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Synthesis of Ni, N co-doped TiO_2 using microwave-assisted method for sodium lauryl sulfate degradation by photocatalyst

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Abstract A titanium dioxide (TiO_2) photocatalyst was modified with nickel (Ni) and nitrogen (N) in titanium tetra-isopropoxide (TTIP) as a precursor through a microwave-assisted method. The Ni and N dopants led to a decrease in the TiO_2 band gap and made it able to function with visible light irradiation. The results of X-ray diffraction analysis demonstrated that the crystalline size of Ni–N–TiO_2 was 13.275 nm in anatase form with a specific peak in $2\theta = 25.32°$. Ni–N–TiO_2 was analyzed by scanning electron microscopy, which showed the smaller morphology and thin particles, and this was further supported by energy-dispersive X-ray data regarding the elemental composition of Ni and N being 4.50 and 2.39%, respectively. Fourier transform infrared spectroscopy results demonstrated the absorption spectrum in wavenumbers of 1197 and 1149 cm^{-1}, indicating an N–TiO_2 bond, a Ti–O bond at 648 cm^{-1}, and an Ni–O bond at 469 cm^{-1}. TiO_2 modified by Ni and N exhibited a decrease in the band gap at 1.95 eV, suggesting the Ni and N dopants successfully inserted onto the TiO_2 crystalline surface to be visualized with visible light. Photoactivity testing was carried out to degrade sodium lauryl sulfate surfactants under visible irradiation, where the degradation efficiency was 93.75%.

Keywords Photocatalyst, TiO_2, Nitrogen, Nickel, Surfactant, Microwave assisted

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Introduction

Surfactant waste processing requires serious attention in nature where human life can be endangered, such as with rivers, groundwater, and sediment pollutions.[1] One of the major pollutant types in water is sodium lauryl sulfate (SLS), an anionic surfactant category that comprises detergents, toothpaste, and shampoo.[2] SLS can degrade naturally in aerobic conditions (sufficient oxygen and microorganisms) and with UV light irradiation from sunlight, degradation requires a long time to take place.[3,4]

The technology necessary for wastewater treatment development over the last decade is represented by photocatalysis, one of the most promising technologies because it quickly and safely makes use of oxidation and reduction reactions under light irradiation.[5,6] There are certain semiconductor types used for the photocatalytic processes, such as TiO_2, CdS, ZnO, GaP, SiC, and Fe_2O_3.[7] TiO_2 is a semiconductor that has attracted much attention because it has high photocatalytic activity and is nontoxic and resistant to corrosion, not dissolving in water.[8] TiO_2 can be found in nature in metamorphic and igneous rocks known as ilmenite ($FeO{\cdot}TiO_2$).[9,10] In addition, TiO_2 can degrade organic waste and dyes while also acting as a disinfectant for medical equipment.[11] A TiO_2 semiconductor is only active under UV light conditions because it has a band gap energy of 3.2 eV.[12,13] This is a constraint when utilizing sunlight because UV light abundance is just 10%.[14,15] There are efforts regarding the improvement of TiO_2 photocatalysis by shifting the band gap energy so that it is active under visible light by modifying via insertion of metals and nonmetals.[16]

A nonmetallic dopant is generally added to TiO_2, i.e., nitrogen (N),[12] carbon (C),[17] sulfur (S),[18] phosphorus (P),[19,20] and fluorine (F),[21] but N as a dopant is more effective because it has an atomic size that is the same as oxygen (O) and a low ionization energy.[22] A

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number of studies have also shown that using transition metal dopants, such as Fe, La, Ni, Mn, Au, or Ag, to decrease the band gap and to improve photocatalytic activity in the visible light region is possible.[23–26] A transition metal dopant in TiO_2 can serve as an electron trap to improve electron–hole pair separation.[27]

This study examined Ni and N co-doped within a TiO_2 catalyst process using a microwave-assisted method because it has the benefits of being environmentally friendly and energy efficient. The improved particle kinetics through the microwave-assisted synthesis of the material was observed in a relatively short time with lower energy consumption,[28] so it was considered a quite promising method for the modification of TiO_2 photocatalysts

