



Photocatalytic Degradation of Methylene Blue by NiS₂-Graphene Supported TiO₂ Catalyst Composites

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Titanium dioxide mediated semiconductor, nickel sulfide (NiS₂) doped graphene photocatalysts were prepared by simple hydrothermal method for the treatment of dye contaminated aqueous solutions. The characterizations of synthesized composites were studied by X-ray diffraction, scanning electron microscope, transmission electron microscope and energy dispersive X-ray. The as-synthesized NiS₂-graphene/TiO₂ composites promptly removed methylene blue dye under visible light irradiation, exhibiting high photocatalytic efficiency. For the purpose of comparison, the photocatalytic effect of NiS₂-graphene composite was also analyzed. The photodegradation of methylene blue was evaluated by the steady decline in the concentration of the dye with increasing time. The rates of the photocatalytic reactions were analyzed giving an insight about the efficiency of each composite.

Keywords: NiS₂-graphene/TiO₂, Visible light, Photocatalytic degradation, Methylene blue, Kinetic study.

INTRODUCTION

Among various oxides semiconductor photocatalysts titanium dioxide has proven to be suitable candidate for photocatalytic activity because of its biological and chemical inertness, cost effectiveness, environmental friendliness, availability and long term stability against photo- and chemical corrosion^{1,2}. Titanium dioxide is well known and the most investigated functional material in semiconductor photocatalysis. It has been widely used in degradation of environmental pollutants in air or water, as well as selective organic transformations to fine chemicals. A growing interest in heterogeneous photocatalysis, to initiate interfacial redox reactions, has generated great interest due to its unique physico-chemical properties, caused by their nanosized dimensions and large surface/volume ratios^{3,4}. Suitable semiconductor materials have been extensively studied possessing suitable band gap energy that corresponds well with the spectrum of sunlight in recent years. This property is advantageous as this property can be further explored for the decomposition of waste organic materials. Carbon materials such as 0 D fullerene (C₆₀), 1D carbon nanotubes (CNT), 2D graphene and 3D graphite are increasingly becoming a popular choice for the formation of nanocomposites doped with semiconductor particles. Among the promising carbon materials, graphene, a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice structure, is expected to have great potential as a nanoscale building block

for developing hybrid materials due to its unique sheet morphology, ultrahigh electron conductivity and mobility⁵⁻⁷. The studies on graphene-based photocatalysts often focus on binary nanocomposites *i.e.* graphene is coupled with only another single component however, beyond dual-ingredient hybrid systems, multicomponent hybrid nanomaterials are expected to provide improved photoactivity and new insight into the development of novel 3D architecture with versatile and extraordinary properties⁸⁻¹³. In the present work, we fabricated ternary hybrids of NiS₂-graphene TiO₂ by an *in situ* strategy on the flatland of graphene and utilize them in selective oxidation importance for industrial uses¹⁴⁻¹⁶. It was found that NiS₂ and graphene nanoparticles carpet the graphene nanosheets and the photoactivity of ternary nanocomposites surpasses the binary one.

In this study, NiS₂-graphene/TiO₂ composite was investigated for its photocatalytic activity. Various characterizations of photocatalysts were studied by XRD, EDX, SEM and TEM techniques. The photocatalytic activity of as prepared samples was evaluated by degrading methylene blue under visible light and the kinetics of the photocatalytic reactions was investigated.

EXPERIMENTAL

Graphene oxide was prepared in the laboratory following the Hummer-Offeman's method in our previous works¹⁷⁻¹⁹, it

was used in the formation of the composites. Titanium (IV) oxysulfate hydrate ($\text{TiO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$) which was the source of titanium dioxide was purchased from Sigma Aldrich, Germany. Sodium sulfide pentahydrate ($\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$) was purchased from Daejung Chemicals Co. Ltd., Korea, whereas nickel(II) nitrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] was purchased from Duksan pharmaceutical Co. Ltd, Korea. Methylene blue trihydrate ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{S} \cdot 3\text{H}_2\text{O}$, 98 %) was purchased from Samchun pure chemicals Co. Ltd., Korea. All the chemicals were used without further purification and all experiments were carried out using distilled water.

