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Preparation of C_{60} Nanowhisker-Nb_2O_5 Nanocomposites and Kinetics Study of Photocatalytic Degradation of Organic Dyes

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The C_{60} nanowhiskers prepared by the liquid-liquid interfacial precipitation method were characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, UV-visible spectrophotometry and Raman spectrophotometry. Niobium pentoxide nanoparticles were prepared using niobium(V) chloride as a precursor and pluronic F108NF as a templating agent. The C_{60} nanowhisker-Nb_2O_5 nanocomposites were heated in an electric furnace at 700 °C under an inert argon gas atmosphere for 2 h. The crystallinity, morphology and photocatalytic degradation activity of the Nb_2O_5 nanoparticles and C_{60} nanowhisker-Nb_2O_5 nanocomposites were confirmed by X-ray diffraction, transmission electron microscopy, scanning electron microscopy and UV-visible spectrophotometry. The Nb_2O_5 nanoparticles and C_{60} nanowhisker-Nb_2O_5 nanocomposites were examined for their use as a photocatalyst in the photocatalytic degradation of organic dyes such as methylene blue, methyl orange, rhodamine B and brilliant green under ultraviolet light at 254 nm. The kinetics for the photocatalytic degradation of organic dyes with C_{60} nanowhisker-Nb_2O_5 nanocomposites were investigated.

Keywords: C_{60} nanowhiskers, Nb_2O_5 nanoparticles, C_{60} nanowhisker-Nb_2O_5 nanocomposites, Photocatalytic degradation, Organic dyes.

INTRODUCTION

Organic dyes used in the laboratory, leather and textile industries are ubiquitous and are one of the main classes of contaminants in wastewater [1,2]. These organic dyes are harmful to humans, microorganisms and aquatic life because of their toxicities [3-5]. Photocatalytic technology is a convenient and effective method for the decomposition of organic dyes from industrial and domestic wastewater [6]. Many important semiconductor materials have been used as photocatalysts such as TiO_2, SnO_2, ZrO_2, Fe_2O_3, CdS and ZnO [7-10]. Niobium pentoxide nanoparticles have an wide band gap (3.4 eV) and are n-type transition metal oxide semiconductor that have chemical inertness, thermodynamic stability and low cytotoxicity [11,12]. Niobium pentoxide nanoparticles are used effectively in numerous reactions including pollution control, selective oxidation, electrochemistry, dehydration and hydration, hydrogenation and dehydrogenation, polymerization and photocatalysis [13-20]. Despite the advantages of their application in various technological fields, so far, only a few studies have focused on the use of Nb_2O_5 nanoparticles [21].

Fullerene (C_{60}) has gathered much interest in materials chemistry owing to their peculiar structural characteristics [22,23]. Fullerene (C_{60}) is used in a range of industrial applications such as optoelectrical devices, semiconductors, superconductors and composite materials [24,25]. Recently, C_{60} nanowhiskers have been prepared using a liquid–liquid interfacial precipitation (LLIP) method [26]. C_{60} nanowhiskers are thin single crystal nanofibers composed of C_{60} molecules [27]. The liquid-liquid interfacial precipitation method uses the interdiffusion process between a solution of fullerene in a good solvent and a poor solvent of fullerene [28]. These C_{60} nanowhiskers are pure carbon semiconductors and have wide potential applications in the fields of electronics, optics, MEMS, catalysts, energy and the environment [29].

The photocatalytic degradation of organic dyes such as methylene blue, methyl orange, rhodamine B and brilliant green were examined under ultraviolet irradiation at 254 nm by UV-visible spectrophotometry [30]. This paper reports the preparation and photocatalytic activity of Nb_2O_5 nanoparticles and C_{60} nanowhisker-Nb_2O_5 nanocomposites. The aim of this study is to investigate the kinetics of the photocatalytic degradation of organic dyes by C_{60} nanowhisker-Nb_2O_5 nanocomposites.

