

### Diamond and Related Materials

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# Sonochemically prepared bismuth doped titanium oxide\_reduced graphene oxide (Bi@TiO<sub>2</sub>-rGO) nanocomposites for effective visible light photocatalytic degradation of malachite green

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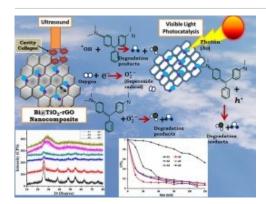
# Highlights

- Ultrasound assisted synthesis of Bi@TiO<sub>2</sub>-rGO nanocomposites with varied loading of Bi.
- Successful degradation of malachite green dye in sunlight using Bi@TiO<sub>2</sub>-rGO nanocomposites.
- Bi@TiO<sub>2</sub>-rGO nanocomposites prepared by ultrasound assisted sol-gel method showed better activity.
- Ultrasound helps to achieve uniform distribution of <u>nanoparticles</u> on the reduced GO sheet

### **Abstract**

In the present work, rGO (reduced graphene oxide) was used as a support material for the preparation of Bi@TiO<sub>2</sub>-rGO nanocomposites with uniform morphology with using ultrasound assisted process. Bi@TiO<sub>2</sub>-rGO nanocomposites samples at various loading of Bi were prepared by a facile sol-gel method assisted by ultrasound waves and their performance was compared with nanocomposites prepared by conventional stirring method. Formation of Bi and Ti based nanoparticles supported with rGO sheet was confirmed by scanning electron microscopy. The successful incorporation of rGO, Bi and Ti in Bi@TiO2-rGO nanocomposites was confirmed by XRD, Raman spectroscopy and EDAX. The XRD study showed phases corresponding to Bi, Ti and rGO and indicated the formation of crystalline Bi@TiO<sub>2</sub>-rGO nanocomposite. From the morphological analysis of nanocomposites, uniformly decorated layered morphology was observed. XRD and Raman analyses confirmed the presence of Bi, Ti and formation of rGO during preparation of Bi@TiO<sub>2</sub>-rGO nanocomposite using ultrasound assisted and conventional method. Prepared Bi@TiO<sub>2</sub>-rGO nanocomposite was applied for the degradation of malachite green dye. The photocatalytic degradation experiments were carried out in sunlight using Bi@TiO2-rGO nanocomposites prepared with varied loading of Bi using ultrasound and conventional method. At the optimum condition, degradation was found to be 93.34% in sunlight.

### Graphical abstract



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### Introduction

Treatment of waste water containing dyes is a major challenge due to bio-recalcitrant nature of the dye molecule. Photocatalysis proves to be an effective technique for degradation of such pollutants present in water. Metal oxide-based nanocomposites have proved to be effective for degradation of various dye molecules present in wastewater. In case of photocatalysis, generated active species are

responsible for the degradation. Hence the factors such as mobility and separation of charges are important in photocatalysis. Many photocatalytic reactions for the treatment of dyes are reported in literature [[1], [2], [3]]. Materials active in ultra-violet radiation or visible light are being proposed as photocatalysts. The photocatalysts active in visible light enable the efficient utilization of spectrum of the light during degradation of the pollutant. Hence there is an urgent need for exploring visible light active photocatalytic materials.

Bismuth based material is a popular choice among visible light photocatalytically active materials. Many bismuth based photocatalysts such as  $Bi_2O_3$  [4], BiOCI [5],  $BiVO_4$  [6],  $BiWO_3$  [7],  $Bi_2SbVO_7$  [8],  $Bi_2Se_3$  [9],  $BiNbO_4$  [10],  $BiMoO_6$  [11],  $Bi_{12}GeO_{20}$  [12],  $Bi_2Al_4O_9$  [13],  $Ag-C_3N_4/Bi_2OCO_3$  [14], Bi-PANI [15],  $BiPO_4$  [16],  $Bi_2O_3$  [17], BiOCI/rGO [18],  $Bi_2B_4O_9$  [19],  $Bi_2O_3/TiO_2$  [20] and many more are reported in literature for their exceptionally excellent photocatalytic performance. It is also observed that the synergistic effect of bismuth and other nanocomposite leads to efficient utilization of light energy in visible zone with full of spectrum. Solis-Casdos et al. [21] have shown preparation of  $Bi_2O_3/TiO_2$  nanocomposite material by sol-gel process. The sol-gel method has led to the formation of  $Bi_2O_3/TiO_2$  binary crystalline material and has demonstrated an excellent photocatalytic activity for the degradation of malachite green dye.

