 70 mg of Perfluoro-Octane was taken and a slurry was made. It was subjected to sonication for 15 minutes for preparation of the composite.

2.5 Photocatalytic Activity

The solution of methylene blue was prepared in distilled water in a flask having molarity. The prepared solution was covered with aluminum foil to avoid the degradation of dye by laboratory fluorescent light. 0.01 M solution of methylene blue was prepared by dissolving methylene blue in 100 mL water. Absorbance was measured by UV/Visible spectrophotometer. Wavelength with maximum absorbance value was considered λ_{max}. Firstly, the beaker with 50 mL solution from the above dye solution (of maximum wavelength) and then 0.20 g composite was added into it. Then put this beaker into the photoreactor stirring for 30 minutes without any light. The stirring took the value of absorbance in UV/Visible light spectrophotometer which is considered a dark value. Then put the UV/Visible bulb on and fixed the position of the reactor for fixing the distance between the light source and the sample. After 10 minutes took 1 mL solution again and took the second absorption value. It was repeated six to seven times until complete degradation of dye

took place in this way the absorbance values of all samples V-doped TiO_2, V-doped TiO_2/RGO, and V-doped TiO_2/RGO and 1-bromoperfluoroctane.
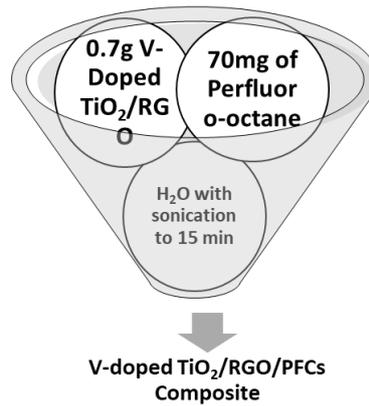
Fig. 4 - V-doped TiO₂/RGO/PFCs composite

3. Results and Discussion

3.1 XRD Analysis

Fig. 5 shows X-ray spectra of Bragg's wide range of angle $20° \leq 2\theta \leq 80°$ with a step size of 0.02 having a scan speed of 1.2(°)/ min showing seven peaks of V-doped TiO_2 /RGO obtained. The four peaks (101), (004), (204), (215) are of high intensity, and the other three (200), (105), and (116) are of low intensity. The peak (021) shows the presence of Vanadium and (002) is the peak for RGO. The JCPDS 89-492 indicates that it is having anatase phase structure [21]. The peak assign to (101) plane is the most intense throughout the pattern, which indicates the preferential orientation of V-doped TiO_2 nanoparticles along (101) direction [22].
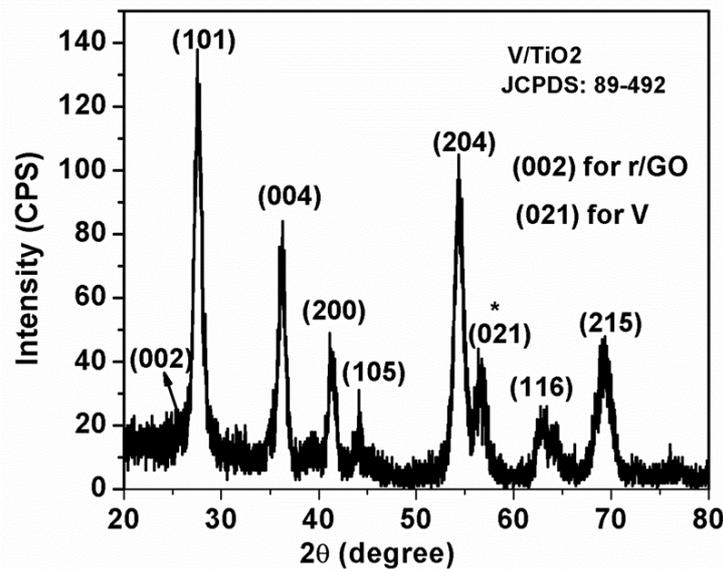
Fig. 5 - XRD spectra showing the V-TiO₂/RGO