EXPERIMENTAL

C_{60} was supplied by Tokyo Chemical Industry Co., Ltd., Japan. Niobium(V) chloride, methylene blue (MB), methyl orange (MO), rhodamine-B (RhB) and brilliant green (BG) were purchased from Sigma-Aldrich. Acetic acid, hydrochloric acid, tetrahydrofuran (THF), isopropyl alcohol (IPA), benzene and anhydrous ethanol were obtained from Samchun Chemicals. Pluronic F108NF was acquired from Kumkang Chemical Co., Ltd., Korea.

The samples were heat-treated in an electric furnace (Ajeon Heating Industry Co., Ltd). The samples were also analyzed by Raman spectroscopy (Thermo Fisher Scientific, DXR Raman Microscope). The crystal structure of the samples was investigated by X-ray diffraction (XRD) (Bruker, D8 Advance) using CuK_α radiation (λ = 1.5406 Å). The morphology and particle size of the samples were examined by transmission electron microscopy (TEM) (JEOL Ltd., JEM-2010) at an acceleration voltage of 200 kV. The surface of the samples was observed by scanning electron microscopy (SEM) (JEOL Ltd., JSM-6510) at acceleration voltages ranging from 0.5 to 30 kV. The UV-visible spectra of the samples were obtained using a UV-visible spectrophotometer (Shimadzu, UV-1601 PC). A UV lamp (8 W, 254 nm, 77202 Marne La Valee Cedex 1, France) was used as the ultraviolet light irradiation source.

Preparation of C_{60} nanowhiskers: 10 mg of C_{60} powder was dissolved in 3 mL of benzene and ultrasonicated for 45 min followed by filtration to remove the undissolved C_{60} powder. The saturated solution of C_{60} was poured into a 20 mL vial and maintained at 5 °C in a refrigerator. Then, 15 mL of isopropyl alcohol was added slowly to the saturated solution of C_{60} to form a liquid-liquid interface. The above mixture solution was stirred with manually and stored in a refrigerator at 5 °C.

Synthesis of Nb_2O_5 nanoparticles: Niobium(V) chloride (2.7 g) and 1 g of pluronic F108NF were dissolved in 5 mL of anhydrous ethanol. After stirring for 5 min with a magnetic bar, 0.40 g of acetic acid and 0.18 mL of hydrochloric acid were added to the above solution under vigorous stirring condition. The produced sol was maintained at 40 °C for 48 h and changed into the formation of gel type sample. The gel was heated in an electric furnace at 700 °C under an inert argon gas atmosphere for 2 h to obtain a black powder.

Preparation of C_{60} nanowhisker-Nb_2O_5 nanocomposites: 10 mg of Nb_2O_5 nanoparticles and 10 mg of C_{60} nanowhiskers were dissolved in 10 mL of tetrahydrofuran. After stirring for 40 min with a magnetic bar, the mixture was poured into a vessel and dried for 30 min. The vessel was heated in an electric furnace at 700 °C under an inert argon gas atmosphere for 2 h. Then, the prepared C_{60} nanowhisker-Nb_2O_5 nanocomposites were placed at room temperature for 5 h.

Evaluation of photocatalytic degradation of organic dyes: Niobium pentoxide nanoparticles and C_{60} nanowhisker-Nb_2O_5 nanocomposites were examined as potential photocatalysts for the degradation of organic dyes, such as methylene blue, methyl orange, rhodamine-B and brilliant green. 5 mg of the Nb_2O_5 nanoparticles and C_{60} nanowhisker-Nb_2O_5 nanocomposites were placed separately into 10 mL vials, each containing 10 mL of an aqueous organic dye solution. Each vial was then irradiated with light at a wavelength of 254 nm using a UV-lamp and the organic dyes that were degraded by the photocatalysts were analyzed using a UV-visible spectrophotometer.

Kinetics study of photocatalytic degradation of organic dyes: A kinetics study of the photocatalytic degradation of organic dyes using the C_{60} nanowhisker-Nb_2O_5 nanocomposites have been carried out by applying the first-order reaction kinetics equation.

