**Supporting Information**

**Enhanced Sunlight-driven Photocatalysis Owing to Synergetic Effect of Gold Nanoparticles-incorporated ZnO/rGO Ternary Heterostructures**

**1. Experimental**

***1.1.******Materials Required***

Gold (III) chloride trihydrate/HAuCl4·3H2O (99.99%), sodium hydroxide/NaOH (99%), zinc acetate/ZnC4H6O4 (99.99%), sodium nitrate/NaNO3 (98%), potassium permanganate/KMnO4 (97%), sodium borohydride/NaBH4 (99%), hydrogen peroxide/H2O2 (97%), ethylene glycol (EG) 99%, and sulfuric acid/H2SO4 (99.99%) were procured from Sigma Aldrich. All mentioned chemicals and solvents were used without any treatment.

***1.2. Synthesis of Graphene***

Graphene (Gr) was synthesized by adopting a revised procedure (Parvez et al., 2014) where 200 mL of 0.5 M ammonium sulphate (NH4)2SO4 salt solution was poured into a 250 mL beaker. A graphite rod was hung at one corner in this beaker and a platinum (Pt) wire at the other corner. The Pt wire was connected with the negative terminal of the power supply and the graphite rod was connected with the positive terminal. After a gradual increment of the voltage up to 12 V, the reaction was run for 1.5 h. The particular voltage was maintained until the graphite rod got reduced by the Pt wire. After reduction of graphite rod, the blackish solution was filtered by using a vacuum filtration pump, washed with DI water and air-dried.

***1.3. Graphene Oxide Synthesis***

Graphene oxide (GO) was synthesized via modified Hummer’s method (Wang et al., 2019). In this chemical oxidation and thermal exfoliation method, a 25 mL of H2SO4 and a 2 g of NaNO3 were taken in a beaker and stirred slowly for 10 min. The beaker was placed in an ice tub to maintain the temperature of the solution. Then 0.5 g of graphite powder was added in stirring condition. After few minutes, 2 g of KMnO4 was mixed in the solution and stirred for next 2 h. Then a thick dark brown paste was visible, and in the meanwhile, the water tub was removed from the stirrer. The solution was stirred for 15 min and when the solution reached up to 50 , a 100 mL of DI water was added into the solution to maintain its temperature. In addition, a 0.68 mL of H2O2 was added dropwise in that solution. After 5 min of stirring, the beaker was removed from the stirrer and the solution was filtered as well as washed with DI water twice. The thick brown paste was then dried in atmosphere.

***1.4. Synthesis of Zinc Oxide Nanostructures***

Synthesis of zinc oxide nanostructures (ZnO NSs) was held by adopting a modified protocol (Bargardi et al., 2020) where a 13 g of ZnC4H6O4 was taken in a conical flask with the addition of 45 mL of ethylene glycol. The conical flask was placed in a mustard oil tub on the hot plate and the temperature was raised until it approached 180. At 122, the solution started bubbling. At 160, it became turbid in color. At 174, the solution gave the sign of nucleation of ZnO NSs by showing off-white color. After 30 min, the reaction was stopped and the conical flask was taken off from the mustard oil tub, it was cooled down to room temperature (RT) and washed with DI water at 6000 rpm at 25, twice.

***1.5. Gold Nanoparticles Synthesis***

Gold nanoparticles (Au NPs) were synthesized by the Turkevich procedure (Tabrizi et al., 2009), one of the most recognized ways to synthesize gold nanocrystals rapidly. In that method, 40 mL of the aqueous solution of HAuCl4·3H2O was added in a beaker and set to boil. At approximately 90, 1 mL of trisodium citrate (Na3C6H5O7) aqueous solution was added in the previous yellow-colored solution. The solution turned transparent on adding Na3C6H5O7 dropwise and then turned into black color. After few minutes, ruby color was aroused showing the sign of Au NPs. The resultant nanoparticles were centrifuged at 8000 rpm at 20 repeatedly.

4HAuCl4 + 6C6H8O7  4Au + 6C5H6O5 + 16HCl + 6CO2

***1.6. Binary Nanocomposites Synthesis***

The binary nanocomposites (BNCs) of ZnO/rGO were synthesized via a hydrothermal procedure. Firstly, 200 mg of GO was added in 150 mL of DI water and stirred for 1 h. Then, 20 mL of 70 mM zinc acetate dihydrate (Zn(CH3CO2)2·2H2O) solution was mixed into the previous mixture following a 30 min of stirring. After that, a solution of NaOH was added gradually to bend the pH to 11. The solution was stirred for next 30 min and then 400 mg of NaBH4 was added and stirred for few minutes. The mixture was shifted into an autoclave for hydrothermal treatment at 150 for 30 min. The obtained reaction solution was filtered. The sediments that remained on filter paper were washed with DI water many times. The yield was calcined at 250 for 4 h to obtain a fine powder of BNCs.

