ORIGINAL RESEARCH PAPER

Chemistry

PHOTOCATALYTIC DESTRUCTION OF ESCHERICHIA COLI IN WATER OVER rGO/TiO2 NANOCOMPOSITES

KEY WORDS: Photocatalyst, Graphene Nanocomposite, UV light, Visible light, E-coli

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ABSTRACT

In the present study, Graphene-TiO2 catalysts are prepared by solvothermal method with varied graphene concentrations (1%, 2.5% and 5%). The prepared nanocomposites were characterized by FTIR, Raman and TEM. The photocatalytic activity towards the destruction of Escherichia coli in water under UV and UV-visible irradiations were studied. Graphene-TiO2 nano composite destructs the bacteria significantly at higher rates than unmodified TiO2 and graphene. The results indicates that, at the beginning, the inactivation of E. coli cells is more due to the generation of reactive oxygen species (ROS) like, OH, H2O2, and O2− . Among all samples, the nano composite containing 2.5 wt.% of graphene exhibits a complete E. coli destruction in a minimum irradiation time of 15 and 20 min under UV–Visible and UV light irradiation respectively. The high photocatalytic activity is achieved with the optimum loading concentration of 2.5 wt. % graphene on titania.

INTRODUCTION

Titanium dioxide is a well-established photocatalyst owing to its UV activity and high chemical stability. Effective utilization of photocatalytically-activated TiO_2 materials is largely entertained in disinfecting water-habitant microorganisms and degrading organic pollutants as they can accommodate photo-induced redox reactions of adsorbed pollutant substances combined with photo-induced hydrophilicity of modified-TiO_2 itself [1-2]. Application of TiO_2 and its derived materials towards water disinfection has been thoroughly reviewed [3-4]. Many studies have been done to investigate the photocatalytic destruction of Escherichia coli by TiO_2 [5-6].

As an extraordinary material, graphene has high chemical stability, notably high specific surface area (~2600 m2 g□1), excellent mobility of charge carriers (20,000cm2 V□1 s□1) and relatively good optical transparency [7-9]. So with this understanding, so many graphene composites have been studied for different applications out of which graphene-TiO_2 have shown advantageous enhancement of photocatalytic activity in a number of studies because the graphene can facilitate charge separation and do a function when used as an electron carrier in composite materials.

In the present study, we have prepared a series of Graphene-TiO_2 nanocomposite catalysts and studied there photocatalytic activity against disintegrating Escherichia coli, a gram-negative bacterium, under UV and UV-visible irradiation conditions. This study suggests the possible application of the prepared nano composites for efficient water disinfection systems.

MATERIALS AND METHODS

The graphene TiO_2 nanocomposites were prepared by a solvothermal method using dimethyl formamide (DMF) as solvent. DMF was used for dual purpose of as a solvent for the reaction and as a reducing agent for reduction of GO (Graphene Oxide) to rGO (reduced Graphene Oxide) For a particular composition, required amount of GO (1%, 2.5% and 5%) was dispersed in 25 mL of DMF and sonicated in a bath sonicator for 20 min. Then, 500 mg of TiO_2 (prepared from Titanium isopropoxide as precursor in a sol gel process) was added to the clear brown GO suspension in DMF and stirred for 30 min at room temperature. This mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave, heated at 180 °C for 8 h. After the solvothermal process, the product was washed with double distilled water and ethanol for several times and dried in an oven at 60 °C. The series of nano composites were characterized by TEM and XRD.

