

Preparation of NiS₂-Graphene Nanocomposites and Photocatalytic Degradation of Organic Dyes

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Nickel disulfide nanoparticles were prepared by nickel(II) chloride hexahydrate and sodium thiosulfate pentahydrate under microwave irradiation. The NiS₂-graphene nanocomposites were calcined in an electric furnace at 700 °C under an argon atmosphere for 2 h. The crystallinity, morphology and optical properties of the NiS₂-graphene nanocomposites were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and UV-visible spectrophotometry. The photocatalytic activity of the NiS₂-graphene nanocomposites in the degradation of organic dyes, such as methylene blue, methyl orange, rhodamine B and brilliant green under ultraviolet light at 254 nm was confirmed by UV-visible spectrophotometry.

Keywords: Nickel disulfide nanoparticles, NiS₂-graphene nanocomposites, Photocatalytic activity, Organic dyes.

INTRODUCTION

Because of their magnetic, optical and catalytic properties, transition metal chalcogenide nanomaterials have attracted considerable attention¹⁻³. Copper disulfide, iron disulfide and nickel disulfide are transition metal disulfides that have been studied widely⁴. In a range of fields, such as photoactive materials, magnetic materials, solid-state lubricants and hydrodesulfurization catalysts, these disulfides have drawn substantial interest^{5,6}. Nickel disulfide (NiS₂) is found in the two main phases, the cubic phase and the triclinic phase⁷. Cubic pyrite NiS₂ has significant electronic and magnetic characteristics⁸. Solid-state reactions, wet chemical thermal techniques and chemical vapor deposition are some of methods for the synthesis of nanoscale nickel disulfide particles have been reported^{6,9-12}. The applications of microwave irradiation in the synthesis of nanoparticles have also been reported¹³. One of the better methods for nanoscale synthesis is the microwave-assisted hydrothermal technique¹⁴. This method has several advantages, such as a higher reaction rate, rapid volumetric heating and energy savings¹⁵⁻¹⁷. Because of these advantages, many studies have used microwave heating for a range of applications in chemistry¹⁸⁻²⁰.

The atom layer planar structure with a honeycomb shape comprised of *sp*²-hybridization bonded carbon atoms is graphene, an allotrope of carbon, with the *sp*² hybridized carbon bonds consisting of in-plane σ bonds and out-of-plane π bonds^{21,22}. The π bonds affect both the electronic conduction in graphene and the weak interaction between graphene and the substrate²³.

Graphene has been favored because of its superior strength, electrical and thermal conductivity²⁴. Moreover, its novel significant properties have drawn considerable attention in both fundamental studies and practical technology applications²⁵.

Discharged wastes containing dyes from various industries and laboratories are toxic to microorganisms, aquatic life and humans²⁶. Therefore, an effective and economical treatment of these organic dyes is an important issue in many developed countries²⁷. Photocatalysis technology is an effective technique for the decomposition of organic compounds from industrial and domestic wastewater²⁸. In addition, it is a cost-effective, highly stable, nontoxic and environmentally-friendly treatment technology²⁹.

This paper reports the preparation of nickel disulfide nanoparticles and NiS₂-graphene nanocomposites. The NiS₂-graphene nanocomposites were heated in an electric furnace³⁰. The photocatalytic effects of nickel disulfide nanoparticles and NiS₂-graphene nanocomposites on the photocatalytic degradation of organic dyes, such as methylene blue, methyl orange, rhodamine B and brilliant green, were examined under ultraviolet light at 254 nm using a UV-visible spectrophotometer.

EXPERIMENTAL

NiCl₂·6H₂O was purchased from Daejung Chemicals & Metals. Na₂S₂O₃·5H₂O was purchased from Shinyo Pure Chemicals. Organic dyes, such as methylene blue (MB), methyl orange (MO), rhodamine B (RhB) and brilliant green (BG), were purchased from Sigma-Aldrich. Ethanol and tetrahydrofuran

(THF) were obtained from Samchun Chemicals. Graphene was supplied by ENano Tec.

The samples were heat treated in an electric furnace (Ajeon Heating Industry Co., Ltd). The structure of all samples was characterized by X-ray diffraction (XRD, Bruker, D8 Advance). The morphology and size of all the samples were examined by transmission electron microscopy (TEM, JEOL Ltd, JEM-2010) at an acceleration voltage of 200 kV. The surface of all samples was examined by scanning electron microscopy (SEM, JEOL Ltd, JSM-6510) at an acceleration voltage of 0.5 to 30 kV. Microwave irradiation was performed by continuous heating at the maximum power in a domestic oven (2450 MHz, 700 W). UV-visible spectroscopy of the all samples was performed using an UV-visible spectrophotometer (Shimadzu, UV-1601 PC). The UV-visible spectra of all samples were obtained using an UV-visible spectrophotometer (Shimadzu, UV-1601 PC).

