Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2015, 4 (2): 525-532

(International Peer Reviewed Journal)

Synthesis of TiO_2 and ZnO Nano Composites With Graphene Oxide. Photo Catalytic Reduction and Removal of Chromium (VI) In Aqueous Solution

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Accepted on 25th February 2015

ABSTRACT

In this work TiO_2 and ZnO nanaoparticle composites with Graphene oxide (GO/TiO_2, GO/ZnO) photocatalyst have been prepared by sol-gel method and characterised by Scanning Electron Microscope (SEM), X-ray Diffraction, UV– visible spectroscopy and UV–Visible Diffuse Reflectance Spectra (DRS). These nanocomposites were used in photocatalytic reduction, under UV visible light, of Chromium (VI) which is highly environment polluting and causes human health problems. The GO/ZnO composite showed increased photocatalytic performance in reduction of Cr (VI) with a maximum removal rate of 65 % under UV light irradiation as compared with GO/TiO_2, which has 35 % removal rate. This may be due to the increased light absorption intensity and range as well as the reduction of electron–hole pair recombination in ZnO and TiO_2 with the introduction of GO.

Keywords: Graphene oxide, ZnO, $TiO_{2,}$ Photocatalytic, Cr (VI).

INTRODUCTION

Graphene is a single layer of carbon and it is nearly a supreme 2D material. It has involved a great deal attention of scientific interest and acquire possible potential applications in various fields, in such as composite materials, batteries, solar cell, photocatalysts, sensors and many others fields [1,2], due to its unique electronic property, high transparency, flexible structure, large specific surface area and good thermal conduction [3,4]. The potential way to utilize these properties in various applications could be to integrate graphene sheets in composite materials such as in the preparation of highly photoactive composites materials based on TiO_2 and ZnO [10-12].

However, graphene is poorly soluble in water and polar organic solvents, which makes it complicated to deposit metal or metal oxide on its surface to synthesize graphene-based hybrid materials [5, 6]. Unlike hydrophobic graphene, graphene oxide (GO) is hydrophilic due to the oxygen-containing functional groups on the sheet surface. Titanium dioxide (TiO_2) and ZnO are nearly all attractive photocatalysts, because they are nontoxic [7], chemically stable, and relatively cheap [8, 9]. The well-known drawback in using TiO_2 and ZnO in the superior oxidation photocatalytic process is the recombination of e^- and h^+ pairs.

As an environmental-friendly and capable approach, ultraviolet (UV)-assisted photocatalytic reduction of chromium (VI) using Graphene Oxide (GO) - semiconductor oxides, typically TiO_2 and ZnO, has been applied. The one-step strategy has been used to construct high quality graphene based composite without using any stabilizing reagent. The fabricated ZnO–graphene (GO/ZnO) and TiO_2–graphene (GO/TiO_2) composites by hydrothermal method are used in carrying out UV-assisted photocatalytic reduction of chromium (VI) in aqueous solution. [1, 13-16] In this work the nanocomposites of TiO_2/GO and ZnO/ GO have been prepared via facile hydrothermal reaction of graphene oxide and TiO_2 and ZnO in aqueous ethanol solvent. The nanocomposite TiO_2/GO exhibits much superior photocatalytic activity and stability than pure TiO_2. The tendancy towards the photocatalytic activities of the samples were evaluated by the photoreduction of Cr (VI) in an aqueous solution under the irradiation of visible light.

The visible light photocatalytic activity for reduction of Cr (VI) pragmatic in the GO/ZnO nanocomposite is due to fact that, under visible light irradiation, GO can be photoexcited and transfer electrons to the conduction band of ZnO.This transforms ZnO to be a visible light photocatalyst for reduction of Cr (VI) instead of photoexcitation of ZnO. On the basis of the above principles, we have designed the GO−ZnO nanocomposite system to show the photosensitizer role of GO on semiconductors. The ZnO nanoparticles are in situ grown on the GO nanosheet to ensure the strong interfacial bonding between ZnO and GO for facilitating the electron transfer between them. The photo catalytic reduction of Cr (VI) in aqueous solution is adopted to show the photosensitizer role of GO in the synthesized GO−ZnO nanocomposites to avoid the self-induced photosensitization effect of the reaction substrate.