The photocatalytic activity of all samples was examined by using Escherichia coli as an indicator strain. 25 ml of sterilized water was spiked with 107 CFU/ml of E. coli and subsequently mixed with catalyst sample in a beaker. The catalyst sample concentration was maintained at 0.5 mg/ml of sterilized water in the test solution. For the photocatalytic experiments, a bioreactor was fabricated which consists of UV-C (Philips TUV 8 W G8T5) and visible light (Philips T5 8 W) sources at the top and a magnetic stirrer at the bottom on which a beaker containing the test solution was placed. The height of 12 cm was maintained from test solution surface to the light source. The major intensities of 8 W UV and 8 W visible light sources were found to be 50 lm/m2 and 505 lm/m2 respectively at the solution surface. At various intervals of time, 1 ml of the sample drawn from the beaker and was serially diluted up to 10-4 dilution. From each diluted solution, 0.1 ml was drawn and spread plated on the LBA plates before incubation at 37°C under the dark condition for 24 hr. After incubation, the number of colonies present on the plates was counted. The Colony Forming Units (CFU) per ml was calculated for each sample at different time intervals

RESULTS AND DISCUSSIONS

The TEM images of reduced graphene oxide (rGO) and graphene TiO_2 nanocomposite are shown in figure 1 and figure 2 respectively. The morphology of rGO, consisting of thin well defined few layer. structures at the edge, as clearly seen in figure 1. The nanocomposite reveals a homogeneous dispersion of nanoparticles of TiO_2 in the rGO surface. It seems TiO_2 nanoparticles having average size of 5-8 nm are entrapped possibly inside the rGO sheets. From the TEM, TiO_2 nanoparticles are found to be linked via graphene sheets. TEM micrograph confirms the formation of composites by solvothermal method.