Experimental

Preparation of Ni–N–TiO_2

The preparation of Ni and N was done by the sol–gel method. These were made by two solutions (A and B). For solution A: 8 mL TTIP was put in 1 mL of acetylacetone containing 30 mL ethanol and for solution B: 30 mL ethanol was put in 4 mL of distilled water containing 2 mL glacial acetic acids. The two solutions were mixed to obtain the TiO_2 sol. The sol was added to 30 mL of 1 M urea solution. Then, it was added by $Ni(NO_3)_2{\cdot}6H_2O$ with the ratio of 1%, 3%, 5%, and 7%. Subsequently, the solution was heated in a microwave for 30 min. Finally, it was washed with distilled water, filtered, and dried in an oven at 100°C, then calcined at 500°C for 1.5 h to obtain the Ni–N–TiO_2 crystal.

Characterization of the synthesized Ni–N–TiO_2

The surface morphology of the synthesized Ni–N–TiO_2 crystal was observed using SEM (JEOL, Model 5900LV). The surface composition was analyzed by EDS (Oxford Links ISIS) and the FTIR spectra by Jasco FT/IR 6600. The band gap was obtained by LAMBDA 950 UV–Vis spectrophotometer PerkinElmer, and the X-ray diffraction spectra of the Ni–N–TiO_2 were obtained using a Philips PW 1050–3710 diffractometer under Cu Ka radiation.

Preparation of SLS solutions

Preparation of SLS solution consists of 0.4, 0.8, 1.2, and 1.4 mg/L. The 3 mL of SLS solution with a concentration of 0.4 mg/L was extracted using separating funnel by adding 5 mL methylene blue and 2 mL chloroform for 30 min. Phases of chloroform were combined and absorbance measured at a wavelength of 640–659 nm using a UV–Vis spectrophotometer to obtain a wavelength maximum from SLS.

Degradation test of SLS solutions

The degradation test of SLS was performed by using 300 mg of catalysts added into 400 mL SLS with concentrations of 0.4, 0.8, 1.2, and 1.4 mg/L, respectively. The photocatalysts processed for 120 min with irradiation by visible light (Philips Halogen lamp 150 W Halolite) and were analyzed by using a UV–Vis spectrophotometer. The absorbance values have integrated into the linear regression equation: y = ax + b, to obtain the concentration and percentage of sample degradation of the measurement with:

$$\%D = \frac{C_0 - C_1}{C_0} \times 100\%$$

where % D is the percentage of SLS concentration degradation, C_0 the initial concentration of SLS, and C_1 the concentration degraded of SLS.

Results and discussion

Preparation of Ni–N–TiO_2 catalyst

In this research, the kinetics of molecules was improved with microwave assistance at a power of 450 watts for 30 min based on Jaimy et al.[29] The composition variations of Ni dopant were obtained by the addition effects of Ni on TiO_2 photocatalytic activity. The hydrothermal treatment was calcined at 500°C for 1.5 h to obtain a TiO_2 powder with an anatase crystalline structure that was advantageous in terms of photocatalytic activity.[30] Table 1 lists the physical properties of the material synthesized photocatalyst, where the addition of Ni and N dopants also increased the yield to an optimum of 83.17% Ni(1%)–N–TiO_2.

Characterization of Ni–N–TiO_2 catalyst

X-ray diffraction (XRD)

Characterization by XRD to obtain data on the Ni–N–TiO_2 crystal structure was performed. Figure 1 shows 17 peaks in the XRD pattern of Ni–N–TiO_2, specifically $2\theta = 25.32°$, 25.52°, 37.88°, 44.011°, 48.16°, 53.922°, 54.42°, 54.9°, 55.44°, 62.64°, 65.22°, 68.623°, 69.106°, 69.515°, 70.165°, 74.782°, and 76.02°. The XRD data demonstrated that the Ni and N dopants were distributed in the lattice of anatase, seen at $2\theta = 25.3°$; 37.9°, 48.1°, 54°, 54.9°, 62.6°, 69.05°, 70.1°, 75.2°, and 82.7°, with field diffractions of (101), (004), (200), (105), (211), and (204), respectively. Crystal anatase

Table 1: The physical properties of the material synthesized by using microwave-assisted hydrothermal method

