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Full Length Article

Investigation of photocatalytic performances of sulfur based reduced graphene oxide-TiO_2 nanohybrids

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ABSTRACT

Hypothesized the incorporation of direct elemental sulfur (S) into graphene-oxide (GO) via simple sonication. Initially S@GO was prepared using simple ultrasonication and evaluated its photocatalytic property. In S@GO instead of photocatalytic activity the adsorption was predominant due the amphiphilic property of GO. Later, S@GO was utilized to prepare sulfur based rGO-TiO_2 [S@rGO-TiO_2 or SRT] hybrids using solvothermal method. Herein the addition of ubiquitous sulfur has been hypothesized to improve the efficiency of photocatalyst. When S@GO subjected to solvothermal treatment, unpredicted reaction took place and it is discussed later briefly, yet this S@rGO-TiO_2 hybrid demonstrated high photocatalytic activity. Some essential characterization such as SEM, EDAX, XRD and Raman analysis were carried out and its photocatalytic performance were evaluated and compared with TiO_2 and reduced graphene-oxide-TiO_2. Our investigations will create a new pathway in futuristic development of SRT hybrids suitable for photocatalytic and waste-water treatment/remedial applications.

1. Introduction

The distressing emission of pollution due to urbanization deteriorated the water quality of river and underground water. More specifically the dye effluent has become a great menace to all living kinds from aquatic, domestic animals to human being, further the river bodies has been greatly polluted [1]. Still the affected river bodies are facing serious consequence and many who lived along the river basin lost their livelihood. Several hundred acres of agriculture land in India had been tremendously affected by the reckless discharge of untreated dye effluent [2]. Therefore the proposed study deals with the preparation of ternary nanohybrids namely sulfur(S) based reduced graphene oxide (rGO)-TiO_2 [S@rGO-TiO_2 or SRT] hybrids to combat the dye pollutant via photocatalysis. Herein, the particular attention is given to sulfur as it is a powerful disinfectant from ancient times and it itself is being a photocatalyst [3]. So it is a noncontroversial element for the introduction in order to obtain synergistic effect. Graphene oxide (GO) is an excellent two dimensional material, which is facilitating in building several nanohybrids successfully. GO is employed owing to its two-dimensional structure with exceptional surface area. Therefore initially combined S-GO. Literature reports S-GO preparation using various approaches such as chemical deposition and subsequent low temperature thermal treatment [4], Sulfur wrapped reduced graphene-oxide was prepared via one pot oxidation and reduction of sulphide & graphene-oxide and subsequent freeze casting process [5]. NaS_2 were also used as sulfur precursor to prepare S@GO via one pot hydrothermal method [6]. The wrapping of sulfur onto graphene attracted a huge interest in the field lithium sulfur battery cathodes in order to improve the electronic conductivity and limit polysulphide dissolution mainly [7]. Herein simple ultrasonication is performed to combine S and GO. Though TiO_2 is considered to be an extensively studied material yet the real competence cannot be denied [8–13]. So it was chosen as a sole material to develop photocatalyst. Many researchers successfully prepared sulfur doped TiO_2 in order to narrow down the band gap [14,15]. For instance, Wang et al. demonstrated the preparation of S-TiO_2 using TiS_2 as a precursor and achieved enhanced visible light photocatalysis [16]. As mentioned before, the addition of sulfur to GO is noncontroversial and expected to bring synergistic effect. Yet, this addition and its subsequent solvothermal treatment gave new insight for real time dye effluent treatment; it is discussed in results

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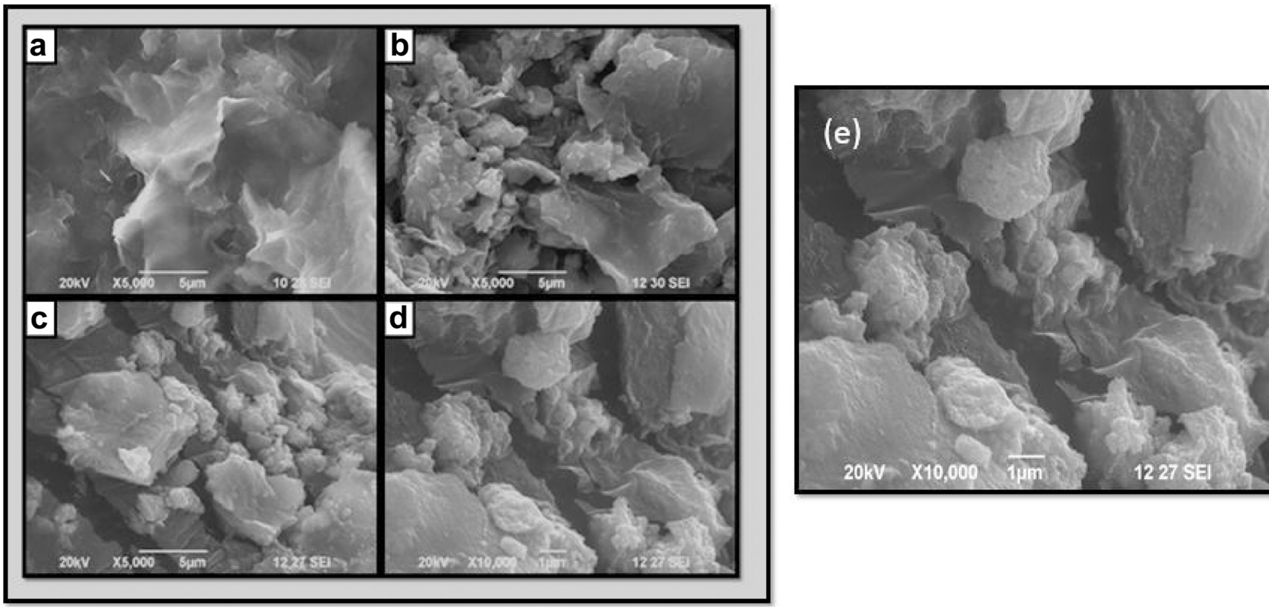