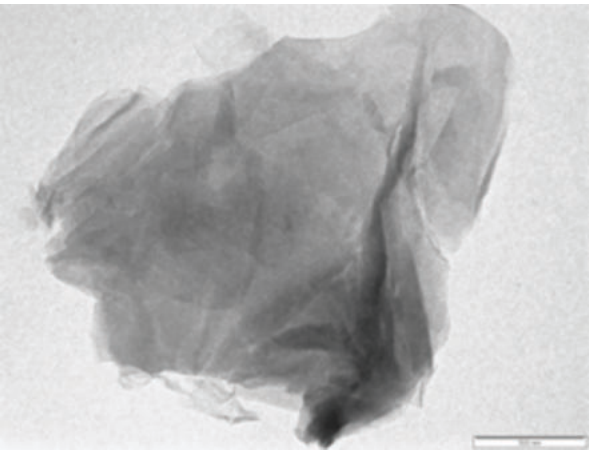

Figure.1: TEM image of rGO

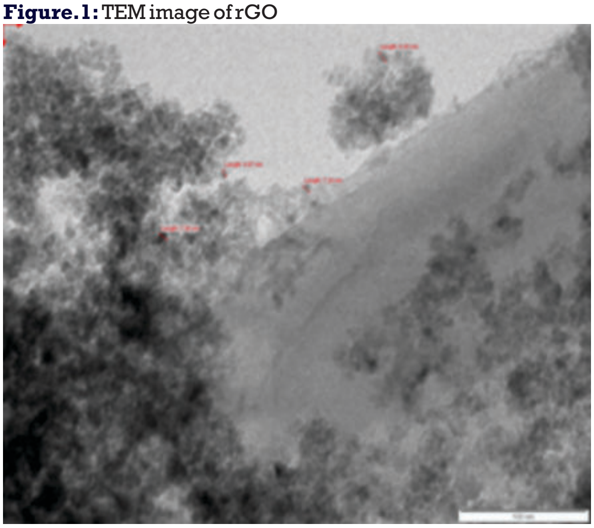

Figure.2: TEM image of rGO-TiO2 nano composite

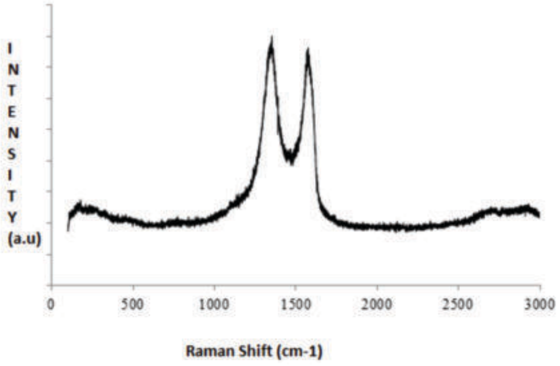

Figure.3: Raman Spectra Of rGO-TiO2 Nano Composite

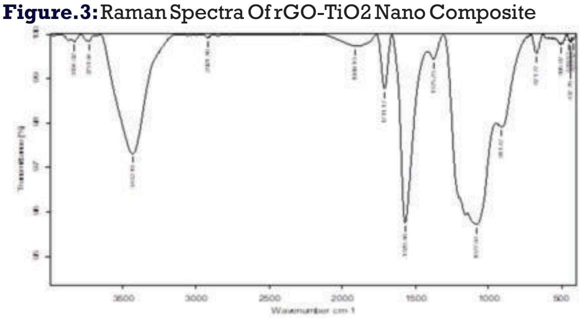

Figure.4: FTIR Spectra Of rGO

Raman spectra of the nanocomposites is presented in figure. 3. The peaks at 1345 and 1595 cm^{-1} correspond to D band and G band. The higher D/G intensity ratio indicates the formation of sp2 carbon domains of smaller average size during the solvothermal synthesis of the composites. [10].

Figure 4 represents the FTIR spectra of rGO. In graphene oxide synthesized by the modified Hummers method, epoxy and hydroxyl groups are attached to basal plane carbon atoms, while carbonyl and carboxyl groups are present in edge carbon atoms [11].

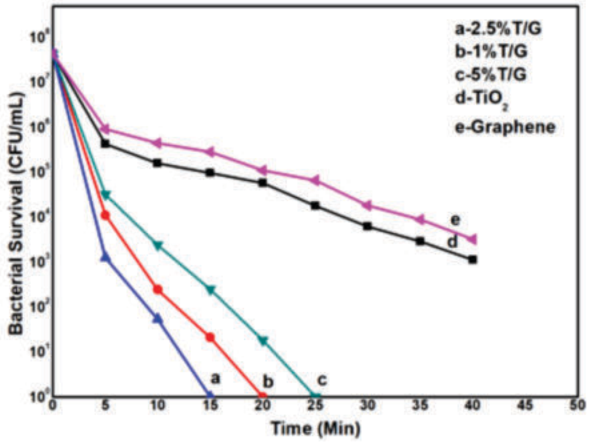

Figure.5: Photocatalytic activity of graphene-TiO2 nanocomposites under UV-Visible irradiation.

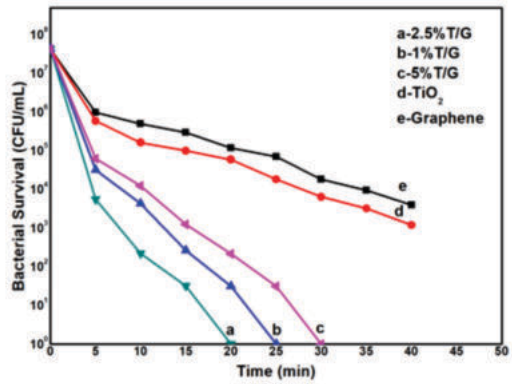

Figure.6: Photocatalytic activity of graphene-TiO2 nanocomposites under UV irradiation

The broad band from 2900 to 3300 cm^{-1} corresponds to stretching and bending vibration of hydroxyl group present in the basal plane and edge carbon atoms. The band near 1590 cm^{-1} can be assigned to C=C stretching vibrations and adsorbed water molecule in between the sheets. The band appearing at 1720– 1750 cm^{-1} is due to carbonyl groups attached at the edge of sheets. The bands at 1222 and 1051 cm^{-1} are attributed to C-OH vibration and C-O-C groups, respectively.