Preparation of NiS_2 -graphene TiO_2 composites: The NiS_2 -graphene TiO_2 composites were prepared by using simple hydrothermal method. Table-1 lists the preparation conditions and the nomenclatures of the photocatalysts used in the present work. Firstly, defined amount of NiCl_2 was dissolved in 70 mL distilled water, then 0.1 M of $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ was added to the solution which was vigorously stirred in a magnetic churn dasher. Afterwards, 0.6 g of graphene was added to the mixture and sonicated (using 750 W, ultrasonic Processor VCX 750, Korea) for 0.5 h under 80 °C. To prepare two different molar solutions of NiS_2 -graphene TiO_2 composites, in one part 0.1 mol of $\text{TiO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ and another part 0.2 mol of $\text{TiO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ was suspended in distilled water and added to the above mixture. The resultant mixture was transferred into a 500 ml borosilicate glass beaker and was sealed with aluminium foil tightly. A thermometer was inserted in the reaction vessel in order to maintain a constant temperature of 80 °C. The solution was continuously stirred for 5 h at a stretch. After the temperature of the mixture was brought down to room temperature, the mixture was filtered using 0.7 μm Whatman filter paper and washed with distilled water. Finally, it was dried in a vacuum at 100 °C and then heat treated in heating furnace at 500 °C for 1 h. The dried catalysts were grounded in a ball mill and marked as 0.1 M NGT and 0.2 M NGT.

TABLE-1
NOMENCLATURE OF THE SAMPLES PREPARED

Preparation method	Nomenclature
1. $\text{NiCl}_2 + \text{Na}_2\text{S} \cdot 5\text{H}_2\text{O} + \text{graphene}$	NG
2. $\text{NiCl}_2 + \text{Na}_2\text{S} \cdot 5\text{H}_2\text{O} + \text{graphene} + 0.1 \text{ mol } \text{TiO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$	0.1 NGT
3. $\text{NiCl}_2 + \text{Na}_2\text{S} \cdot 5\text{H}_2\text{O} + \text{graphene} + 0.2 \text{ mol } \text{TiO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$	0.2 NGT

To identify the crystallinity of the prepared composites, XRD data using Shimadzu XD-D1 was obtained with monochromatic high intensity $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). JSM-5600 JEOL, Japan; was used to obtain SEM images of the composite surface to observe the surface state and structure of the prepared composites. Additionally, EDX analysis (attached to SEM) was studied in order to perform the elemental analysis of the desired region of the prepared NiS_2 -graphene and NiS_2 -graphene TiO_2 composites. A more detailed surface state of the nanostructures of the composite particles were characterized by TEM images using JEOL, JEM-2010, Japan.

Photocatalytic test: The decomposition experiment of $1 \times 10^{-5} \text{ M}$ aqueous solution of methylene blue was performed to analyze the photocatalytic effect of NiS_2 -graphene, 0.1 M NiS_2 -

graphene TiO_2 and 0.2 M NiS_2 -graphene TiO_2 composites. Prior to illumination, 0.05 g of powdered samples were dispersed in 100 mL of aqueous methylene blue solution using magnetic stirrer under dark ambient for 0.5 h. The first thirty minute interval were necessary to achieve adsorption/desorption equilibrium. For irradiation, a LED lamp (8 W, Fawoo, Lumidas-H) was used at a distance of 90 mm from the solution in the dark box. The suspension was irradiated with visible light as a function of irradiation time. Then samples were withdrawn regularly from the reactor at regular intervals of 0, 30, 60, 90, 120 and 150 min, respectively and the dispersed powders were removed using a centrifuge. The clean transparent solution was analyzed by UV/visible spectroscopy.

The percentage degradation of both of the dyes were also obtained by the following formula:

Percentage of dye degraded (%) = $(C_0 - C) / C_0 \times 100 \%$ (1) where, C_0 = Concentration of the dye in control after the reaction system reaches the adsorption/desorption equilibrium; C = Concentration of the dye effected by the catalyst composites at various irradiation times.

RESULTS AND DISCUSSION

The crystal phase structures of as-prepared NiS_2 -graphene TiO_2 composite photocatalysts were characterized by X-ray diffraction measurement (Fig. 1). NiS_2 -graphene being the starting foundation of the ternary hybrids like 0.1 NGT and 0.2 NGT. It was evident that the introduction of NiS_2 -graphene particles did not change the XRD pattern of TiO_2 drastically. It can be confirmed from Fig. 1. the TiO_2 in the two as prepared composites (0.1 NGT and 0.2 NGT) had anatase-phase, while the NiS_2 is predominantly cubic crystalline phase. Both samples showed crystal planes at (101), (004), (200), (105), (211) and (204) originated from the anatase TiO_2 phase (JCPDS file, No. 21-1272), while all the peaks can be indexed as a simple cubic lattice with cell constant $a = 5.678$, which is consistent with the previous results²⁰.