RESULTS AND DISCUSSION

The C_{60} nanowhiskers were characterized by Raman spectroscopy and UV-visible spectroscopy. Fig. 1 shows the Raman of the C_{60} nanowhiskers. The Raman shifts of the C_{60} nanowhiskers were observed at 265, 491 and 1457 cm^{-1} which can be associated with the Hg(1) squashing, Ag(1) breathing and Ag(2) pentagonal pinch modes of the C_{60} molecules, respectively [31]. Fig. 2 shows the UV-visible spectrum of the C_{60} nanowhiskers. The optical properties of C_{60} nanowhiskers were observed at λ_{max} = 542 nm, 597 nm and 622 nm.

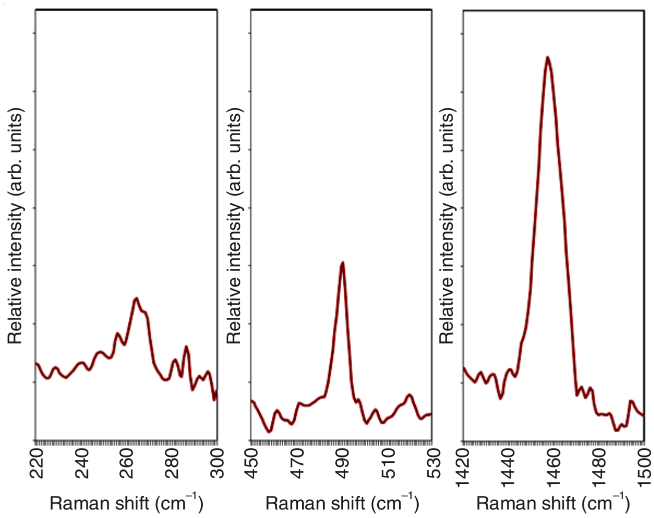

Fig. 1. Raman spectra of the C_{60} nanowhiskers

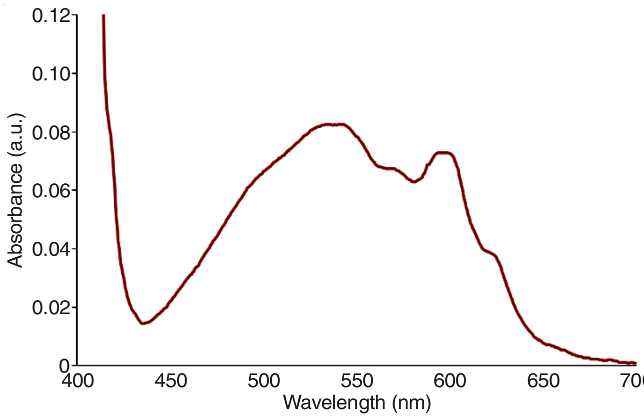

Fig. 2. UV-visible spectrum of the C_{60} nanowhiskers

Fig. 3 shows the XRD patterns of the (a) C_{60} nanowhiskers, (b) Nb_2O_5 nanoparticles and (c) C_{60} nanowhisker-Nb_2O_5 nanocomposites. The characteristic peaks of the C_{60} nanowhiskers were observed at 2θ values of 10.79°, 17.70°, 20.72°, 27.98°, 30.76° and 32.63°. The characteristic peaks of the Nb_2O_5 nanoparticles were observed at 2θ values of 22.66°, 28.41°, 36.64°, 46.17°, 50.70°, 55.22°, 63.69° and 71.09°. The