3.2 Photocatalytic Degradation Activity

Fig. 6 shows the comparative study of photodegradation of methylene blue by Vanadium doped TiO_2, Vanadium doped TiO_2/RGO, and Vanadium doped TiO_2/RGO with 1-bromoperfluroctane from zero to ninety minutes. It was observed the absorbance of the samples taken after every ten minutes of regular intervals. It was observed that absorbance of the MB decreases with the increasing time. The methylene blue activity decreases rapidly with time and the slope of the curve is steep which shows only vanadium-doped titanium photocatalytic behavior. When the addition of RGO in vanadium-doped titanium the activity slope becomes less steep, and it shows that the more time it requires to degrade from the methylene blue. The most promising results were obtained when the addition of 1-bromoperfluroctane was added with vanadium-doped titanium RGO. The degradation delay shows increased activity[23,24].
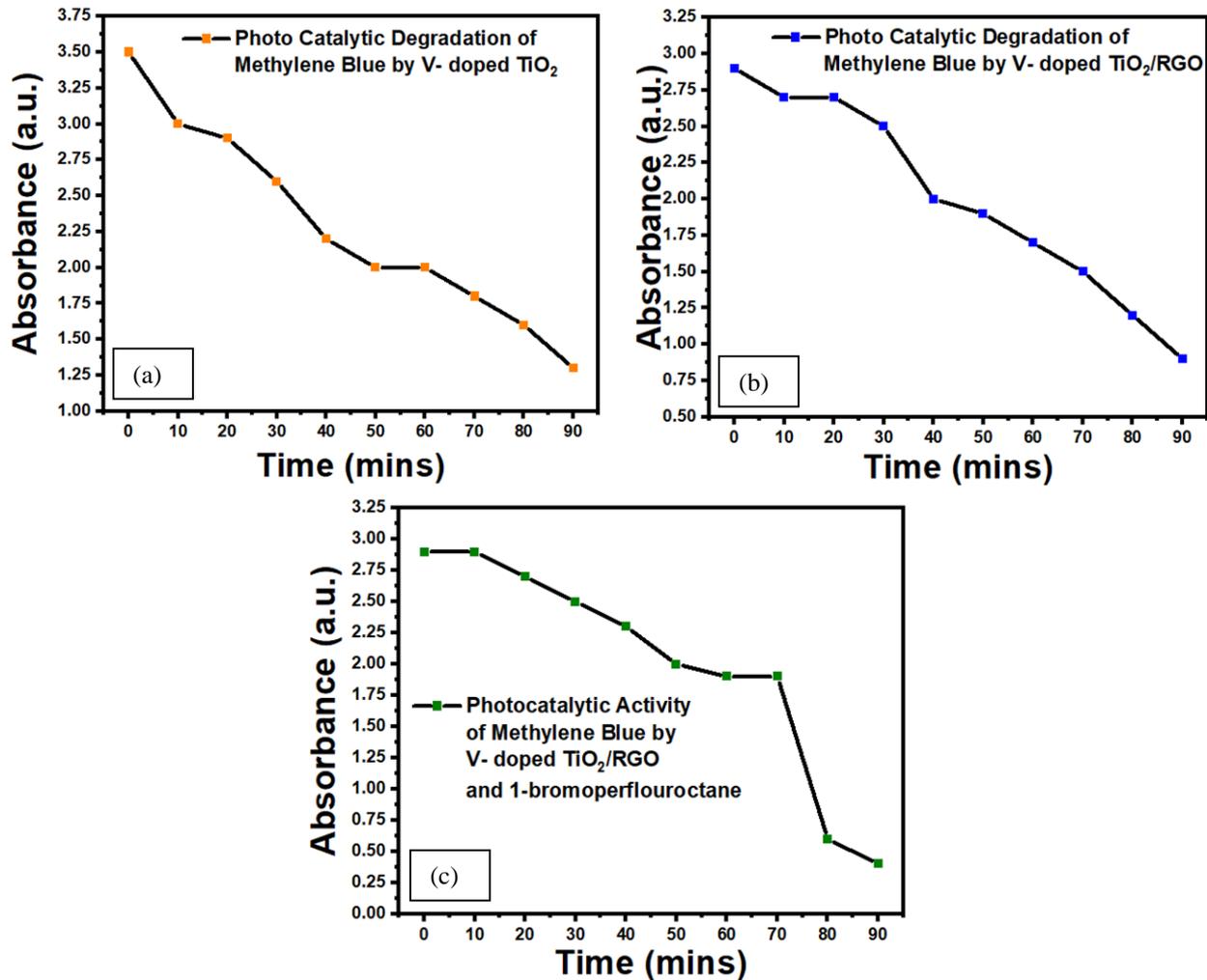
Fig. 6 - (a) Photodegradation of methylene blue by V-doped TiO$_2$; (b) photodegradation of methylene blue by V-doped TiO$_2$/RGO; (c) photodegradation of methylene blue by V-doped TiO$_2$/RGO/PFCs

4. Conclusion

The photodegradation of prepared composite V-doped-TiO$_2$/RGO for the removal of methylene blue from the polluted water was studies having applications in the industrial effluents was analyzed. The compositions were made using the hydrothermal synthesis method and confirmed by the X-ray diffraction technique. The ultraviolet spectroscopy confirmed that the addition of reduced graphene oxide with adding 1-bromoperflurooctane will increase the activity of degradation and remove more and more methylene blue by changing the color of the solution to crystal clear. The method will be utilized for the industrial cleaning of water. The future work will be the composition or prototype of a filter that will work for the cleaning and maintain the pH of industrial wastewater.

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