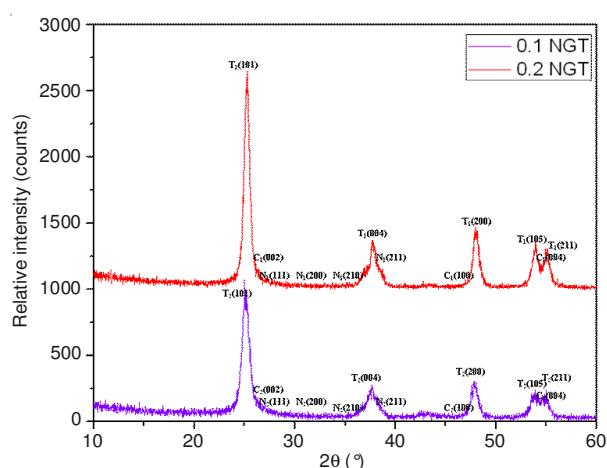


Fig. 1. XRD analysis of 0.1 mol and 0.2 mol of NiS_2 -graphene TiO_2 composites

Energy dispersive X-ray was carried out to probe composition and element weight percentage of the attached nanoparticles. Fig. 2. shows the spectrum of NiS_2 -graphene TiO_2 composites containing (a) 0.1 mol of TiO_2 (b) 0.2 mol of

TiO₂. The data of EDX analyses of the as prepared composites have been listed in Table-2. The EDX spectra showed that the primary elements present in the composites were C, O, Ni, Ti and S. 0.1 mol and 0.2 mol NiS₂-graphene/TiO₂ composites showed strong Ti peaks at 4.5 eV in both cases. As expected due to the difference in the amount of TiO₂ present, the peak intensities were little different with 0.2 mol NiS₂-graphene/TiO₂ composites having greater intensity peaks. However the graph representing the quantitative results of the weight percentages suggested that 0.2 mol NiS₂-graphene/TiO₂ had lesser C content than 0.1 mol of NiS₂-graphene/TiO₂ composites. There were some minute amounts of impurities which were attributed to the instrumental contaminations.

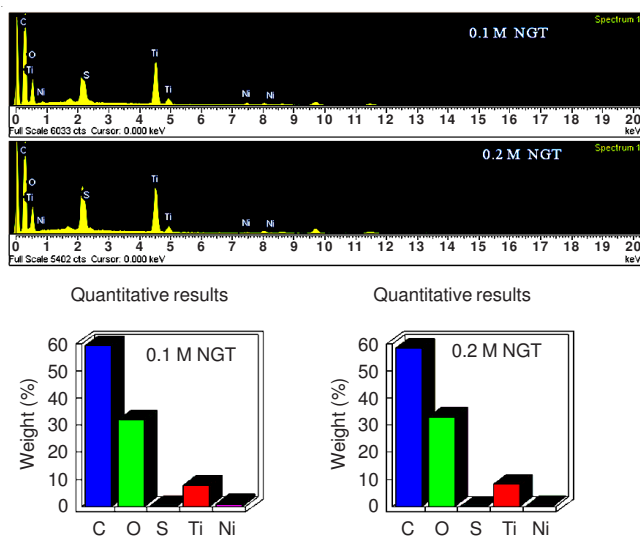


Fig. 2. EDX analysis of (a) 0.1 mol NiS₂-graphene TiO₂ and (b) 0.2 mol of NiS₂-graphene TiO₂

Samples	C	O	Se	Sn
SnSe	6.75	25.72	22.23	45.30
SnSe-graphene	37.32	35.99	3.52	23.17

Scanning electron microscopic images provide information about the micro-surface structures (Fig. 3). Non-uniform particles of NiS₂ were scattered on graphene surface as seen from the high magnification image in Fig. 3 (a). From Fig. 3 (b) and 3 (c) the uniformly formed TiO₂ were distributed unevenly on the graphene surface. The nanoscaled NiS₂ particles were found attached on the surface of TiO₂ and graphene surfaces as highly agglomerated structures formed by the hydrothermal method. The NiS₂/TiO₂ particles comprised of smooth surfaces and had a high tendency to agglomerate. This may have occurred due to the small crystal size that tends to agglomerate easily because of weak surface forces.