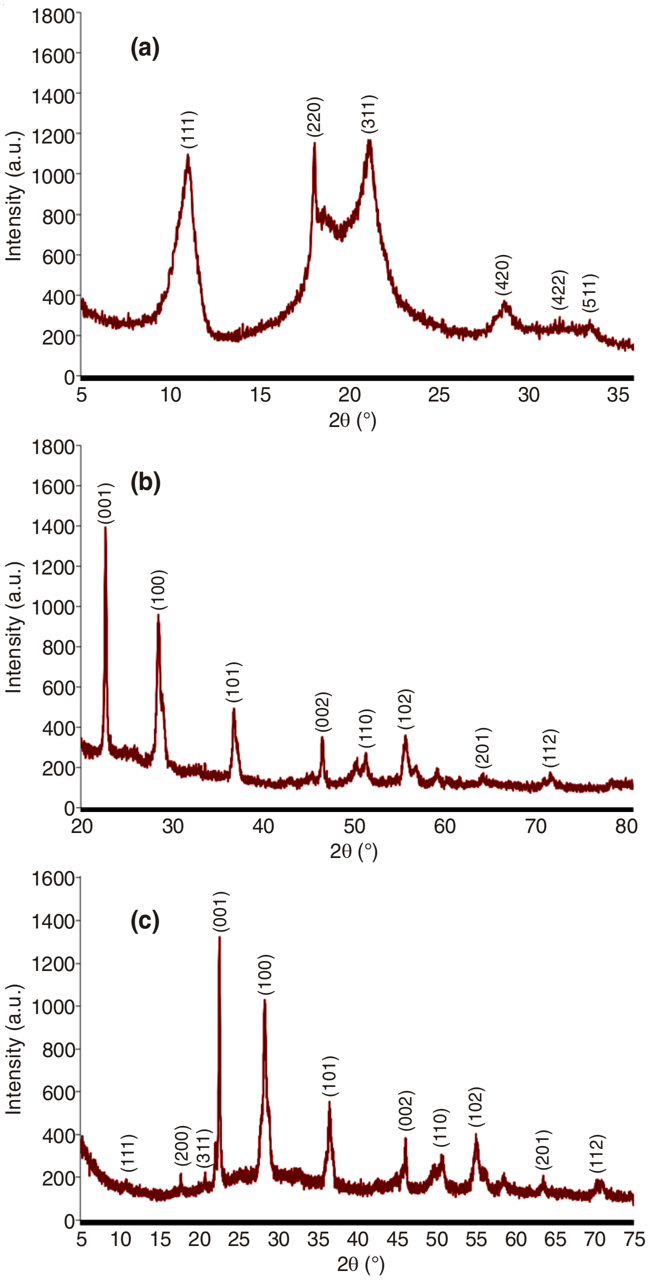

Fig. 3. XRD patterns of (a) C_{60} nanowhiskers, (b) Nb_2O_5 nanoparticles and (c) C_{60} nanowhisker-Nb_2O_5 nanocomposites

characteristic peaks of the C_{60} nanowhisker-Nb_2O_5 nanocomposites were observed at 2θ values of 22.62°, 28.39°, 36.61°, 46.15°, 50.69°, 55.19°, 63.66° and 71.07° due to the Nb_2O_5 nanoparticles and 2θ values of 10.78°, 17.71° and 20.71° due to the C_{60} nanowhiskers.

Fig. 4 shows the TEM images of the (a) C_{60} nanowhiskers, (b) Nb_2O_5 nanoparticles and (c) C_{60} nanowhisker-Nb_2O_5 nanocomposites. The synthesized C_{60} nanowhiskers had needle and rod-like shapes. The length of the nanowhiskers ranged from 100 nm to 2 μm. The Nb_2O_5 nanoparticles had a triangular, quadrangular and quasi-spherical shape that appeared to agglomerate. The average size of the Nb_2O_5 nanoparticles was 45 nm. In the C_{60} nanowhisker-Nb_2O_5 nanocomposites, the Nb_2O_5 nanoparticles were placed above the C_{60} nanowhiskers.

Fig. 5 shows the SEM images of the (a) C_{60} nanowhiskers, (b) Nb_2O_5 nanoparticles and (c) C_{60} nanowhisker-Nb_2O_5 nanocomposites. The SEM image showed that the C_{60} nanowhiskers had rectangular, needle and rod-like shapes. The SEM image showed that the Nb_2O_5 nanoparticles had a stone shape. A comparison of the two figures showed that the Nb_2O_5 nanoparticles in the C_{60} nanowhisker-Nb_2O_5 nanocomposites were smaller than the synthesized Nb_2O_5 nanoparticles.

As a result of the heat treatment, the Nb_2O_5 nanoparticles in the C_{60} nanowhisker-Nb_2O_5 nanocomposites were quite small compared to the synthesized Nb_2O_5 nanoparticles, while their surface areas were larger.