MATERIALS AND METHODS

Materials: Graphite fine powder (99.99 %) was purchased from sigma Aldrich Chemical Corporation USA. Titanium (IV) isopropoxide (99.99 %), Zinc sulphate ($ZnSO_4$), concentrated sulphuric acid (H_2SO_4, 98%), Sodium nitrate ($NaNO_3$), Hydrogen peroxide (H_2O_2 30 %), Ammonium bicarbonate (NH_4HCO_3), and Ethanol were of analytical grade, purchased from SD fine chemicals, Mumbai.

Synthesis of Graphene Oxide (GO): GO was prepared from natural graphite powder through modified Hummers method [18]. In this synthesis, 2 g of graphite was further into 46 mL of 98% H_2SO_4, followed by stirring at room temperature over a period of 24 hrs. After that, 200 mg of $NaNO_3$ was introduced into the mixture and stirred for 30 min. Consequently, the mixture was kept below 5 ^{0}C by ice bath, and 6 g of $KMnO_4$ was gradually added into the mixture. Subsequent to heating to 35–40 ^{0}C, the mixture was stirred for a further 30 min. After that, 92 mL of water was added into the above mixture during a period of 25 min. Finally, 280 mL of water and 20 mL of H_2O_2 were added into the mixture to stop the reaction. After the unexploited graphite in the resulting mixture was removed by centrifugation, the precipitant GO was dispersed into distilled water and ultrasonicated, dried in air oven at 100 ^{0} C. Finally the product was calcinated at 400 ^{0} C for 3 h.

Synthesis of TiO_2 nanoparticles (TiO_2 NPs): 10 mL titanium (IV) isopropoxide was slowly introduced 35 mL into ethanol in an ice bath (0 ^{0} C) under constant stirring for 30 min until it was completely dissolved and then 10 mL of double distilled water was added to this suspension. The generated white titanium oxide (TiO_2) was allowed to stand for 2 h. Then, the obtained TiO_2 NPs were filtered, washed with double distilled water and dried at 100 ^{0} C in a vacuum oven for 3 h. The product was calcinated at 400 ^{0} C for 1 h to obtain white powder of TiO_2.

Synthesis of ZnO Nanaoparticles (ZnO NPs): 50 mL of 1.0 M $ZnSO_4$ solution was further drop wise into 60 ml of 2.0 M NH_4HCO_3 solution under vigorous stirring at 60 ^{0} C in a water bath for 1 h. The white precipitate formed was isolated by filtration, washed thrice with distilled water and ethanol, and then dried in a vacuum oven at 60 ^{0} C for 24 h. Finally, the product was calcinated at 600 ^{0} C for 1 h to obtain white powder of ZnO.

TiO_2 and ZnO Nanoparticle Composites with Graphene Oxide (GO/TiO_2/ZnO): The TiO_2 and ZnO naanopaticles composite with graphene oxide were prepared by hydrothermal method. 0.500 g of graphene oxide was added in 50 mL of double distilled water and after 1 h ultrasonication, a brown yellow solution was formed. Then 0.500 g of TiO_2 nanoparticles powder was added in to the solution and the mixture was refluxed for 6 hours with constant stirring at 60 – 80 ^{0} C. The product was collected and dried in air oven for 3 h. The same procedure was repeated for preparing graphene oxide composite with Zinc oxide also.

Photocatalytic activity of (GO/TiO_2) and (GO/ZnO): The photocatalytic activities of the samples were evaluated by the photoreduction of Cr (VI) in an aqueous solution under the irradiation of visible light. [17, 19, 20] For this 100 mg of GO/TiO_2 composite material was added to100 mL of 0.0050 mg L^{-1} $K_2Cr_2O_7$ aqueous solution and magnetically stirred in the dark room for 2 h, to attain the adsorption–desorption equilibrium on the surface of the catalyst. The mixed suspension was then, under stirring, exposed to direct sunlight for 1 h. During illumination, 5 mL sample solutions were drawn from the system at certain time intervals. After the removal of the catalyst particles by centrifugation, from the sample solution residual amount of Cr (VI) was analyzed using UV−Vis spectrophotometer. The same procedure was also adopted for (GO/ZnO) composite .

Characterization: Scanning electron microscope (SEM) studies were carried out with the (HITACHI-3000 SH Model). Material phase analysis of the prepared nanocatalysts was done by powder X-ray diffraction (XRD) measurements were carried with (Rigaku diffractometer, Japan, Cu, Kα radiation, λ = 1.5406 A˚). Diffuse reflectance spectra (DRS) of the samples were recorded in the wavelength range 200–800nm using a UV–Vis spectrophotometer (Jasco-650, japan) equipped with an integrating sphere accessory employing $BaSO_4$ as reference material. The extent of during catalytic ozonation was followed spectro photometrically using a UV–Vis spectrophotometer (Jasco-650, japan).