Preparation of NiS₂ nanoparticles under microwave irradiation: NiCl₂·6H₂O (0.95 g, 4 mmol) and Na₂S₂O₃·5H₂O (1.99 g, 8 mmol) were dissolved in 100 mL of deionized water to prepare a 0.04 M NiCl₂ and 0.08 M Na₂S₂O₃ solution. The mixture solution was stirred vigorously for 10 min. The beaker containing the mixture solution was reacted under microwave irradiation for 10 min. After the reaction was complete, the black precipitate was washed several times with ethanol and dried at room temperature.

Preparation of the NiS₂-graphene nanocomposites for testing photocatalytic degradation: To attain the NiS₂-graphene nanocomposites, the synthesized NiS₂ nanoparticles were placed separately in a vessel and heated to 700 °C in an electric furnace under an argon gas atmosphere for 2 h. Subsequently, the sample was cooled to room temperature under an argon atmosphere for 5 h.

To attain the NiS₂-graphene nanocomposites, 20 mg of synthesized NiS₂ nanoparticles and 20 mg of graphene were dissolved separately in 10 mL of tetrahydrofuran. The two solutions were mixed and stirred vigorously for 0.5 h. The mixture of solution was poured into a vessel and dried for 1 h to vaporize the organic solvent. The vessel was heated in an electric furnace to 700 °C under an argon atmosphere for 2 h. Subsequently, the sample was cooled to room temperature under an argon atmosphere for 5 h.

Evaluation of photocatalytic degradation of organic dyes with nanomaterials: The synthesized NiS₂ nanoparticles and NiS₂-graphene nanocomposites were used as a photocatalyst to test the degradation of the organic dyes, such as methylene blue, methyl orange, rhodamine B and brilliant green. 5 mg of each of the synthesized NiS₂ nanoparticles and the NiS₂-graphene nanocomposites were placed separately in a vial containing 10 mL of the aqueous organic dye solution. Each vial was irradiated with 254 nm light using an UV-lamp. The organic dyes degraded by the photocatalysts were analyzed by UV-visible spectrophotometry.

RESULTS AND DISCUSSION

The synthesized NiS₂ nanoparticles were dispersed in distilled ethanol to determine the peak value of the NiS₂ nanoparticles. Fig. 1 shows the optical properties of NiS₂

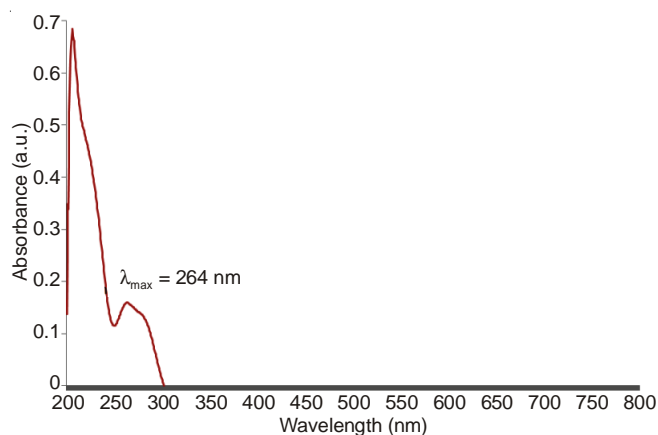


Fig. 1. UV-visible spectrum of the synthesized NiS₂ nanoparticles

nanoparticles synthesized using the microwave method at $\lambda_{\text{max}} = 264$ nm.