Fig. 6 shows the UV-visible spectra of the photocatalytic degradation of (a) methylene blue, (b) methyl orange, (c) rhodamine-B and (d) brilliant green with Nb_2O_5 nanoparticles under ultraviolet irradiation at 254 nm for 5 min. The photocatalytic degradation activity was superior for methylene blue compared to that for methyl orange, rhodamine-B and brilliant green when using the Nb_2O_5 nanoparticles. The order of effectiveness of the degradation of the organic dyes was methylene blue > rhodamine-B > brilliant green > methyl orange.

Fig. 7 shows the UV-visible spectra of the photocatalytic degradation of (a) methylene blue, (b) methyl orange, (c) rhodamine-B and (d) brilliant green with the C_{60} nanowhisker-Nb_2O_5 nanocomposites under ultraviolet irradiation at 254 nm for 1 min. The C_{60} nanowhiskers affected a great effect on the photocatalytic degradation of methylene blue, methyl orange, rhodamine-B and brilliant green. The photocatalytic degradation

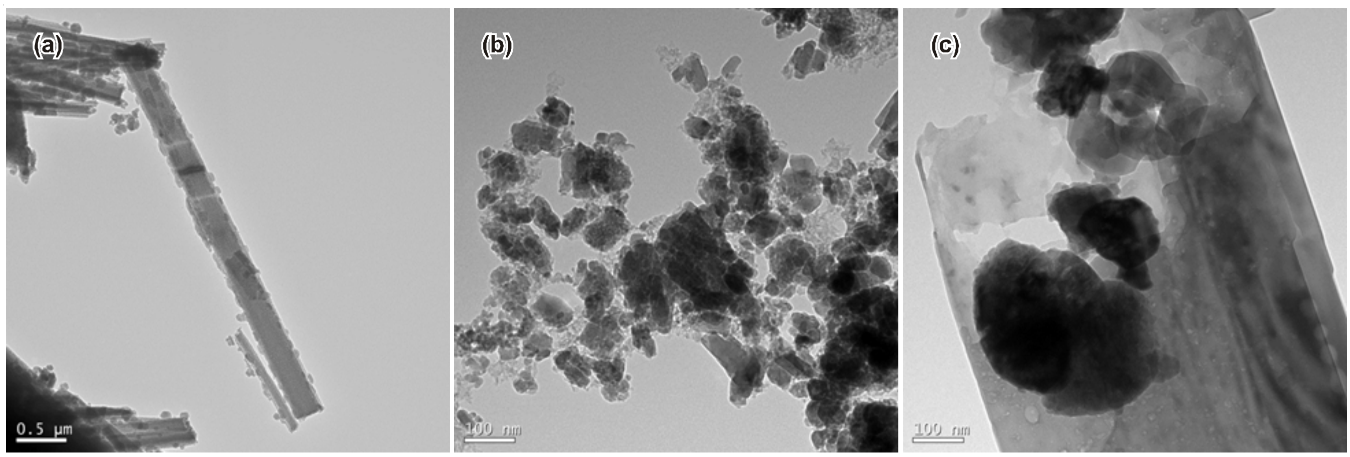

Fig. 4. TEM images of (a) C_{60} nanowhiskers, (b) Nb_2O_5 nanoparticles and (c) C_{60} nanowhisker-Nb_2O_5 nanocomposites