RESULTS AND DISCUSSION

Scanning Electron Microscope (SEM) Studies: TiO_2 nanoparticles prepared by sol gel method and made in to graphene oxide composite by hydrothermal method. The SEM image in Figure 1(a) shows the extend of doping of TiO_2 NPs in graphene oxide. The sizes of TiO_2 nanoparticles can be controlled from 3 µm by the composition of solvent system and the concentration of titanium (IV) isopropoxide. Approximately, the surface area for each particle was inversely proportional to the particle size. The surface areas for the prepared nanoparticles have been calculated by assuming that each particle is a crystalline shape without pores or internal surface. As indicated in figure (b) and (c) the measured surface areas for the 4 µm, and 500 nm nano particles were similar to the calculated values. This suggests that the prepared TiO_2 nano particles are close to crystalline shape, and they are dense in structure without micro pores or internal surface.

It gives an idea about the particle sizes and surface modifications in GO–ZnO photocatalyst affected during doping. It is observed that the particle structures are irregular and ranged in size from 1µm, 10µm to 500 nm. The SEM permits easy differentiation of ZnO nanoparticles (small white areas) and GO sheets (large black areas). That is, ZnO NPs are seen on the surface of the GO sheets particle as black dots. Also, there is a possibility for the ZnO to be incorporated into the interstitial positions. Further, it is observed that the average size of ZnO in GO / ZnO particles is in the range of 1µm to–500 nm. It is also clear that the particles has been increased which is indicated by the increased particle size with well-developed faces. The composition of the prepared materials (GO/TiO_2) and (GO/ZnO) were determined by the EDX spectrum (Fig. 1(d) and (h)), which supports the presence of 35.59 wt % of TiO_2 NP deposited on the GO. The EDX also reveal that 49.08 wt% of ZnO NPs were deposited on the surface of GO. [23, 26]