The reduced graphene oxide (rGO) is known for its excellent surface properties (e.g. higher surface area, 2D structure, higher electron mobility) related to separation of electron and hole and therefore many studies demonstrated the use of rGO as a support material in nanocomposite synthesis [[22], [23], [24], [25]]. The addition of rGO significantly improves charge carrier mobility, also reducing the re-combination of charge carriers [[26], [27], [28], [29], [30]]. Addition of rGO is also desired due to its ability to further prevent the agglomeration of nanoparticles [31,32]. So, in the present work rGO was used as a support material and was incorporated with the use of an ultrasound. Ultrasound proves to be a viable option for the synthesis of nanomaterials [33,34]. Sonication has ability to form products with uniform morphology [35,36]. Synthesis of nanomaterials with the help of ultrasound is demonstrated by many researchers [[37], [38], [39], [40], [41], [42], [43]]. For the present work, Bi, TiO<sub>2</sub> and rGO based photocatalytic material was synthesized by a facile route involving sol-gel method assisted with ultrasound. Further, Bi@TiO<sub>2</sub>-rGO nanocomposites were applied for an efficient degradation of malachite green dye in presence of sunlight.

# Section snippets

### **Materials**

The chemicals required for the synthesis of Bi@TiO<sub>2</sub>-rGO nanocomposite were sulphuric acid (98%, Research Lab Fine Chemical Industry), graphite powder (100-μm, Sd Fine-Chem Limited, India),

hydrochloric acid (35–38%, Qualigens Chemicals & Reagents), sodium nitrate (>99%, S D Fine-Chem Limited, India), potassium permanganate (>99%, Merk, India), hydrogen peroxide (30%, S D Fine-Chem Limited, India), titanium isopropoxide (98%, Avra, India), bismuth nitrate penthydrate (>99%, Merk, India)...

# UV/Vis analysis of nanocomposite

The UV–Vis absorption spectra of nanocomposites were recorded on a double beam spectrophotometer and it indicates presence of rGO. The spectra of nanocomposites prepared by ultrasound and magnetic stirring (conventional) methods are as shown in Fig. 2A and B respectively. The spectra showed one shoulder peak at around 250nm. The absorption band around 250nm indicated presence of Bi@TiO<sub>2</sub>-rGO [21] and Bi<sub>2</sub>O<sub>3</sub> [48]. The bandgap of the nanocomposites prepared by conventional and ultrasound method...

### Conclusion

In the present work, successful preparation of Bi@TiO<sub>2</sub>-rGO nanocomposites was established with and without ultrasonication. The obtained nanocomposites were characterised with UV/Vis, SEM, EDS, XRD and Raman analyses, which confirms the successful formation of Bi@TiO<sub>2</sub>-rGO nanocomposite. Anatase phase of Bi@TiO<sub>2</sub>-rGO nanocomposite is confirmed and incorporation of Bi showed visible light photocatalytic performance. Further, Bi@TiO<sub>2</sub>-rGO nanocomposite prepared with ultrasound assisted process is...

# CRediT authorship contribution statement

**Gauri A. Kallawar**: Conceptualization, Formal analysis, Investigation, Methodology, Writing - original draft. **Bharat A. Bhanvase**: Conceptualization, Supervision, Writing & editing, Project administration. **Bhaskar R. Sathe**: Writing & Editing....

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

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