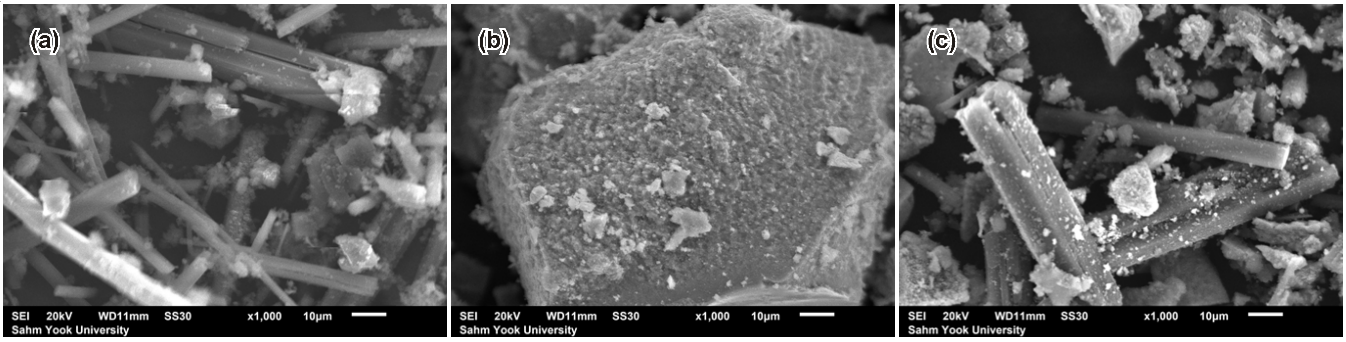

Fig. 5. SEM images of (a) C_{60} nanowhiskers, (b) Nb_2O_5 nanoparticles and (c) C_{60} nanowhisker-Nb_2O_5 nanocomposites