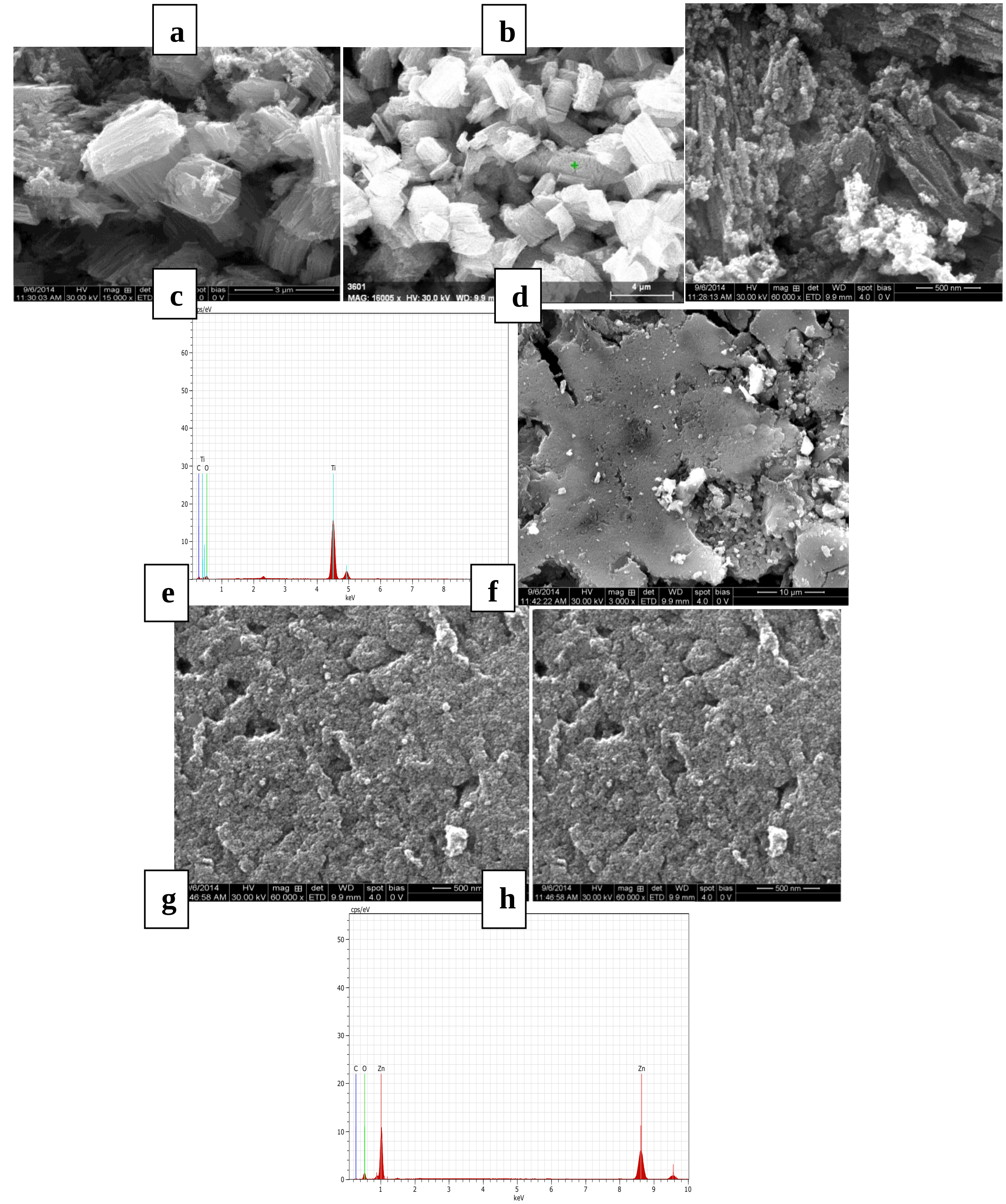

Figure: 1(a). SEM image of GO - TiO_2 (a), (b), (c) for different magnification and (d) EDX Spectrum of the of GO/TiO_2 sample 1 (b) SEM image of (e),(f),(g) for different magnification and (h), EDX Spectrum of the of GO/ ZnO sample

X-Ray diffraction (XRD): The X-ray diffraction (XRD) patterns of TiO_2 NPs with and without GO shown in the above figure (2) indicate that the TiO_2 NPs are consisting of mixed phase of anatase and rutile The diffraction peaks observed at values of 25.28◦ and 36.8◦ correspond to (101) diffraction plane of anatase and (110) diffraction plane of rutile, respectively [8,10,15, 23].