The crystal structure of the synthesized NiS₂ nanoparticles was examined by XRD using CuK α ($\lambda = 1.5406$ Å) radiation. Fig. 2 shows the XRD patterns of the (a) synthesized NiS₂ nanoparticles and (b) NiS₂-graphene nanocomposites. The distinctive peaks of the synthesized NiS₂ nanoparticles were observed at 27.35, 31.68, 35.28, 38.59, 45.42, 53.38, 56.43, 59.43, 61.89 and 72.92° 2 θ , which were assigned to the (111), (200), (210), (211), (220), (311), (222), (023), (321), (331) planes, respectively. The characteristic peaks of the NiS₂-graphene nanocomposites were observed at 31.76, 37.72, 45.46, 54.52, 56.22, 59.13 and 72.58° 2 θ due to the NiS₂

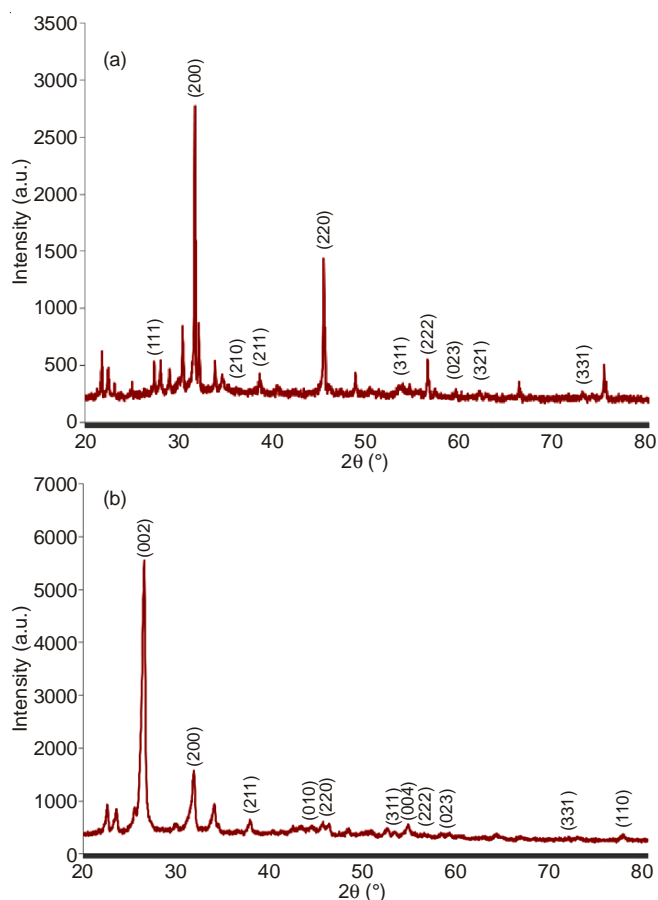


Fig. 2. XRD patterns of the (a) synthesized NiS₂ nanoparticles and (b) NiS₂-graphene nanocomposites

nanoparticles and 26.46 , 44.36 , 55.25 and 77.37° 2θ due to graphene.

TEM images of the (a) synthesized NiS_2 nanoparticles and (b) NiS_2 -graphene nanocomposites are shown in Fig. 3. The synthesized NiS_2 nanoparticles had a quasi-spherical shape that appeared to agglomerate. The mean size of the synthesized NiS_2 nanoparticles was observed to 70 nm. The NiS_2 nanoparticles in Fig. 3b were located above the graphene nanoparticles. A comparison of the two figures showed that after heat treatment, the NiS_2 nanoparticles in the NiS_2 -graphene nanocomposites were broken into smaller parts.

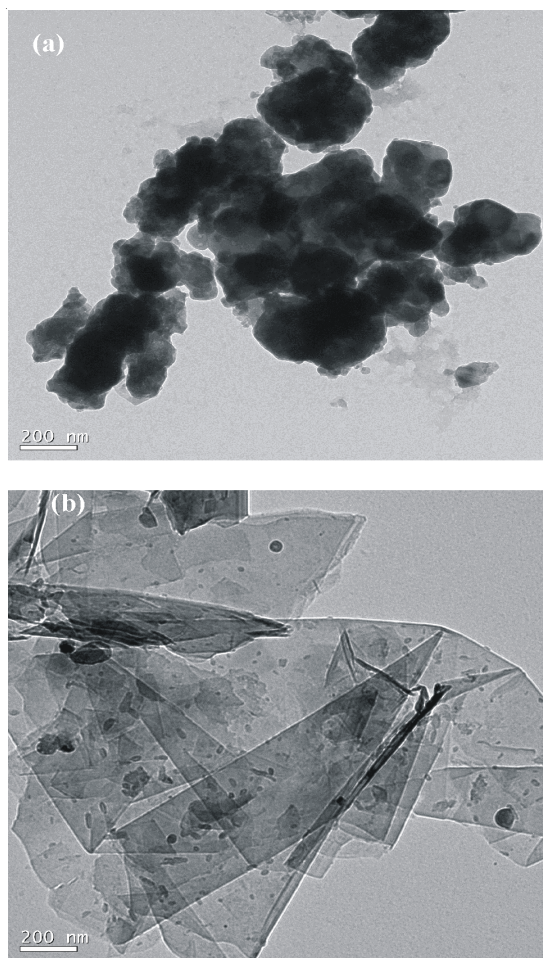


Fig. 3. TEM images of the (a) synthesized NiS_2 nanoparticles and (b) NiS_2 -graphene nanocomposites