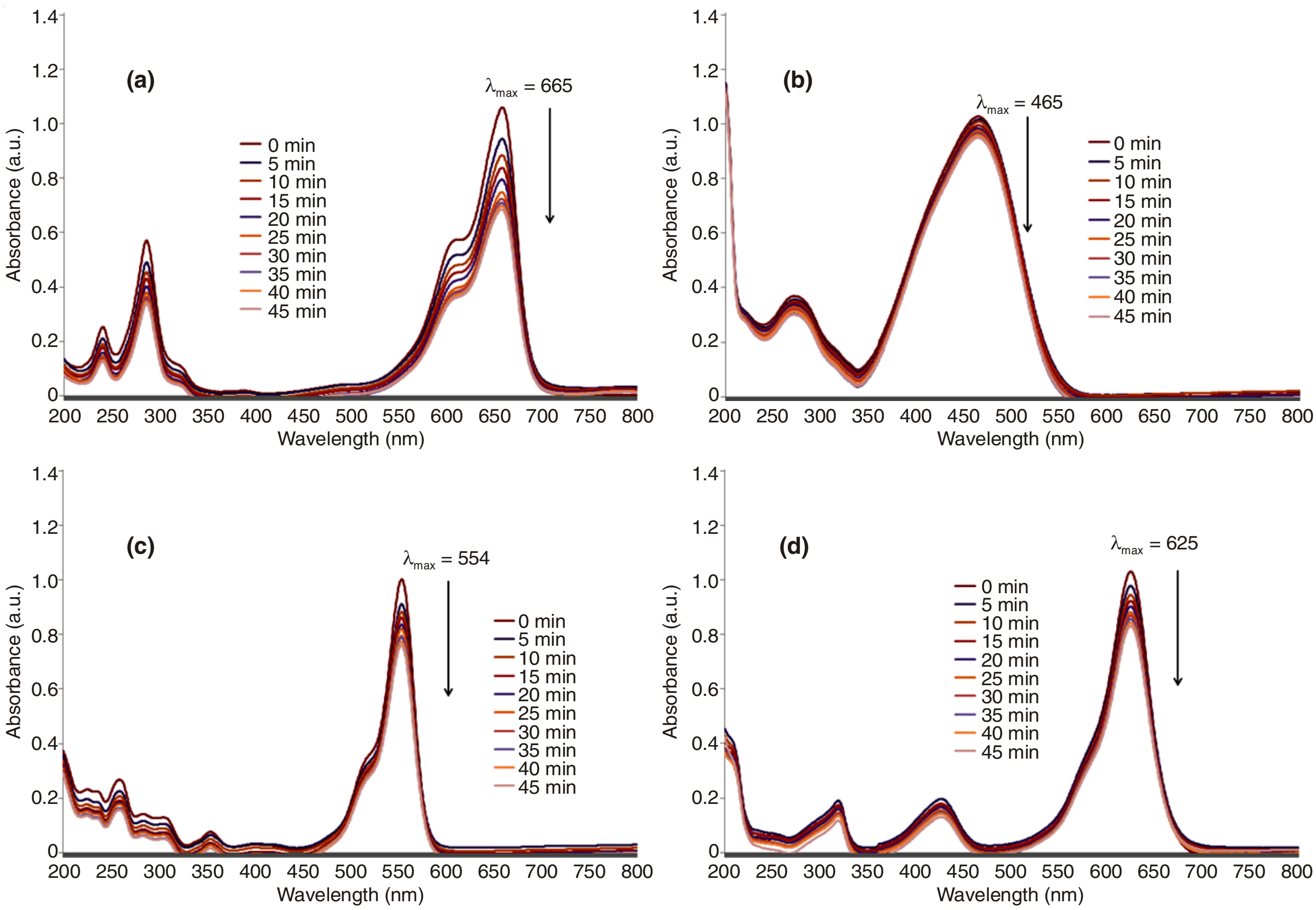

Fig. 6. UV-visible spectra of degradation of (a) methylene blue, (b) methyl orange, (c) rhodamine-B and (d) brilliant green with Nb_2O_5 nanoparticles

activity was effective for methylene blue and rhodamine-B. The order of the photocatalytic degradation of the organic dyes was methylene blue > rhodamine-B > brilliant green > methyl orange.

Fig. 8 shows the kinetics study of the photocatalytic degradation of methylene blue, methyl orange, rhodamine-B and brilliant green with C_{60} nanowhisker-Nb_2O_5 nanocomposites under ultraviolet irradiation at 254 nm. The photocatalytic degradation of the organic dyes followed first-order reaction kinetics according to the kinetics equation:

$$\ln\left(\frac{C}{C_o}\right) = -kt$$

where k is the apparent first-order rate constant, t is the reaction time, C is the concentration according to the reaction time and C_0 is the initial concentration. Table-1 presents results of the kinetics study of the photocatalytic degradation of methylene blue, methyl orange, rhodamine-B and brilliant green by a first-order reaction which is based on the kinetics equation. The order of the kinetics of the photocatalytic degradation of the organic dyes was methylene blue > rhodamine-B > brilliant green > methyl orange.

Conclusion

The C_{60} nanowhiskers had rectangular, needle and rod-like shapes. The lengths of the C_{60} nanowhiskers were 100 nm to 2 µm. The Nb_2O_5 nanoparticles had triangular, quadrangular