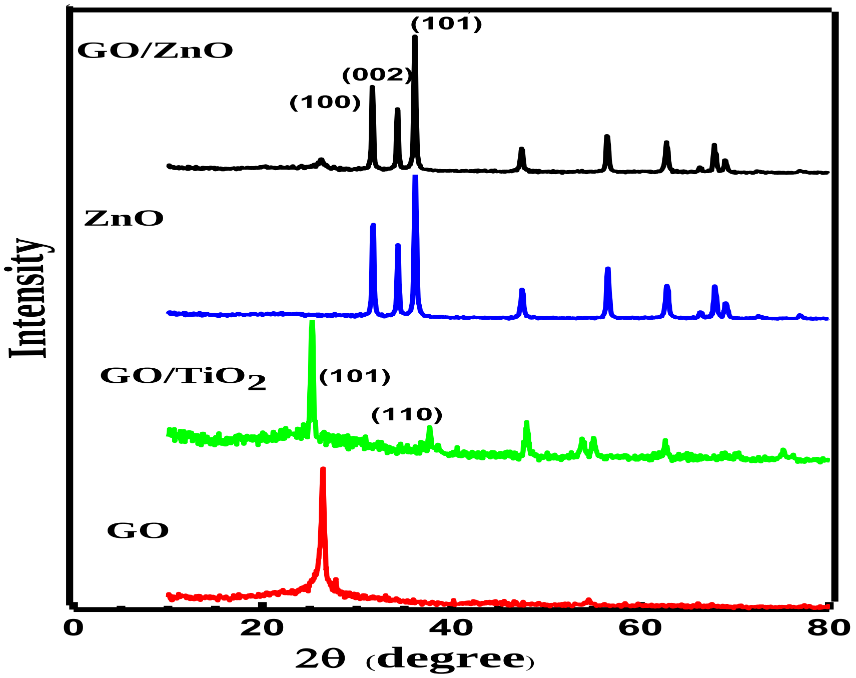

Fig: 2 XRD spectrums of GO/TiO_2 and GO/ZnO

The samples exhibit analogous diffraction peaks in terms of TiO_2 framework. The dominant peaks located at can be 25.2, 36.8, are indexed to (101), and (110), crystallographic planes of TiO_2. The phase purity of ZnO in samples is confirmed by the XRD patterns as shown in figure: (2). It can be seen that for the obtained blank ZnO, GO/ZnO nanocomposites with 1:1 % weight addition ratios of GO and the sample of GO/ZnO, they show similar XRD patterns. [1, 18,] The dominant peaks located at can be. 31.7, 34.4, 36.3, are indexed to (100), (002), and (101) coincides of crystallographic planes of ZnO, Notably, no diffraction peaks for GO can be observed in the nanocomposites. [21 ,22,27] one possible reason might be due to the low amount and relatively low diffraction intensity of GO in comparison with the diffraction intensity of TiO_2 and ZnO the other is probably due to the disappearance of the layer-stacking regularity after reduction of Graphene oxide.

UV–Visible Diffuse Reflectance Spectra (DRS): The UV−Vis diffuse reflectance spectra (DRS) measurement has been performed to determine the optical property of the samples. As shown in figure. (3). it can be seen that the presence of different amounts of Graphene oxide has a significant manipulate on the Optical property of light absorption for the GO/TiO_2 and GO / ZnO nanocomposite.

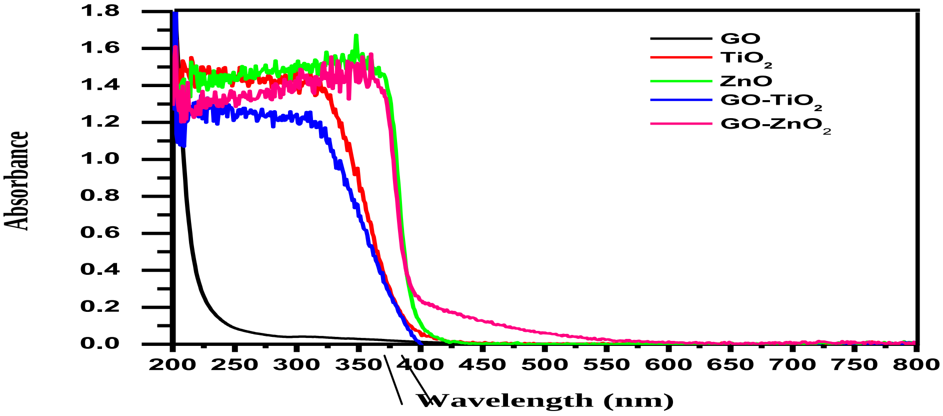

Fig: 3 UV-visible Diffuse reflectance spectroscopy (DRS) spectrum of GO, TiO_2, ZnO, GO/TiO_2 and GO/ZnO

The addiation of Graphene oxide it induced the increased light absorption intensity in the visible light region ranging from 200 to 800 nm in comparison with blank TiO_2 and ZnO which can be described to the broad absorption of GO in the visible light region. In the addition, it could be noted that the GO/TiO_2, GO/ZnO and GO blank TiO_2 and ZnO nanocomposites all display the sharp absorption band edge onset at 385 nm. [1, 11, 18.23, 29] Additionally, it is noteworthy that GO/TiO_2 and GO/ZnO shows a weaker absorbance than that of TiO_2 to change ZnO in the visible light region. According to the formula λ= 1240/Eg the band gap energy of TiO_2 and GO/TiO_2 are 3.30 eV and 3.01 eV respectively. The band gap energy of ZnO and GO/ZnO are 3.01 eV and 2.08 eV respectively This results confirmed that the absorption off visible light of TiO_2, ZnO nanoparticles has been effectively enhance by the incorporation GO/ TiO_2 and GO/ZnO which is beneficial for improving the photocatalytic of activity of TiO_2 and ZnO.[24,25,28]

Photocatalytic Degradation of Chromium (VI): The photocatalytic activity when GO/TiO_2 and GO/ZnO evaluated for instantaneous photocatalytic decontamination of Cr (VI) under the UV light irradiation. For the comparison purpose the photocatalytic decontamination of Cr (VI) where alone conducted shown the figure 4. Among the GO−TiO_2 and GO/ZnO Nanocomposites with different GO addition ratios, 1:1% GO−TiO_2 and GO/ZnO exhibits the best visible light photo activity.