***1.7. Characterization Techniques***

The absorption spectra of all three samples were measured from 200800 nm via Epoch Biotech UV-vis absorption spectrophotometer. An X-ray diffractometer (D8 advance A25 Bruker, Germany) was employed to examine the crystalline structure through Cu-K radiation in the domain of 2080. Scanning electron microscopy (JEOL SEM Japan operated at 5 kV) was employed to characterize the surface morphology of all samples.

**2. Photocatalytic Activities**

***2.1. Photocatalysis by Pristine ZnO Nanostructures***

The results of MB photodegradation by pristine ZnO NSs are given in **Figure S1**. Since electron-hole pairs are not produced in ZnO due to its broad *Eg*, so its photocatalytic performance is limited. The merely chances of high efficiency are due to UV light which contributes only 5% in the energy spectrum (Rafique et al., 2020). ZnO NSs possess few surface imperfections and few disorders. Therefore, the slow charge transfer over grain boundaries occurs due to potential barrier lying at the interface between ZnO grain boundaries which results in the fast charge recombination (Rodwihok et al., 2019). The basic mechanism in the photocatalysis by pristine ZnO NSs is given below in the reaction equation form;

***ZnO + hν ZnO ()***(1)

***+ MB MB oxidation***(2)

***+ H2O H+ + OH\**** (3)

***OH\* + MB MB degradation*** (4)

The efficiency of pristine ZnO NSs is 87% with the rate constant (*k*) and degradation factor (*R2*) value are found to be 0.012 min-1 and 0.970, respectively. **Figure S1** is showing the recycling graphs of pristine ZnO NSs. Certainly, the photocatalytic efficiency is reduced from first recycle to third recycle, as clear from **Figure S1**.

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## Figure S1. (a) UV-vis spectra of MB with pristine ZnO NSs as photocatalysts during the degradation process under sunlight exposure and (b-d) their reusability tests for SPC activity.

***2.2. Photocatalysis by ZnO/rGO Binary Nanocomposites***

To enhance the photodegradation efficiency of pristine ZnO NSs, BNCs had been synthesized hydrothermally. The ZnO NSs wrinkled on the rGO layers are responsible to transfer the electrons from conduction band (CB) of ZnO NSs to the conductive rGO sheet under sunlight exposure. As the size of BNCs photocatalyst reduces due to the addition of rGO in ZnO NSs, the surface to volume ratio also enhances, hence resulting in the improved charge separation. The chemical reactions of this process are given below;

***ZnO/rGO ZnO/rGO***  (5)

***ZnO + ( ZnO (***(6)

***rGO + ( rGO ()***(7)

***+ ZnO(***(8)

***+ rGO (***(9)

***ZnO/rGO (h+) + (OH-) ZnO/rGO + (OH•)***(10)

***(MB) Degraded product*** (11)

BNC shows the photodegradation effectiveness more than the pristine ZnO NSs that is approximately 92% with the *k* and *R2* values as 0.016 min-1 and 0.988, respectively. **Figure S2**(a) reveals the photodegradation of MB dye while **Figure S2**(b)-(d) shows the reusability tests of BNCs in three recycles.

bnc pca

## Figure S2. (a) UV-vis spectra of MB with ZnO/rGO BNCs as photocatalysts during the degradation process under sunlight exposure and (b-d) their reusability tests for SPC activity.

In ZnO/rGO nanocomposites, CB level of ZnO is higher than the work function of rGO. So, an alternative pathway of carrier creates which prohibits charge recombination. Because of high surface imperfections, disorders and narrow *Eg*, the oxygen molecules in large number shift to rGO layer resulting in the increase in photocatalytic efficiency. Reduced *Eg* of BNCs is explained by the increment of surface charge between ZnO as well as rGO. Due to surface charge increment, the optical *Eg* shifts to higher wavelength (Rodwihok et al., 2019). The mechanism of photocatalysis by BNCs sample is depicted in **Figure S3**.

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**Figure S3.** Mechanism of sunlight-driven photocatalysis by ZnO/rGO BNCs sample.

**Table S1.** First-order kinetic constants and relative coefficients for sunlight-driven photocatalytic degradation of MB dye by pristine ZnO NSs, BNCs and TNCs nanocatalysts.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample ID | *Eg* (eV) | Photocatalytic efficiency (%) | *k* (min-1) | R2 |
| ZnO | 3.56 | 87 | 0.012 | 0.970 |
| ZnO/rGO | 3.37 | 92 | 0.016 | 0.988 |
| ZnO/rGO/Au | 3.17 | 96 | 0.019 | 0.992 |

**Reference**

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