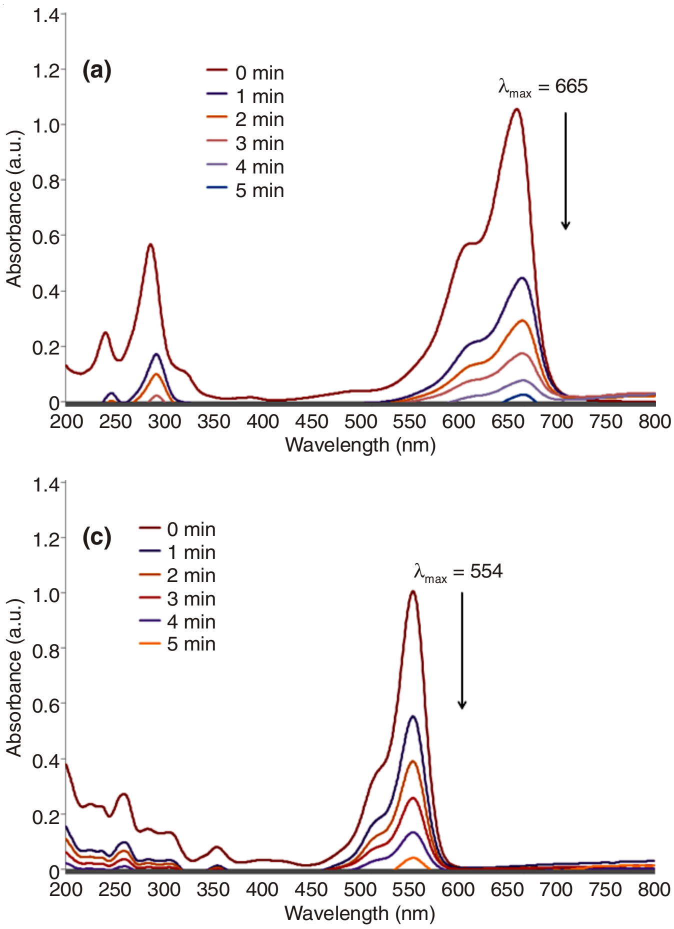

Fig. 7. UV-visible spectra of degradation of (a) methylene blue, (b) methyl orange, (c) rhodamine-B and (d) brilliant green with C_{60} nanowhisker-Nb_2O_5 nanocomposites

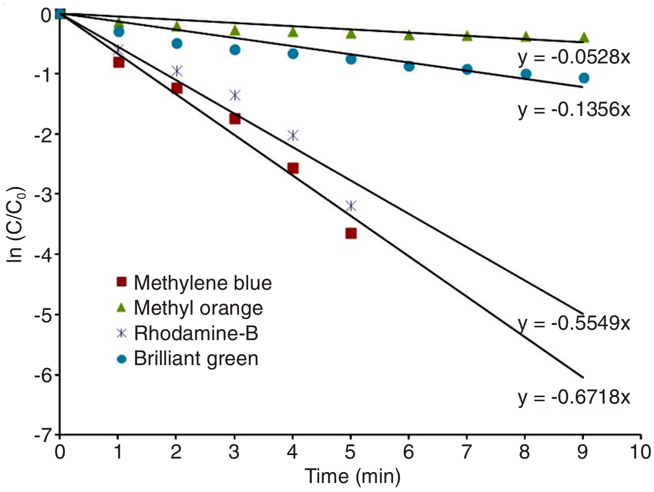

Fig. 8. Kinetics study of the degradation of (a) methylene blue, (b) methyl orange, (c) rhodamine-B and (d) brilliant green with the C_{60} nanowhisker-Nb_2O_5 nanocomposites

TABLE-1
KINETICS DATA OF THE PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE, METHYL ORANGE, RHODAMINE-B AND BRILLIANT GREEN WITH THE C_{60} NANOWHISKER-Nb_2O_5 NANOCOMPOSITES BY FIRST-ORDER KINETICS EQUATION

Time (min)	Methylene blue (ln C/C_0)	Methyl orange (ln C/C_0)	Rhodamine-B (ln C/C_0)	Brilliant green (lnC/C_0)
0	0	0	0	0
1	-0.8061	-0.1341	-0.5920	-0.2963
2	-1.2279	-0.1989	-0.9403	-0.4878
3	-1.7447	-0.2606	-1.3560	-0.5874
4	-2.5614	-0.2896	-2.0114	-0.6549
5	-3.6420	-0.3198	-3.1869	-0.7521
6	–	-0.3411	–	-0.8651
7	–	-0.3594	–	-0.9211
8	–	-0.3703	–	-1.0008
9	–	-0.3845	–	-1.0668

and quasi-spherical shapes with average sizes of 45 nm. In the C_{60} nanowhisker-Nb_2O_5 nanocomposites, the Nb_2O_5 nanoparticles were smaller than the synthesized Nb_2O_5 nanoparticles and had larger surface areas. Among the organic dyes such as methylene blue, rhodamine-B, brilliant green and methyl orange, methylene blue was degraded the most effectively using the synthesized Nb_2O_5 nanoparticles and the C_{60} nanowhisker-Nb_2O_5 nanocomposites as photocatalysts. The photocatalytic degradation rate was calculated according to the first-order kinetics equation. The reaction rate for the photocatalytic degradation of the organic dyes with the C_{60} nanowhisker-Nb_2O_5 nanocomposites was the highest for methylene blue compare to rhodamine-B, brilliant green and methyl orange. Therefore, the order of photocatalytic degradation rate of the organic dyes with the C_{60} nanowhisker-Nb_2O_5 nanocomposites was methylene blue > rhodamine-B > brilliant green > methyl orange.

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