For obtaining highly detailed and magnified images of surface nanostructures and particle sizes of the NiS₂-graphene TiO₂ composites, TEM analysis were performed [Fig. 4(a) and (b)]. From the high magnified TEM images of Fig. 4 (a), it was observed that the NiS₂/TiO₂ particles exhibited uniform

size distribution and the spherical TiO₂ particles were of average sizes ranging from 7 to 10 nm whereas NiS₂ particles were from 2 to 5 nm. In Fig. 4 (b) the similar structures were seen of the NiS₂/TiO₂ particles but due to higher molar amount of TiO₂ the NiS₂/TiO₂ particles were more evenly spread on the graphene surface.

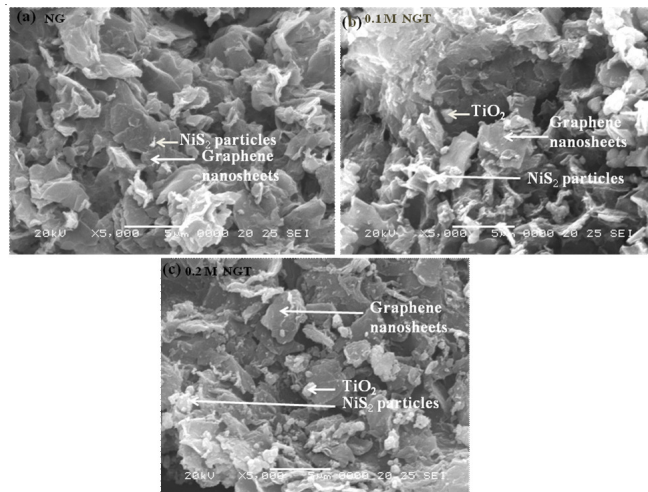


Fig. 3. SEM micrographs of (a) NiS₂-graphene (b) 0.1 mol of NiS₂-graphene TiO₂ and (c) 0.2 mol of NiS₂-graphene TiO₂ composites

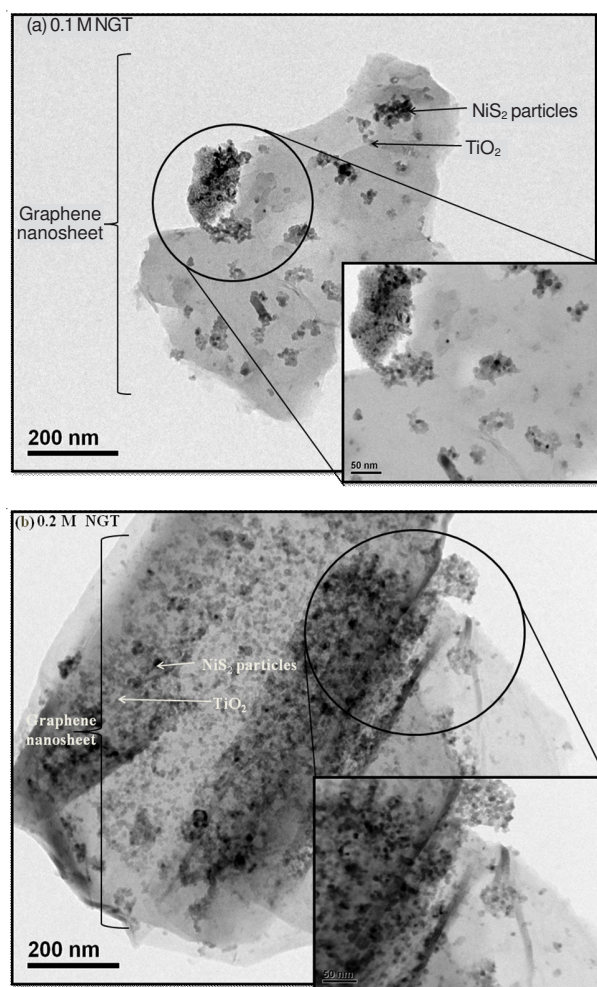


Fig. 4. TEM micrographs of (a) 0.1 mol of NiS₂-graphene TiO₂ and (b) 0.2 mol of NiS₂-graphene TiO₂ composites

Photocatalytic degradation of methylene blue solution:

The visible-light photocatalytic activity of the as-prepared composites photocatalysts were studied *via* mineralization of an aqueous methylene blue. The spectra of the dye solutions showed the relative degradation yields at different time intervals. The decreasing concentration of methylene blue in the photocatalytic reaction was used to evaluate the activity of NiS₂-graphene TiO₂ composites. As the dye solution increasingly lost its colour intensity, the dye concentration continued to decrease. Fig 5(a) and (b) represent the degradation of methylene blue in presence of NiS₂-graphene TiO₂ nanocomposites in visible light from which it was clear that the concentration of methylene blue gradually diminished with increasing time for all of samples. Moreover, the alterations that can be obtained by different molar amounts of TiO₂ in the ternary composites were analyzed by preparing different NGT composites with different molar amounts of TiO₂, *i.e.* 0.1 NGT and 0.2 NGT. However, in this study, the photocatalytic activity of under visible light was improved by the introduction of NiS₂-graphene nanoparticles. In order to demonstrate the positive effect of NiS₂-graphene nanoparticles on TiO₂, their influence was investigated on methylene blue. The decrease in concentration was evaluated at the λ_{\max} value of the dye which were determined from the absorption spectra of the dye. The λ_{\max} value of methylene blue was found to be 665 nm. In case of 0.1 M NGT, 35.4 % of methylene blue was degraded after 150 min and 45.8 % of methylene blue was degraded with

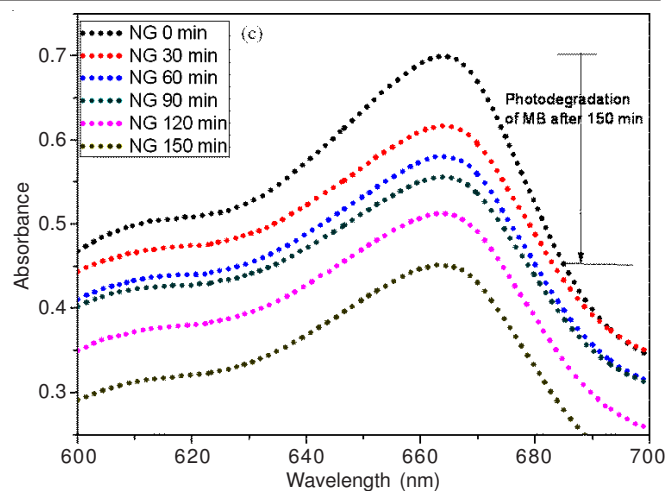
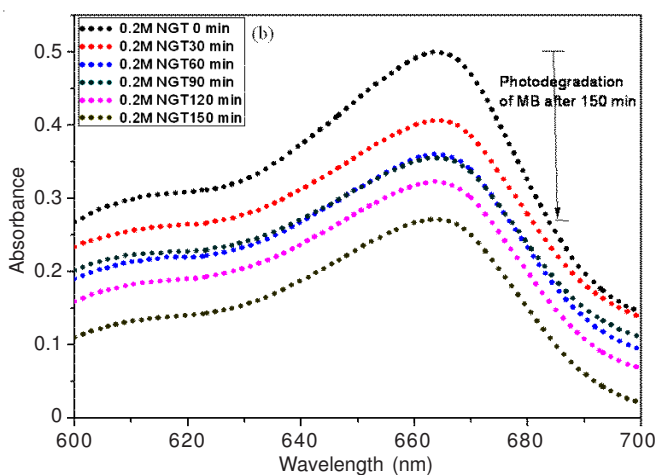
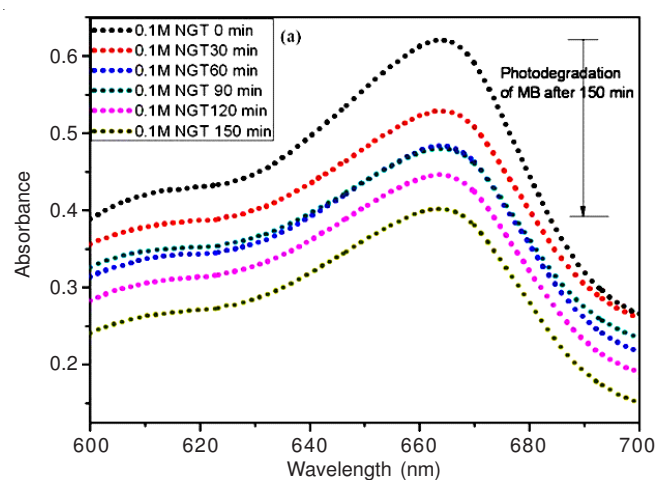


Fig. 5. Degradation of methylene blue by (a) 0.1 mol of NiS₂-graphene TiO₂ (b) 0.2 mol of NiS₂-graphene TiO₂ and (c) NiS₂-graphene composites

0.2 M NGT from the original concentration of the dye (Fig. 6). Additionally 36 % of methylene blue was degraded by NiS₂-graphene composites that proved that it itself has photocatalytic action that can definitely prove to have synergistic effect on TiO₂.