Catalysts	Color	Mass (g)	Yield (%)
TiO_2	White	1.732	82.74
N–TiO_2	Light brown	2.084	82.91
Ni–TiO_2	Light yellow	1.822	82.88
Ni(1%)–N–TiO_2	Light yellow	2.108	83.17
Ni(3%)–N–TiO_2	Light yellow	2.138	82.98
Ni(5%)–N–TiO_2	Light yellow	2.171	82.91
Ni(7%)–N–TiO_2	Light yellow	2.198	82.62

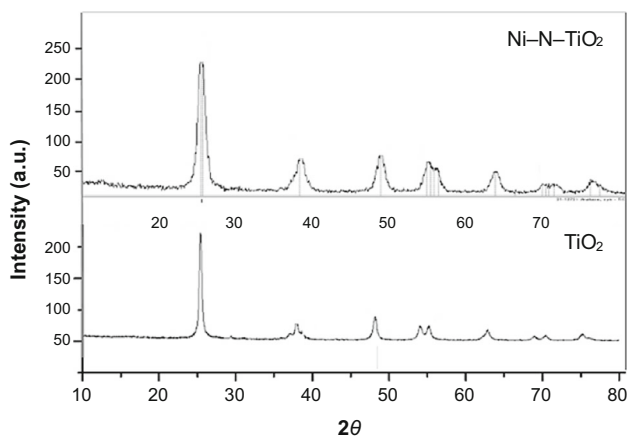

Fig. 1: The result of XRD pattern on Ni–N–TiO_2 catalyst

(101) had a robust influence on TiO_2 photocatalytic activity. According to Nurdin et al.,[24] the TiO_2 anatase has the large surface area to enhance the high photocatalytic activity. It can be calculated using the Scherer equation.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is crystal size (nm), λ is the wavelength of the X-ray (0.15406 nm), β is the half width of the diffraction peak (rad), and θ is the angle of the diffraction peaks (°). From the Scherer equation, the obtained TiO_2 crystal size was 13.275 nm.

UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS)

UV–Vis DRS was employed to obtain the band gap of synthesized Ni–N–TiO_2. The higher the band gap value, the greater was the effect on semiconductor performance that was observed because there was still the requirement for large amounts of energy to excite the electrons from the valence band to the conduction band. The presence of Ni and N dopants was very effective in increasing TiO_2 performance because these dopants could separate the electron–hole from the valence band onto the conduction band. The band gap of Ni–N–TiO_2 was calculated by using the Kubelka–Munk factor [F(R)], with the band gap value of 1.9534 eV (Fig. 2). This was smaller than the pure TiO_2 (3.2 eV),[31] N (2.6 eV),[12] and Ni (2.33 eV).[32] The successful Ni–N–TiO_2 synthesis using a microwave-assisted method demonstrated that there was a smaller band gap than conventional methods of 2.28 eV.[33] This was caused by the microwave-assisted where the material receives energy emitted to accelerate the reaction. The decrease in the band gap value to form the photo hole (valence band) and photoelectron (conduction band) in visible light was influenced by the dopants.

Based on Ruslan et al.,[25] the band gap can be used to calculate the corresponding wavelength (UV–Vis) spectra regions by Plank–Einstein relation [$E = hc/\lambda = (1239.8\ \text{eV nm})/\lambda$]. In this study, the synthesized Ni–N–TiO_2 has been activated in visible wavelength regions at 634.68 nm.

Fourier transform infrared spectroscopy (FTIR)

FTIR measurements were carried out to identify the formation of the bond with Ti, N, Ni, and O as the resulting effect of adding Ni and N dopants to TiO_2.

The wavenumber at 1197 and 1149 cm^{-1} was indicative of the N–TiO_2 bonds. The absorption at wavenumber of 648 cm^{-1} and 469 cm^{-1} were presented a Ti–O and Ni–O bonds, respectively. According to Ruslan et al.[25] the vibration of the metal with an O group was expected to appear at the wave number 600–400 cm^{-1} (Fig. 3).

Scanning electron microscopy energy-dispersive x-ray (SEM-EDX)

The SEM-EDX measurement results were utilized to explain the surface morphology from the elements on the Ni–N–TiO_2 catalyst. Figure 4 shows the morphology measurements of the TiO_2 and Ni–N–TiO_2 catalysts.