SEM images of the (a) synthesized NiS_2 nanoparticles and (b) NiS_2 -graphene nanocomposites are shown in Fig. 4. The SEM image of the synthesized NiS_2 nanoparticles showed a triangular shape with fine agglomerates. A comparison of the two shapes revealed that the NiS_2 nanoparticles in the NiS_2 -graphene nanocomposites to be more collapsed than the synthesized NiS_2 nanoparticles. As a consequence of heat treatment, the NiS_2 nanoparticles in the NiS_2 -graphene nanocomposites were smaller than the synthesized NiS_2 nanoparticles and the surface area was larger.

Fig. 5 presents UV-visible spectra showing the degradation of (a) methylene blue, (b) methyl orange, (c) rhodamine B and (d) brilliant green with the synthesized NiS_2 nanoparticles under ultraviolet irradiation at 254 nm for 5 min. The photo-

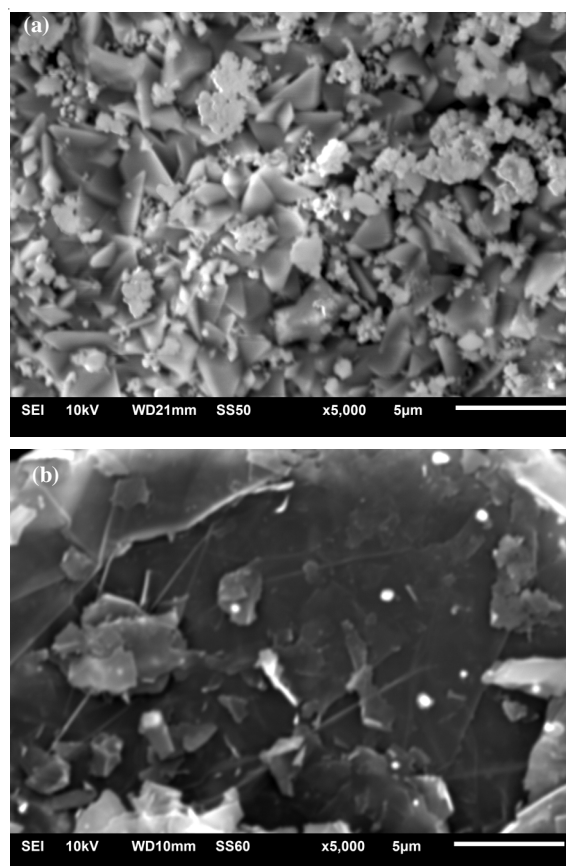


Fig. 4. SEM images of the (a) synthesized NiS_2 nanoparticles and (b) NiS_2 -graphene nanocomposites

catalytic performance of the synthesized NiS_2 nanoparticles was superior for methylene blue than for rhodamine B, brilliant green and methyl orange. The order of effectiveness among the organic dyes degraded was methylene blue > rhodamine B > brilliant green > methyl orange.

Fig. 6 shows the UV-vis spectra of the degradation of (a) methylene blue, (b) methyl orange, (c) rhodamine B and (d) brilliant green using the NiS_2 -graphene nanocomposites under ultraviolet irradiation at 254 nm for 1 min. The addition of graphene nanoparticles had a significant effect on the degradation of organic dyes, such as methylene blue, methyl orange, rhodamine B and brilliant green as a photocatalyst. The addition of graphene nanoparticles to the matrix of suitable semiconductor materials (NiS_2) can lead to a smaller band gap due to chemical bonding between the semiconductor nanoparticles and graphene³¹. The photocatalytic effect was greater in methylene blue than in rhodamine B, brilliant green and methyl orange as shown in Fig. 6. The order of effectiveness among the organic dyes degraded was methylene blue > rhodamine B > brilliant green > methyl orange.