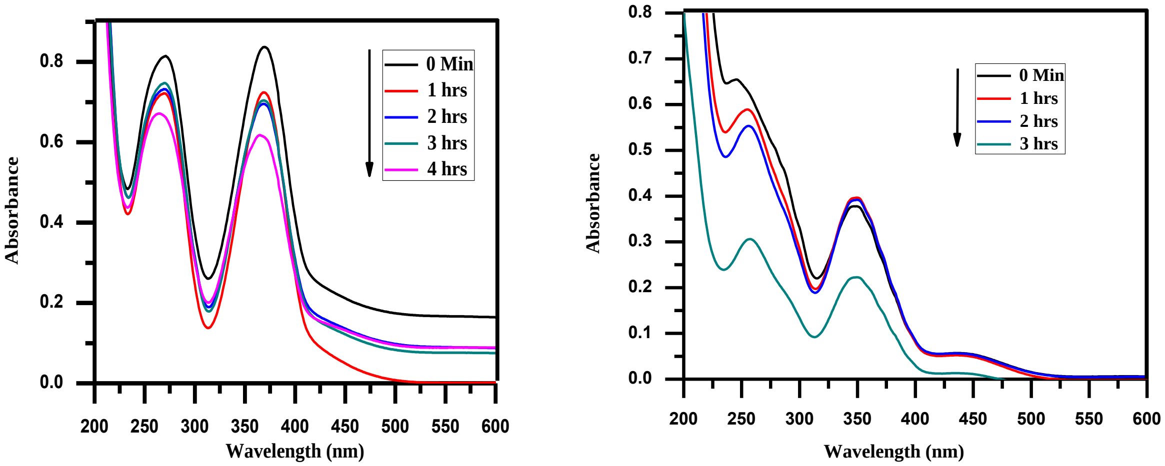

Fig: 4 UV-visible spectrums of (a) GO/TiO_2 (b) GO/ZnO nanocomposites for photocatalytic performance was reduction of Cr (VI) in aqueous solution under visible light.

The whole reduction process is monitored by measuring the time-dependent UV−Vis absorption spectra of the reaction mixture solution. As shown in figure 4(a), during the reaction process, the absorption intensity of Cr (VI) at 375 nm 275 nm decreases gradually with the irradiation time, indicating the successful reduction of Cr (VI). The GO−TiO_2 nanocomposite removes 35 % Cr (VI) from the solution. As shown in the figure 4(b), during the reaction process, the absorption intensity of Cr (VI) at 350 nm and 250 nm decreases gradually with the irradiation time, indicating the successful reduction of Cr (VI). The GO/ZnO nanocomposite removes 65 % Cr (VI) from the aqueous solution. Besides, it is clear that the addition ratios of GO are crucial to determine the photocatalytic performance of the GO/TiO_2 and GO/ZnO nanocomposites, indicating the synergetic effect between TiO_2, ZnO and GO. It is also notable that there is no reduction of Cr (VI) in aqueous solution over the bare GO implying that GO by it cannot directly act as photocatalyst for reduction of Cr (VI) under visible light irradiation. [1, 18]. It is known that throughout photocatalysis, the light absorption and the charge transportation and departure is essential factors. The enhancement of the photocatalytic performance should be approved to the increase of the light absorption intensity and range, and the reduction of electron–hole pair recombination in ZnO and TiO_2 with the introduction of GO in the composite, which can be confirmed from absorption and UV measurements. However, when the GO content is further increased above its most favourable value, the photocatalytic performance deteriorates. GO may absorb some UV light and thus there exists a light harvesting competition figure 4 Photocatalytic reduction of Cr (VI) by ZnO and TiO_2 under the UV irradiation.

APPLICATIONS

Graphene oxide composite with GO/TiO_2, and GO/ZnO was applicable for photocatalytic performance for reduction of Cr (VI) and removal of Cr (VI) in aqueous solution.

CONCLUSIONS

This summery of the work GO well known could be effectively reduction the removal of Cr (VI) using of GO/TiO_2, and GO/ZnO. Graphene oxide synthesis of natural graphite powder. Graphene oxide composite with GO/TiO_2, and GO/ZnO was used for photocatalytic performance was reduction of Cr (VI). GO/ZnO composite was used for photocatalytic performance was reduction of Cr (VI) aqueous solution under visible light the removal of Cr (VI) was 65 % and 35 % of the GO/TiO_2. GO/TiO_2 composite was used for low photocatalytic performance for reduction and removal of Cr (VI). Another GO/ZnO composite was used for high photocatalytic performance when compared to GO/TiO_2 composite. GO/ZnO composite has the best photocatalytic performance for reduction and removal of Cr (VI) in aqueous solution.

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