Materials Science in Semiconductor Processing 30 (2015) 321–329

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Enhanced photocatalytic degradation of methylene blue by reduced graphene-oxide/titanium dioxide/zinc oxide ternary nanocomposites

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ARTICLE INFO

Available online 7 November 2014

Keywords:
Photocatalytic degradation
Reduced graphene-oxide nanosheets
ZnO nanorods

ABSTRACT

In this report, an attempt has been made to prepare reduced graphene-oxide/Titanium dioxide/Zinc oxide ($rGO/TiO_2/ZnO$) ternary photocatalyst system via a facile two step solvothermal method and their results were compared with rGO/TiO_2 and TiO_2. The structural, morphological and optical properties were explored using X-Ray diffraction (XRD), Scanning electron microscope (SEM), Energy Dispersive Spectra (EDS), Raman and Photoluminescence (PL). SEM images noticeably present the 2D sheet morphology of GO, irregular spherical morphology of TiO_2 and nanorods morphology of ZnO. XRD pattern depicted the formation of TiO_2 anatase and wurtzite hexagonal structure of ZnO, which is highly desirable for photocatalysis application. Further, the results of Raman spectra are in good agreement with the XRD data. The PL spectra evidently revealed the quenching effect of electron–hole recombination process. The photocatalytic degradation of the system was investigated using a model dye methylene blue (MB). The efficiency of the ternary system was evaluated and compared using rGO/TiO_2 and TiO_2. The degradation efficiency of $rGO/TiO_2/ZnO$, rGO/TiO_2 and TiO_2 was found to be 92%, 68% and 47% within 120 min respectively. Our results will pave the way for the development of futuristic rGO based ternary nanocomposites for photocatalytic applications.

1. Introduction

Water is the most essential resource for the existence of all beings; nevertheless nowadays water pose a serious threat to all beings, from aquatic to human being. Around the globe, it has become the chief carrier of all contaminants such as carcinogenic dye [1] effluent, heavy metals [2], and Pharmaceutical waste [3] despite carrying essential natural minerals such as sodium, magnesium, calcium etc. It is mainly due to the reckless discharge of untreated industrial effluents into the water bodies. Synthetic dye production has been increased tremendously to meet the demand of textile industries. On the other hand, environmentalists are striving hard to combat the dye effluents effects. It is high time; the industrial effluents treatment has to be carried out forcibly, in order to curtail the harmful effects of pollutants in water, eventually to save the planet earth and to prevent diseases. There are several approaches to treat industrial effluents, such as Precipitation Ion–Exchange, Evaporation, Reverse osmosis, Ultrafiltration, Microfiltration, Solvent extraction [4,5]. Each approach has its own prospective and constraints. With intense literature review of each method, photocatalytic degradation technique was employed, because other methods merely transfer the industrial waste from one phase to another phase, i.e. detrimental sludge remains even after the treatment. Therefore the photocatalytic technique is undoubtedly the finest method to convert harmful organic contaminants into carbonaceous products [6].

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http://dx.doi.org/10.1016/j.mssp.2014.09.019
1369-8001/