Conclusion

Nickel disulfide nanoparticles were synthesized using a microwave irradiation technique. Using an electric furnace at 700°C under an argon atmosphere for 2 h, the NiS_2 -graphene nanocomposites were prepared. The NiS_2 nanoparticles and NiS_2 -graphene nanocomposites were synthesized for use as a photocatalyst for the degradation of methylene blue, methyl orange, rhodamine B and brilliant green under UV-light at

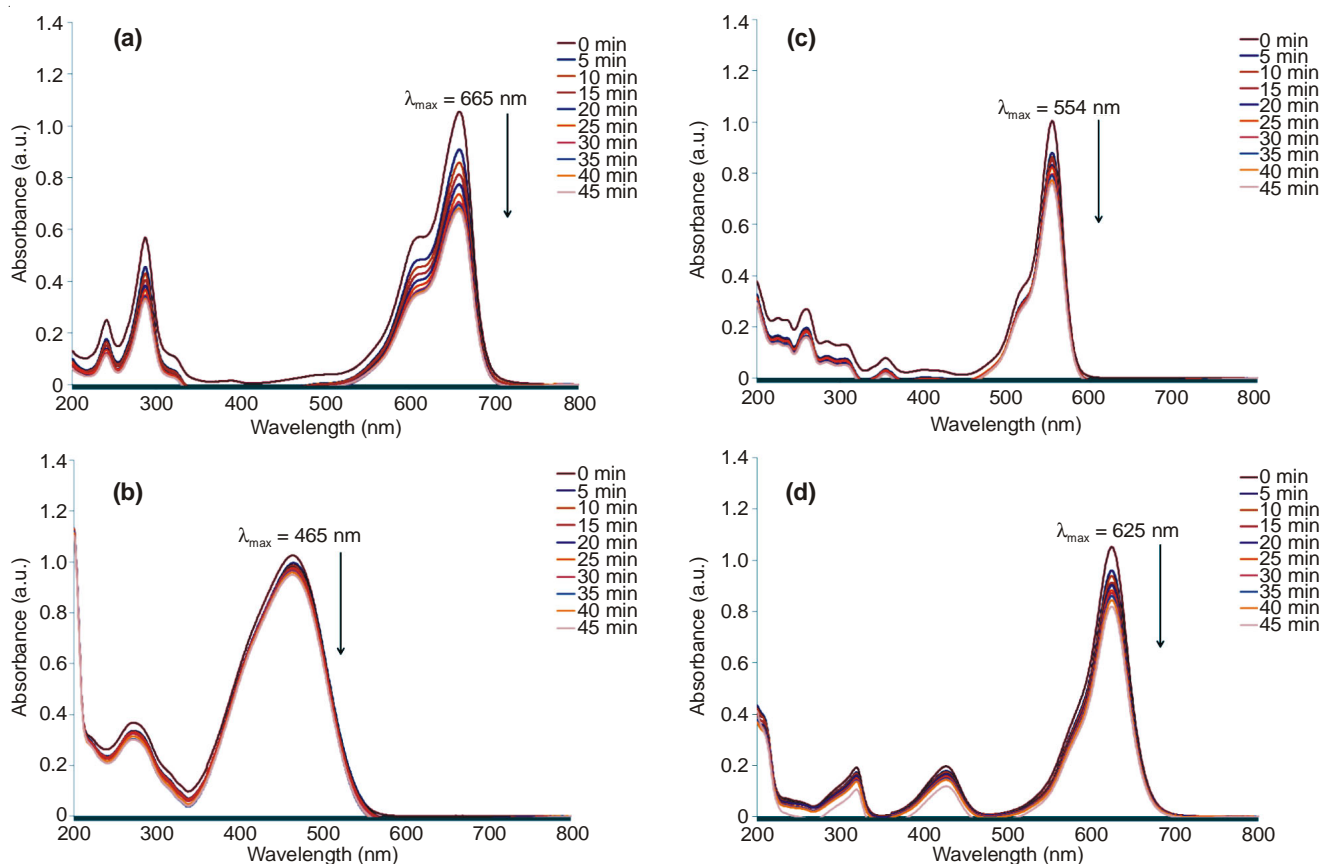


Fig. 5. UV-visible spectra of the degradation of (a) methylene blue, (b) methyl orange, (c) rhodamine B and (d) brilliant green with the NiS₂ nanoparticles