Figure 4a is a morphology of TiO_2 synthesized by the sol-gel method, while Fig. 4b is the physical changes of the Ni–N–TiO_2 that had a smaller size than TiO_2. The smaller particle size was obtained with the large active surface area on the photocatalyst. It

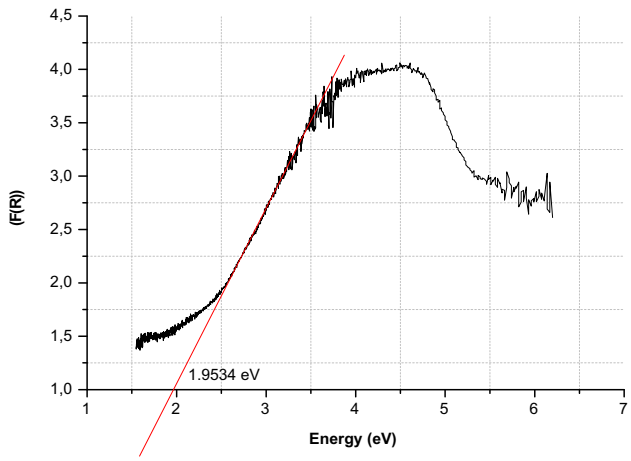

Fig. 2: The result of band gap of Ni–N–TiO_2 catalyst

permitted collisions with the materials to be a catalyst for the rapid reaction.

The composition of the catalyst using the EDX catalyst meant that Ni–N–TiO_2 possessed atoms of C, O, N, Ti, and Ni at proportions of 6.04, 34.94, 2.39, 52.12, and 4.5%, respectively (Fig. 5).

Degradation test using SLS solution

Effect of dopants nitrogen (N) and nickel (Ni) on the performance of TiO_2 catalyst

The addition of dopants into the TiO_2 matrix showed that TiO_2 can be active under visible light such that the SLS surfactant is degraded as can be seen in Fig. 6. The presence of the N dopant in TiO_2 im-