The photocatalytic activity of TiO_2, rGO and TiO_2/rGO (1, 2.5 and 5%) composite samples were investigated for their efficacy towards E. coli inactivation (MTCC-739), a Gram –ve bacteria in the presence of UV and UV–Visible light irradiation, the results are displayed in figure 5 and figure 6 respectively. Results revealed that the all the synthesised materials except bare TiO_2 and rGO achieved excellent bactericidal activity, as during the first 5 min of irradiation, from initial concentration all the samples able to inactivate the bacterial cell in the range of 4-5.5 log reduction, however a gradual reduction is observed with subsequent irradiation time, however the inactivation rate decreased in the later period of time. This indicates that, at the beginning, the inactivation of E. coli cells is more due to the generation of reactive oxygen species (ROS) like, OH, H_2O_2, and O_2– but with the subsequent irradiation time the rate of inactivation becomes slow as the competition for ROS between the remaining active E. coli cells and the cell materials released during photocatalysis.

Although photocatalytic inactivation on E. coli was observed for all composites under both the UV and UV–visible conditions, the maximum inactivation was observed for 2.5%TiO_2/rGO. The sample 2.5% TiO_2/rGO show 7 log (complete) reduction in 15 and 20 min under UV–Visible and UV light irradiation respectively. But, photocatalytic activity differs for each sample. Pure graphene oxide exhibits inferior activity than TiO_2. However, when graphene oxide is modified with titania, its photocatalytic effect towards inactivation of E. coli is increased compared to TiO_2. The photocatalytic activity of TiO_2 increases after coupling with G derivatives, remarkable electron conductivity is attributed so that the carbon nanomaterial provides a 2D network reservoir to accept as well as shuttle photogenerated electrons from the semiconductor, which results in the separation and prolonged lifetime of hole-electron pairs [12]. Further, GO can interact with TiO_2 via H-bonding and polar forces, while in the case of rGO, the hydrophobic interactions play a dominant role. The photocatalytic activity of GO- TiO_2 nanocomposites against E. coli was investigated, and a complete inactivation was observed at 30 min under light irradiation [13]. Akhavan and Ghaderi [14] also observed high-performance of GO/ TiO_2 thin films towards inactivation of E. coli bacteria than bare TiO_2 and GO in an aqueous solution under solar light irradiation. Under both the irradiation condition bare TiO_2 and GO does not show complete log reductions even after 45 min of irradiation from the initial concentration (107 CFU/mL). But loading of TiO_2 on GO helps to improve the activity of GO more under UV–Visible irradiation than UV. Although samples with 1% and 5% TiO_2/rGO show 7 log reductions means complete inactivation of bacteria at different irradiation time of 20 and 25 min under UV -Visible and 25 and 30 min under UV irradiation respectively, they also exhibit lower log reduction values lower under UV–Visible irradiation than UV alone. The excellent photocatalytic activity of TiO_2/rGO nanocomposites has been observed under UV -visible light irradiation than UV alone which may be due efficient separation of photogenerated electron–hole pairs since graphene can be used as an electron acceptor and transporter [12]. This confirms that more no of (ROS) like, OH, H_2O_2, and O_2– involved the photocatalytic activity to wards inactivation of E. coli. Furthermore, the photocatalytic activity decreases when the graphene content exceeds 2.5 wt% in the composite. This result can be explained as follows: a large number of graphene sheets exist in the sample of TiO_2/ 5%rGO, then the active site of TiO_2 might be shielded by other graphene sheets [15], during the photocatalytic process. Thus, the sample of 5% TiO_2/rGO possesses lower photocatalytic activity than 2.5% TiO_2/rGO and the observed result is very well correlated with the result obtained by Cao et al., as they found lower photocatalytic activity of TiO2/7% GSs than TiO_2/4.2 % GSs [16].

CONCLUSIONS

The solvothermal method of synthesis of graphene nanocomposites is one of the best methods for catalytic applications. The percentage of graphene in the nanocomposite plays an important role in the morphological as well as photocatalytic activity. In the present study the photocatalytic activity decreases when the graphene content exceeds 2.5 wt% in the composite, which is the optimum loading for the present study. The results of the present study indicate that the nano composites can be effectively used in waste water treatment method.

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