Fig. 1. SEM images of (a) GO (b) S@GO and (c & d) S@rGO-TiO_2 (e) SEM image of S@rGO-TiO_2 with the distribution of TiO_2.

and discussion section. Sulfur has the tendency to interact with carbon. When compared to oxygen, sulfur shows little tendency to form double bond with carbon and the orbital overlap of carbon and sulfur is less than carbon and oxygen. So it is a non-controversial element for the introduction. Further, the addition of ubiquitous metal-oxide TiO_2 hypothesized to improve the efficiency of photocatalyst. Some essential characterization such as SEM, EDS and XRD has been carried out and its photocatalytic performance has been evaluated and compared with TiO_2 and reduced graphene oxide-TiO_2.

2. Materials and methods

The source for sulfur is direct elemental sulfur purchased from Sigma Aldrich. Carbon sulphide (CS_2) was procured from Merck. High quality expandable graphite powder was purchased from Merck. High grade H_2O_2, H_2SO_4, $KMnO_4$ and HCl were purchased from Rankem, India. Titanium (IV) isopropoxide [TTIP] was purchased from Sigma Aldrich.

2.1. *S@GO preparation*

GO were prepared via modified hummer's method. Three ratios of S:GO (1:1, 1:2, 1: 3) were prepared, initially sulfur was dissolved in 2 ml of CS_2 solvent to make homogenous solution. To GO (2 ml/mL) exfoliated solution, CS_2 dissolved sulfur was added and sonicated for an hour. Then, dried in hot air oven around 60 °C.

2.2. *S@GO-TiO_2 preparation*

The S@rGO-TiO_2 sample was prepared using two pot method. First S@GO is prepared, later know amount of S@GO was exfoliated in 75 ml ethanol via sonication, consequently 1 ml of TTIP was added into the GO dispersed solution and sonicated for 45 min in order to attain homogenous dispersed solution. This solution was transferred to stainless steel based Teflon autoclave and kept at 180 °C for 18 h. Later the sample was washed with deionized water several times in order to remove the loosely bounded TiO_2 and it was dried at 80 °C for 12 h. Thus S@rGO-TiO_2 hybrid was prepared. Similarly rGO-TiO_2 and TiO_2 anatase powder was prepared.

2.3. *Photocatalytic studies*

Photocatalytic investigation was carried out in a closed chamber illuminated with UV light. The reaction solution was irradiated with a 300 W Xenon lamp. Measured amount (0.01 g) of photocatalyst was suspended in 100 ml of 0.3 mg/l concentrated Methylene Blue (MB) solution. Before irradiation, the suspensions were stirred in the dark for 30 min in order to establish adsorption-desorption equilibrium. Subsequently irradiated ceaselessly for 120 min, at regular time interval about 3 ml of the reaction solution was taken out. Consequently, the clear supernatant was taken into a quartz cell (path length 1.0 cm), then analyzed using UV–vis spectrometer (Model: JASCO V-60) at l_{max} = 663 nm, absorption maximum of MB.

3. Results and discussion

The morphology of GO, TiO_2-rGO and S@GO-TiO_2 was characterized by using SEM. Fig. 1 illustrates the SEM image of graphene-oxide (GO) sheet, S@GO and S@GO-TiO_2. Fig. 1b depicts S@GO; the uneven distribution of sulfur. The presence of abundant amount of oxygen containing functional group on GO surface increased the number of active site for S interaction with GO. Fig. 1(c) and (d) shows S@GO-TiO_2 sample at different magnification. The presence of micrometer size aggregates can be seen along with sheet-like morphology of rGO. Initially the aggregates were considered as sulfur enveloped TiO_2 due to chemisorptions because sulfur has strong attraction over TiO_2. Later analyzing the EDS and Raman result, surprisingly the sulfur seems to be missing in S@GO-TiO_2 hybrid system. Further, magnified image of S@GO-TiO_2 (Fig. 1e) clearly reveals that TiO_2 particles aggregated together forming clusters in the diameter of few micrometers. The rGO

Table 1
Elemental composition of S@GO and S@rGO-TiO_2.

Element	Atomic wt%	
	GO@S(1:2)	S@rGO-TiO_2
C	76.64	61.81
O	10.91	31.86
S	12.45	–
Ti	–	6.09