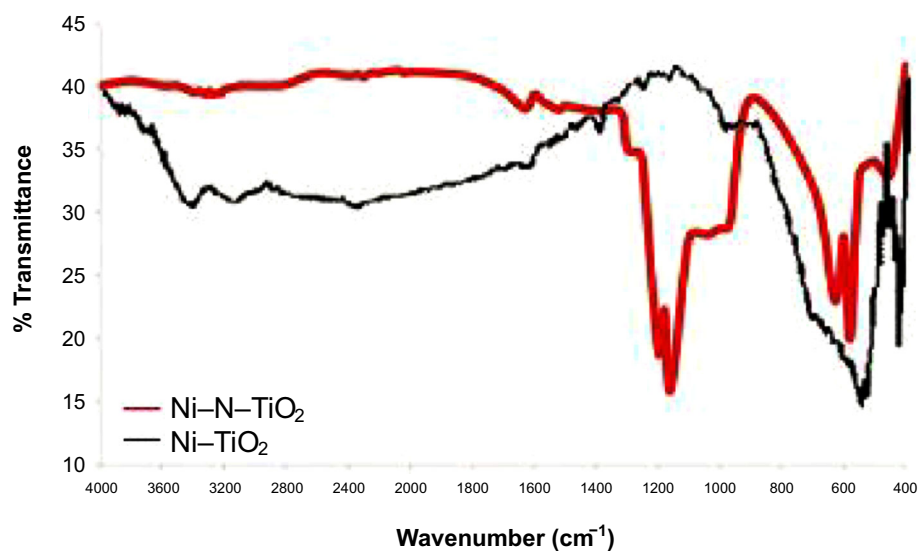

Fig. 3: FTIR spectra of Ni–N–TiO_2 and Ni–TiO_2 catalysts

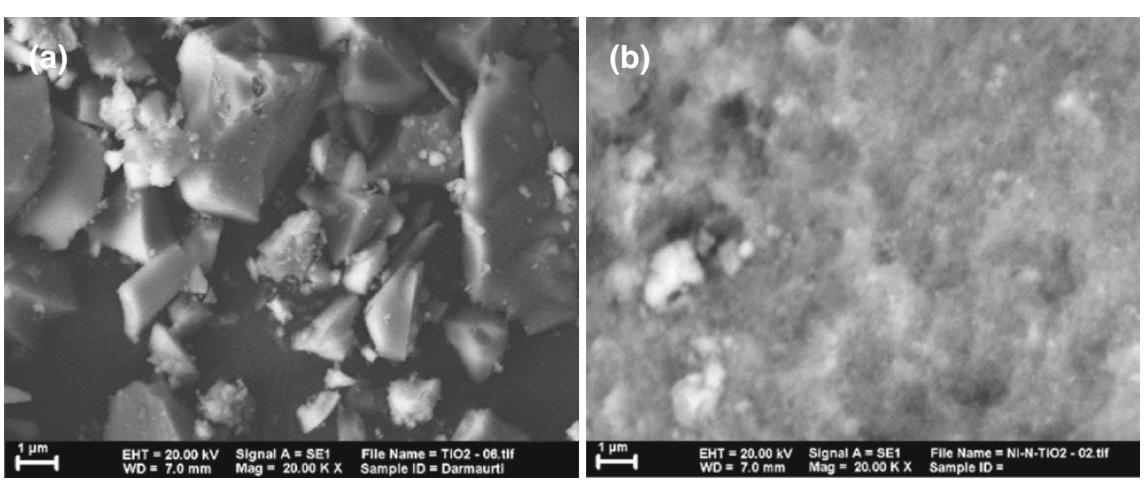

Fig. 4: The morphology of catalysts in scale bar: 1 µm; (a) TiO_2, and (b) Ni–N–TiO_2