TiO_2 is a paramount photocatalyst; it was first explored by Fujisima et al., in the year 1972 [7]; then it started to revolutionize the scientific world in the field of photocatalysis and hydrogen fuel production, owing to its simple, abundant, strong oxidizing and non-toxic nature [8,9]. Yet there are few drawbacks in TiO_2, such as recombination effect and its low photoresponse towards visible light. These two bottlenecks make it an undesirable candidate for effective photocatalysis. Therefore numerous approaches were attempted to develop a TiO_2 hybrid based photocatalyst by either doping it with rare earth metal [10], nitrogen [11], sulfur [12], etc. or by preparing nanocomposites utilizing activated carbon [13], CNT [14], graphene [15] based TiO_2 hybrid, in order to effectively degrade the dye effluents. Despite TiO_2, ZnO is a promising photocatalyst [16] and it has been widely used for photocatalytic degradation of pollutant; furthermore researchers also prepared TiO_2/ZnO binary nanocomposite in order to acquire the best from each metal oxide [17,18]. Apart from this duo, recently graphene and graphene-oxide is yet another excellent entrant in the photocatalysis field, which supports the duo in attaining effective degradation as it scavenges and shuttles electron; thus recombination issue can be minimized tremendously [15]. It is a recent incredible 2D nanosheets, which has astounding electrical [19], mechanical [20] and thermal properties [21]. Reports affirm that metal-oxide nanoparticles can be anchored on the GO sheets via the abundant oxygen-containing functional groups such as epoxy, hydroxyl, carbonyl, and carboxyl groups which are present on the GO sheets [22–28]. Further, GO itself acts as a photocatalyst by itself [29]. Recently, several ZnO/rGO [22–24] and TiO_2/rGO [25–28] systems have been reported in efforts to obtain a composite with superior photocatalytic performance, arising from the synergistic effects between the metal oxide and rGO. Therefore, the incorporation of another photocatalyst active metal oxide (ZnO) into graphene–TiO_2 composites to form ternary composites should be a promising method to design advanced photocatalyst materials for dye degradation. The rGO plays a vital role in the photocatalysis, where it inhibits the undesirable recombination effect. Recently researchers are more interested in the preparation of rGO based ternary composite, solely to deliver a synergistic effect. Ping et al., and Hem Raj et al., prepared Ag–ZnO/rGO and Ag–Ag–Br/TiO_2/rGO [30,31] respectively and found successful in their venture. Yet, Ag is the prime element in the composite; apparently it is not an economic photocatalytic ternary composite. Hence, we proposed a cost-effective rGO/TiO_2/ZnO (RGTZ) ternary system, where each material is abundant and cost-effective. Therefore, herein we attempted to prepare RGTZ nanocomposite via a simple solvothermal process in order to obtain synergistic effect towards the effective degradation of model dye, MB. Eventually the ternary nanocomposite was evaluated with bare TiO_2 (T) and rGO/TiO_2 (RGT).

2. Materials and methods

High quality expandable graphite powder was purchased from Merck. High grade H_2O_2 and HCl were purchased from Rankem, India. Titanium (IV) isopropoxide (TTIP, 98%), Zinc nitrate and Hexamethylenetetramine (HMT) were purchased from Sigma Aldrich.

2.1. Preparation of graphene-oxide

Graphene-oxide was prepared by a universal method, i.e. Modified Hummer's method [19]. Briefly, the expandable graphite powder (2 g) was stirred in 50 mL of concentrated H_2SO_4 acid for 30 min. Subsequently 6 g of $KMnO_4$ was gradually added to the solution, then stirred further and to it 90 mL of deionized water was added. Eventually 5 mL of H_2O_2 was added to the above solution. 5% HCl aqueous solution was added finally in order for washing. Later, repeated centrifugation was done using deionized water until the pH of the solution reaches neutral. Soon after, it was kept at 60 °C for overnight for drying. A homogeneous dispersion of GO nanosheets was obtained after sonication.

2.2. Preparation of rGO/TiO_2/ZnO ternary nanocomposite

Two step solvothermal approach was carried out to prepare rGO/TiO_2/ZnO. In brief, 0.5 wt% of 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 obtain homogenous dispersed solution. This solution was transferred to a 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 rGO–TiO_2 nanocomposite was prepared. Subsequently for the preparation of rGO/TiO_2/ZnO (RGTZ) ternary nanocomposite, 40 mM of zinc nitrate and HMT of equi-molar concentration was prepared, and as prepared and rGO–TiO_2(RGT) was added to the solution and stirred vigorously. Later the solution was transferred to the stainless steel based Teflon autoclave and kept at 90 °C for 5 h and dried at 80 °C overnight. Thus rGO/TiO_2/ZnO ternary nanocomposite was prepared. TiO_2 anatase powder was also prepared using the same method without the addition of GO and ZnO_2 precursor.

2.3. Characterization

The sample thus synthesized was characterized using XRD, SEM, Raman and PL spectroscopy. Powder X-ray diffraction studies were carried out using XRD instrument Shimadzu X-600 Japan, with CuKα radiation, to identify the crystalline phase and also to assess the structural integrity of sample. The XRD patterns of GO, TiO_2, RGT and RGTZ nanocomposite were obtained in the scanning range of $2\theta = 10–90°$ and with scanning speed of 10 (deg/min). SEM images were taken using JEOL 6390, Japan, whereby the samples were dispersed on a carbon tape. The Raman spectra were obtained in order to investigate the carbon based sample; it was done using HORIBA Jobin Yvon Raman spectrophotometer system. The PL spectra were obtained by using a FLUOROLOG, HORIBA Jobin Yvon spectrophotometer in order to study the transfer behavior of photogenerated electrons and holes.