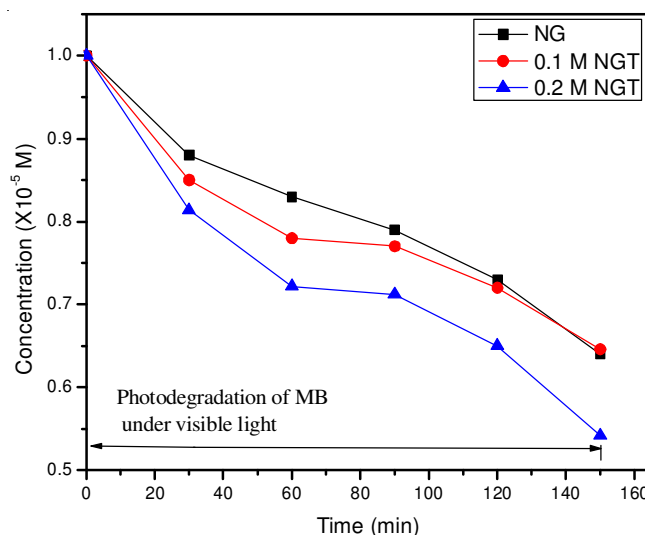
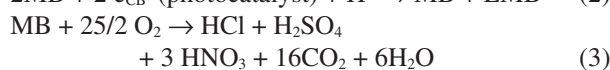
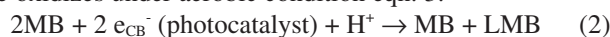


Fig. 6. Dependence of methylene blue concentration on 0.1 mol of NiS₂-graphene TiO₂, 0.2 mol of NiS₂-graphene TiO₂ and NiS₂-graphene composites

Methylene blue was photodegraded by cleavage and demethylation that caused the decoloration of the dye solution. According to previous reports²¹ methylene blue suspended in photocatalyst irradiated with visible light reacts with photogenerated electron (e_{CB}^-) to produce leuco form of methylene blue (LMB) under anaerobic condition eqn. 2, while methylene blue oxidizes under aerobic condition eqn. 3.



Moreover, Zhang *et al.*²¹ suggested that leuco form of methylene blue was generated in the low concentration of dissolved oxygen while the demethylation occurred due to the oxidation of methylene blue with free radicals produced by photocatalysts under aerobic conditions.

Considering their compositions, the improvement in the photocatalytic activity of ternary NiS₂-graphene TiO₂ hybrid should be ascribed to the introduction of the third component TiO₂. Fig. 7 represents the scheme of charge transfer process between NiS₂-graphene and TiO₂ particles for enhancing the photocatalytic performance of the ternary hybrids. From previous reports²², the introduction of graphene into the matrix of a suitable semiconductor material (in this case NiS₂) could possibly lead to a band gap narrowing of the semiconductor material because of the chemical bonding between semiconductor particles and graphene. In this case, the introduction of the third component TiO₂, the same phenomenon is observed. When NiS₂-graphene was illuminated with visible light the semiconductor (metal sulfide) produced electrons (e⁻) and holes (h⁺) that gained enough energy or momentum to jump the forbidden gap or energy barrier denoted as (E_g). The electrons (e⁻) travels from the valence band (VB) to the conduction band (CB), producing increased number of electrons (e⁻) in the conduction band and holes (h⁺) in the valence band. Thus, a number of electrons (e⁻) and holes (h⁺) were generated in NiS₂. Meanwhile, electrons got transferred from conduction band of NiS₂ into graphene and TiO₂ when they were in contact. Graphene attached to the semiconductor material (NiS₂) assisted in the smooth transition transferring electrons (e⁻) to the conduction band of NiS₂, thereby increasing the number of electrons as well as the rate of electron-induced redox reactions. The accumulation of electrons inevitably causes shifting in the apparent Fermi level to achieve equilibrium. The graphene coupled NiS₂ system had enhanced photocatalytic activity of TiO₂ mainly because of the high charge separation induced by the synergistic effects of graphene on NiS₂. The generated electrons (e⁻) react with dissolved oxygen molecules and produce oxygen peroxide radicals O₂^{•-}. The positive charge hole (h⁺) can react with OH⁻ derived from H₂O to form hydroxyl radicals OH[•]. The methylene blue molecules then can be photocatalytically degraded by oxygen peroxide radicals O₂^{•-} and hydroxyl radicals OH[•] to CO₂, H₂O and other mineralization products. The reactions involved in the charge mobility and mineralization of the dyes are as follows:

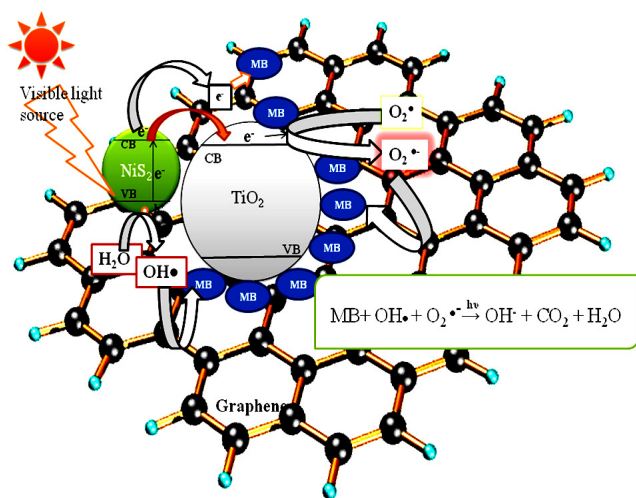
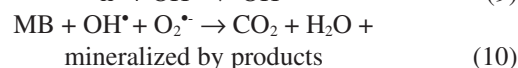
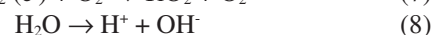
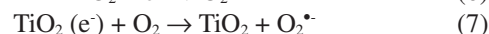
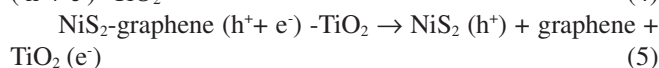
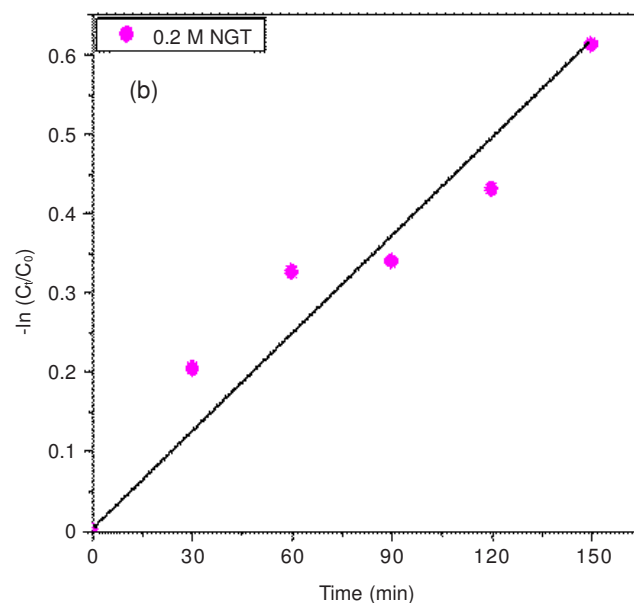
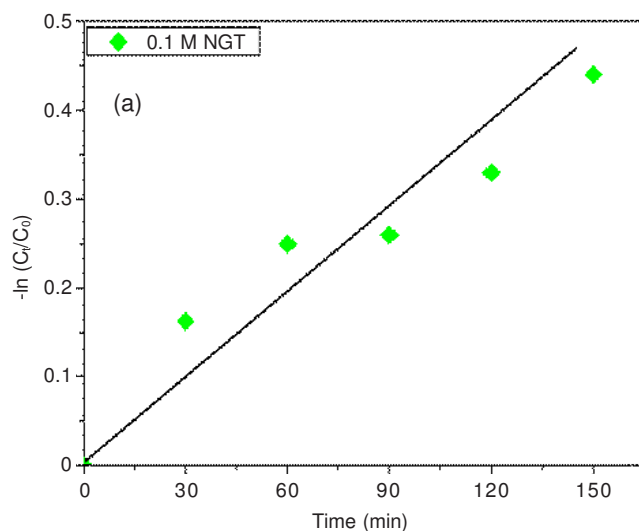