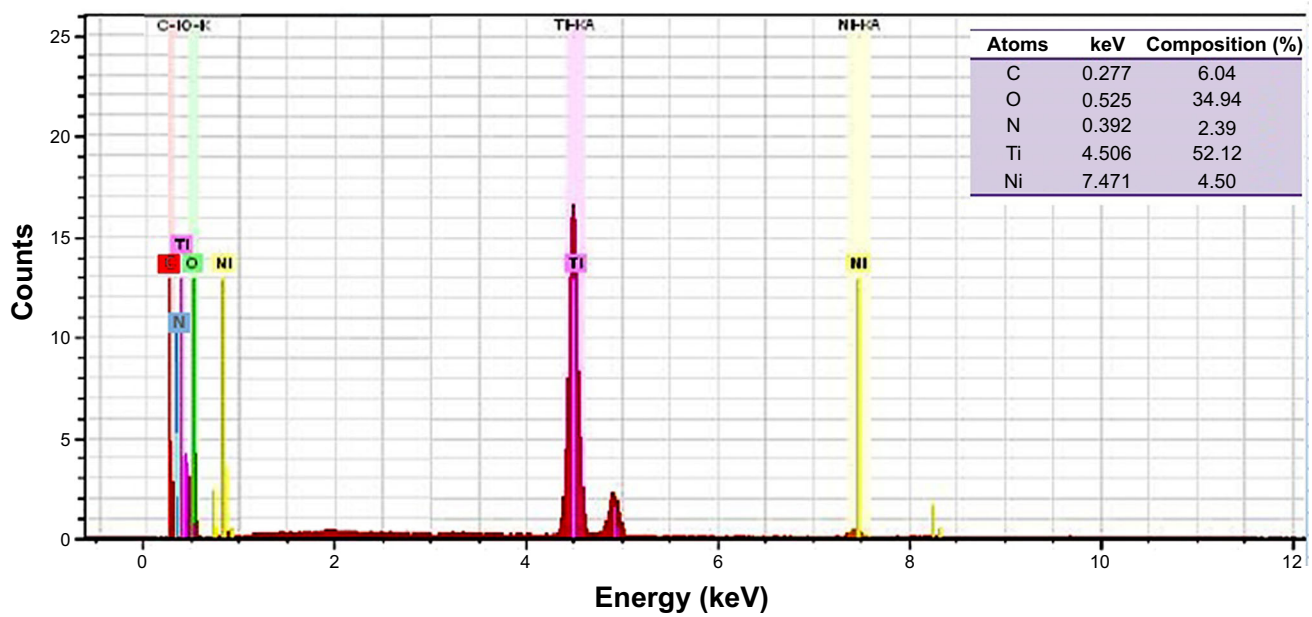

Fig. 5: The result of EDX spectrum on Ni–N–TiO_2 catalyst

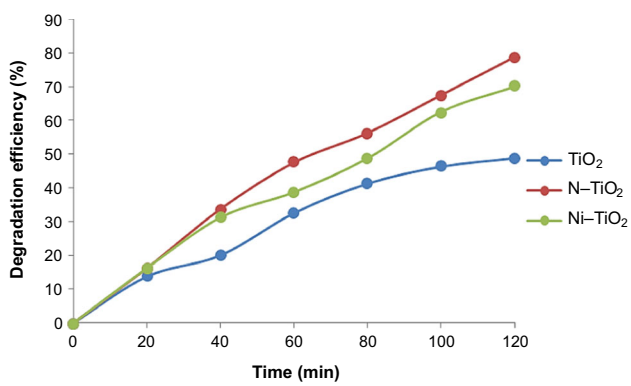

Fig. 6: The performance test comparison on TiO_2 dopants to degrade SLS in visible light combined of TiO_2, N–TiO_2 and Ni–TiO_2 catalysts

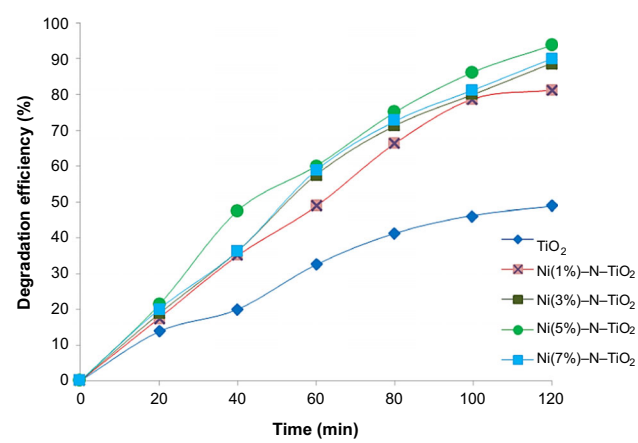

Fig. 7: The composition effect of Ni dopant in N–TiO_2 to degrade 0.8 mg/L SLS under visible light

proved the degradation efficiency of the SLS surfactant by 78.75% compared to the standard TiO_2 catalyst (48.75%). According to Asahi et al.,[34] the mixing of the p states on the N dopant with O in the 2p valence band could decrease the TiO_2 band gap, while the conduction band is steady state position. SLS degradation was obtained using TiO_2 dopant Ni under visible light irradiation with the efficiency of 70% compared with the standard TiO_2 photocatalyst.

Effect variation of nickel (Ni) dopants

The effect of the Ni dopant at composition variations of 1, 3, 5, and 7% to degrade SLS through Ni–N–TiO_2

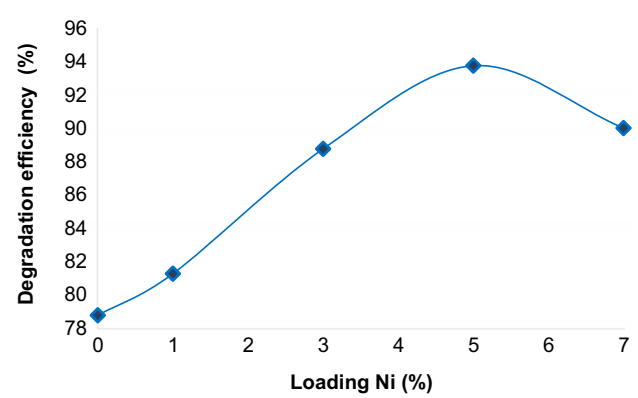

Fig. 8: The loading effect of Ni dopant to degrade the 0.8 mg/L SLS surfactant in visible light irradiation for 120 min