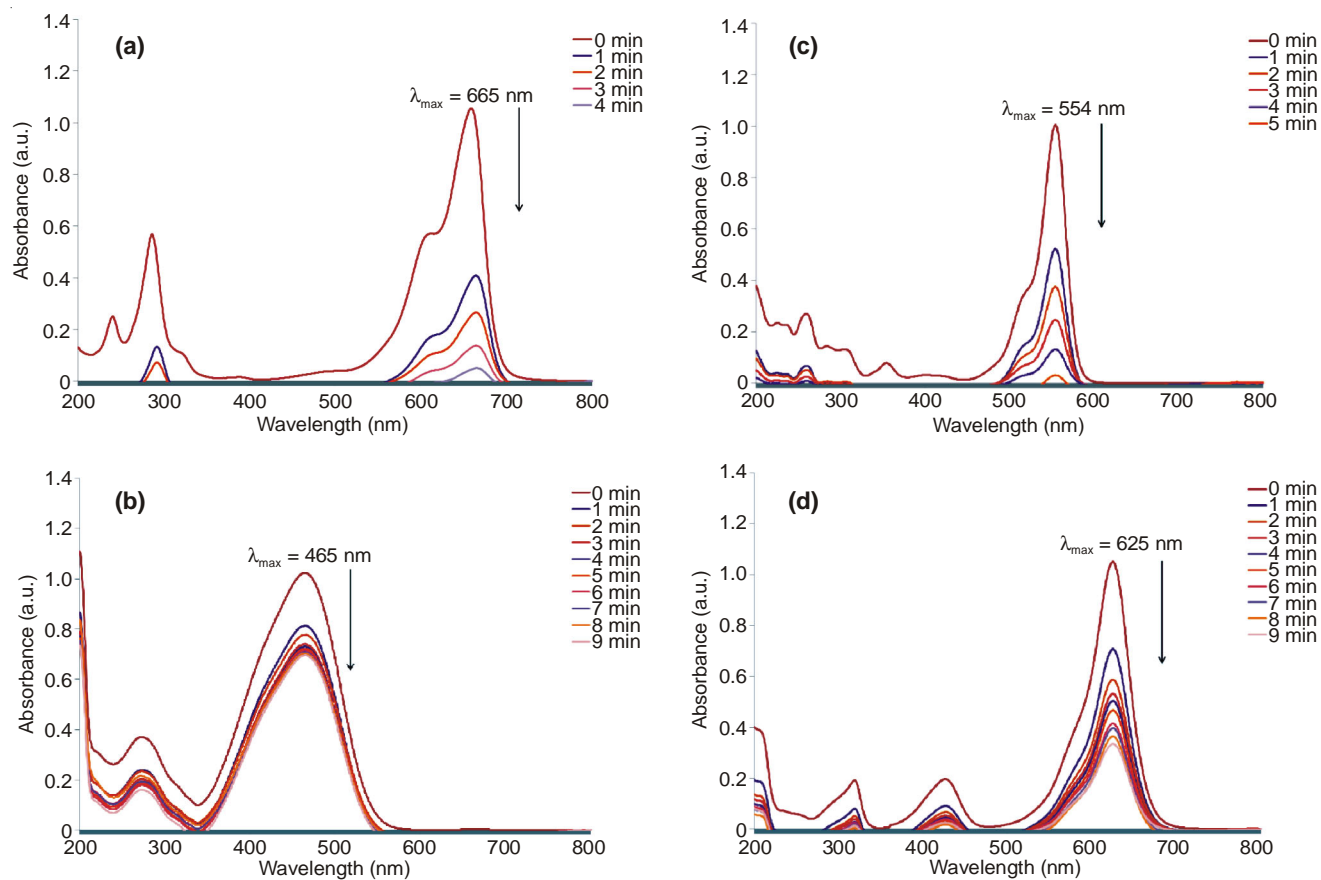


Fig. 6. UV-visible spectra of the degradation of (a) methylene blue, (b) methyl orange, (c) rhodamine B and (d) brilliant green with the NiS₂-graphene nanocomposites

254 nm. The addition of graphene nanoparticles had a significant effect on the photocatalytic degradation of methylene blue, methyl orange, rhodamine B and brilliant green. In addition, heat treatment was found to be effective in producing a photocatalyst for the degradation of organic dyes. After heat treatment, the particle size of the NiS₂ nanoparticles was smaller. The synthesized NiS₂ nanoparticles were more agglomerated than the NiS₂ nanoparticles in the NiS₂-graphene nanocomposites. The NiS₂ nanoparticles in the NiS₂-graphene nanocomposites had a separated quasi-spherical shape with less agglomeration compared to the synthesized NiS₂ nanoparticles. Among the organic dyes, such as methylene blue, methyl orange, rhodamine B and brilliant green, the degradation of methylene blue was most effective using the NiS₂-graphene nanocomposites as a photocatalyst under ultraviolet light at 254 nm.

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