Fig. 7. Schematic representation of excitation and charge transfer process between NiS₂-graphene and TiO₂ composites



Kinetic study of photocatalytic reaction: The graphical lines of $-\ln(C/C_0)$ vs. t at 0-150 min under visible light irradiation time were plotted which can be approximated as straight lines as shown in Fig 8. The kinetic studies were performed on the basis of the rate of disappearance of the dye. The catalytic reactions with as-prepared samples could be expressed by Langmuir-Hinshelwood model. Fig. 8 implies that the photocatalytic degradation of methylene blue followed the pseudo-first order kinetics expressed as:

$$-dC/dt = k_{app}C \quad (11)$$



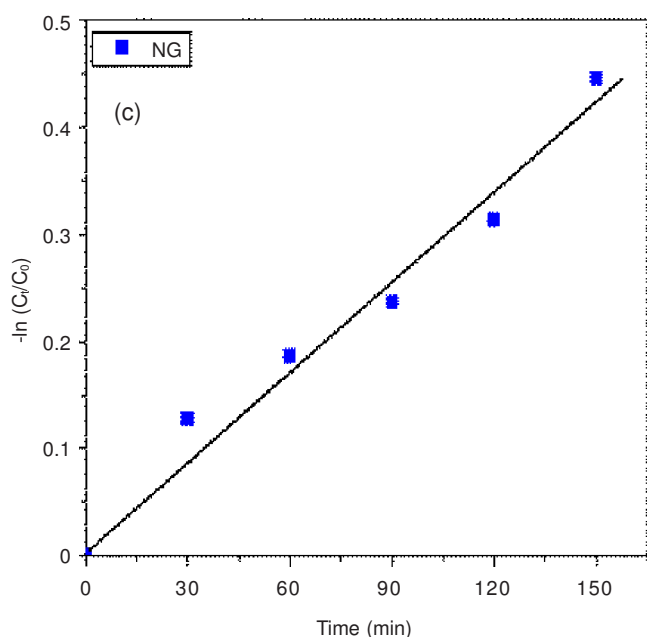


Fig. 8. Apparent first order kinetics of methylene blue degradation in presence of (a) 0.1 mol of NiS₂-graphene TiO₂ (b) 0.2 mol of NiS₂-graphene TiO₂ and (c) NiS₂-graphene composites

Integration of this above equation (with the restriction of $C = C_0$ at $t = 0$, with C_0 being the initial concentration in the bulk solution after dark adsorption and t is the reaction time) will lead to the following expected relation:

$$-\ln (C_t/C_0) = k_{app}t \quad (12)$$

where C_t and C_0 are the reactant concentrations at times $t = t$, respectively and k_{app} and t are the apparent reaction rate constant and time, respectively. So from the graphical plot in Fig. 8, the slope of the linear lines should be equal to apparent first order rate constant (k_{app}). The regression coefficient R^2 and k_{app} values of rate of photocatalytic degradation of methylene blue are listed in Table-3. The methylene blue degradation rate constant for NiS₂-graphene composites with visible light irradiation reached $2.0 \times 10^{-3} \text{ min}^{-1}$. The methylene blue was degraded by the same rate as that of 0.1 NGT. However the rate of degradation of methylene blue using 0.2 NGT was higher than 0.1 NGT and NiS₂-graphene, approximately

Experimental Condition	k_{app} (min ⁻¹)	R^2
0.1 M NiS-graphene TiO ₂ + MB	2.0×10^{-3}	0.936
0.2 M NiS-graphene TiO ₂ + MB	3.0×10^{-3}	0.940
NiS-graphene + MB	2.0×10^{-3}	0.973

$3.0 \times 10^{-3} \text{ min}^{-1}$. The above results suggested 0.2 NGT was the most effective photocatalyst. The excellent photocatalytic activity could be attributed to the synergistic effects of high charge mobility of electrons in the NGT composites.

Conclusion

In this study, we presented the preparation of 0.1 NGT and 0.2 NGT composite photocatalysts synthesized via the facile hydrothermal method. The XRD patterns for the NiS₂-graphene TiO₂ composites showed that the composites contained a typical single and clear anatase phase and a cubic NiS₂ phase. The surface properties were characterized by SEM and the favorable morphology of the 0.1 NGT and 0.2 NGT composites were investigated by the TEM technique. The photocatalytic results showed that the improved degradation rate of methylene blue solution should be considered as a result of the introduction of NiS₂-graphene, which caused shift to visible light region.

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