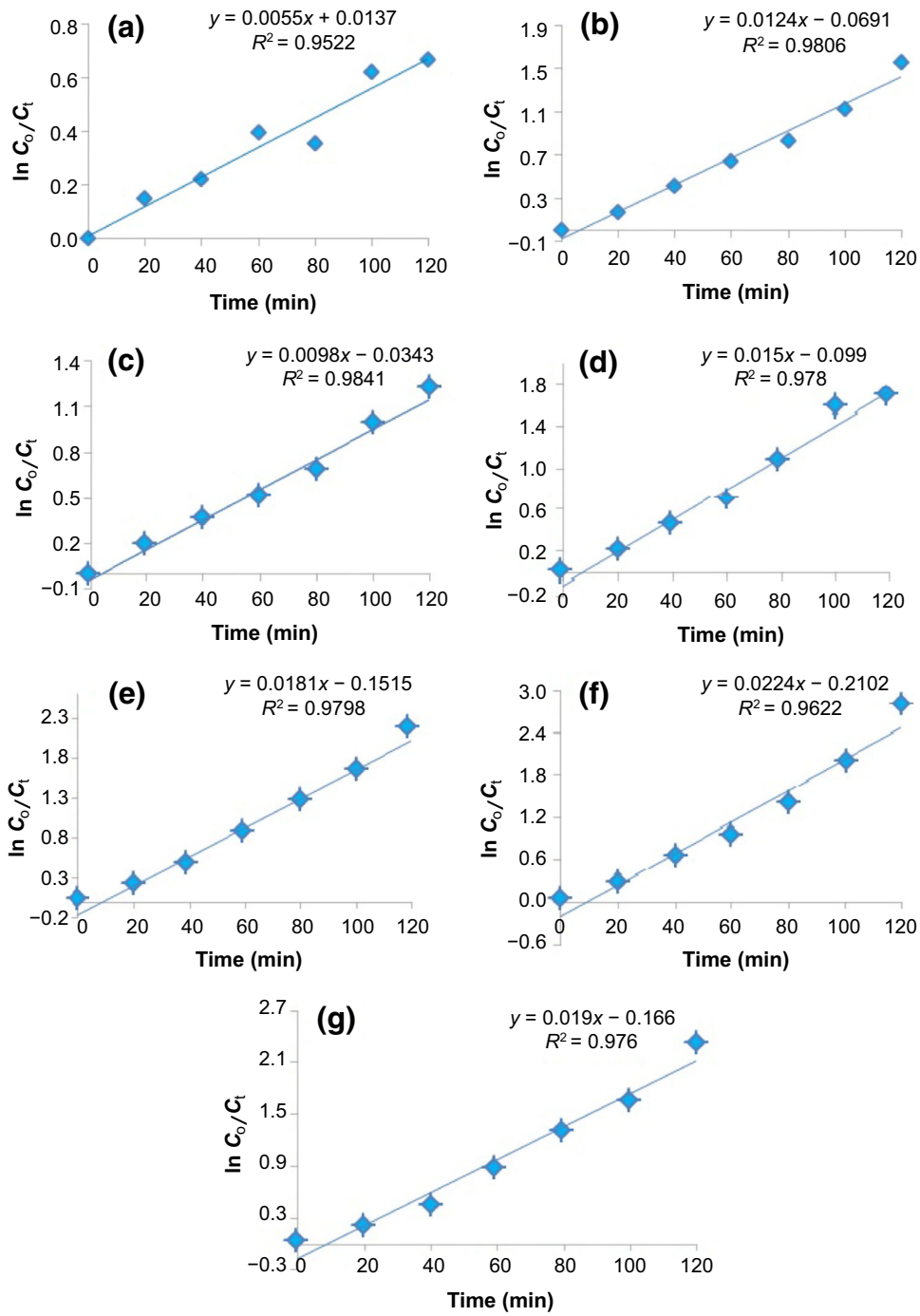

Fig. 9: The kinetics rate of SLS degradation kinetics at 0.8 mg/L using the photocatalyst (a) TiO_2, (b) N–TiO_2, (c) Ni–TiO_2, (d) Ni(1%)–N–TiO_2, (e) Ni(3%)–N–TiO_2, (f) Ni(5%)–N–TiO_2, (g) Ni(7%)–N–TiO_2

photocatalysis exhibited the most optimal degradation results in 120 min at 5% loading of Ni with the degradation equivalent to 93.75% (Fig. 7).

Zhang et al.[35] noted that a metal dopant was inserted into the N–TiO_2 system as an electron trap that enhances photocatalytic activity. Meanwhile, a dopant is required at a precise composition in N–TiO_2 for SLS degradation. This was observed for Ni–N–TiO_2 at 5%, and the specific Ni loading is shown in Fig. 8.

Rate constant for SLS degradation test

The reaction rate constant and reactant concentrations can be determined by examining the reactant concen-

Table 2: The reaction rate constant of SLS degradation on 0.8 mg/L

Variable	k (mg L^{-1}/min)
SLS + TiO_2	0.0055
SLS + N–TiO_2	0.0124
SLS + Ni–TiO_2	0.0098
SLS + Ni(1%)–N–TiO_2	0.0150
SLS + Ni(3%)–N–TiO_2	0.0181
SLS + Ni(5%)–N–TiO_2	0.0227
SLS + Ni(7%)–N–TiO_2	0.0190

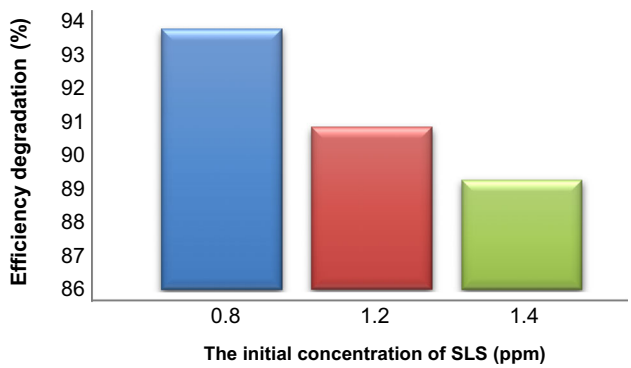

Fig. 10: The initial concentration effect of SLS against efficiency degradation

tration at any time during the reaction. If a reaction occurs at very low concentrations (mg L^{-1}), the reaction takes place as a first-order reaction, i.e.,

$$\ln \frac{[C_0]}{[C]} = kt$$

where C_0 is a concentration during the time of degradation at $t = 0$, C is the concentration during the time of degradation at $t = t$, k is the reaction rate constant, and t is the time in minutes. $\ln \frac{[C]_0}{[C]}$ is plotted against time of irradiation (t) to obtain linear curves with a k slope[16] as shown in Fig. 9.

Table 2 lists the reaction rate constant for SLS by Ni(5%)–N–TiO_2 which is greater than TiO_2 catalyst, N–TiO_2, Ni–TiO_2, and Ni–N–TiO_2 with the loading of Ni at the same time. The rate of the reaction using the Ni–N–TiO_2 catalyst with 5% Ni loading was faster in degrading SLS (Fig. 10).

Variation effect of initial concentration on SLS degradation

The variable effect of initial concentration on SLS degradation using Ni(5%)–N–TiO_2 with SLS concentrations of 0.8 mg/L, 1.2 mg/L, and 1.4 mg/L demonstrated optimum degradation at 93.75, 90.83, and 1.4%, respectively.

When the initial concentration increased, surfactant molecules are adsorbed on the catalyst surface. However, when the molecules are adsorbed on the catalyst, the SLS surfactant does not entirely degrade because of the light intensity and catalyst constant factors.[36] The high concentrations of SLS on the catalyst surface decrease the production of ·OH on the catalyst. Furthermore, the SLS solution will absorb many photons, causing their availability for activation of the catalyst to be reduced.

Conclusion

Modified TiO_2 nanoparticles were successfully synthesized using a microwave-assisted method to produce a photocatalytic material in an anatase crystalline form with a size of 13.27 nm. The Ni and N dopants in TiO_2 decreased the band gap energy of 1.9534 eV—the material could be activated by visible light. The TiO_2 photocatalyst with Ni and N dopants improved catalytic performance in degrading SLS up to 81.25% for Ni(1%)–N–TiO_2, 88.75% for Ni(3%)–N–TiO_2, 93.75% for Ni(5%)–N–TiO_2, and 90.00% for Ni (7%)–N–TiO_2. Furthermore, TiO_2, N–TiO_2, and Ni–TiO_2 as photocatalysts had degradation efficiencies of 48.75, 78.75, and 70.0%, respectively.

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