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Photocatalytic hydrogen production from glycerol and water with NiO_x/TiO₂ catalysts

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Abstract

The surface of a TiO₂ material was modified by loading NiO_x in 10 wt% by impregnation with nickel nitrate followed by calcination in air at different temperatures. The TiO₂ and NiO_x/TiO₂ samples prepared were applied for photocatalytic H₂ production from glycerol and water at 50 °C. The H₂ evolution was enhanced by NiO_x loading and was dependent on calcination temperature. A maximum H₂ evolution was observed with 450 °C calcined NiO_x/TiO₂ sample. The properties of those TiO₂ and NiO_x/TiO₂ samples were characterized by nitrogen adsorption, XRD, UV/Vis, and XPS measurements to examine factors responsible for the enhancement of photocatalytic H₂ evolution with NiO_x loaded and calcined TiO₂ samples.

Keywords: Photocatalytic activity, Glycerol reforming, Hydrogen production, Nickel doping, Titanium dioxide

1. Introduction

The useful application of biomass derived materials is attracting much attention from industry and academia. One of interesting applications is the production of H_2 from chemical and photochemical transformations of those materials [1-3]. The photocatalytic H_2 production can be performed under mild conditions and several authors studied different biomass derived model materials including alcohols, glycerol, glucose, sugars, and so on. Recently a larger amount of glycerol is produced as a byproduct in the production of biodiesel and so it is desirable to find its application [4]. The heterogeneous photocatalytic H_2 production from aqueous glycerol solutions (Scheme 1) were studied by several authors using TiO_2 based catalysts loaded with Pt [5-8], Pd [9], and CuO_x [10-12]. Fornasiero et al. prepared active Cu/TiO_2 catalysts by a water-in-oil microemulsion method, in which Cu nanoparticles were embedded in the TiO_2 , and these were active for the H_2 production from glycerol and water under visible light irradiation conditions [10]. The doping of NiO_x onto the surface of TiO_2 is effective for the preparation of p-type (NiO_x) - n-type (TiO_2) junction [13]. Such NiO_x -doped TiO_2 catalysts were recently reported to show good performance of photocatalytic degradation of organic compounds of methyl orange [14], methylene blue [15], and 2-naphthol and *p*-cresol [16]. In the present work, the authors prepared NiO_x/TiO_2 catalysts by conventional impregnation and tested their performance in photocatalytic H_2 production from a mixture of glycerol and water under UV/Vis irradiation conditions. We could find few published study that has considered the use of NiO_x/TiO_2 photo-sensitive materials for such a H_2 production from biomass derived compounds.

Scheme 1

2. Experimental

2.1. Catalyst preparation

A TiO_2 material supplied by Catalysis Society of Japan was used, which was a mixture of anatase and rutile TiO_2 . The structural properties will be presented later (Table 1). The doping of Ni species was made by conventional impregnation with nickel nitrate (Wako) and the loading of Ni species was 10 % by weight assuming Ni species was in the form of NiO . A weighed TiO_2 (1 g) was dispersed in 10 cm³ $Ni(NO_3)_2$

aqueous solution (0.15 M) and the slurry formed was continuously stirred overnight for sufficient impregnation. The mixture was kept in an oven at 80 °C for 12 h to remove the solvent (water). Then, the solid sample was ground and calcined in a muffle furnace while passing air at 50 cm³ min⁻¹ at 250, 450 and 650 °C for 3 h. The catalysts so prepared are denoted by NiO_x/TiO₂ hereinafter.

2.2. Catalyst characterization

The surface and bulk properties of NiO_x/TiO₂ samples prepared were characterized by different methods. BET surface area was measured by N₂ adsorption at -196 °C (Quantachrome NOVA 1000). Prior to N₂ physisorption, the samples were degassed under vacuum at 150 °C for 2 h. Structural properties were examined by powder X-ray diffraction (XRD) (Rigaku D/Max-2500 PC) with Cu K α radiation and a Ni filter. XRD patterns were measured from 20° to 80° at a rate of 1° min⁻¹. Diffuse reflection UV/Vis spectra were recorded under ambient conditions (Shimadzu UV-3100PC) using BaSO₄ matrix as background under ambient conditions. The spectra measured were converted to the absorption spectra by using the Kubelka-Munk function. X-ray photoelectron spectroscopy (JEOL JPS-9200) was used to examine the surface properties and all the binding energies were referenced with respect to the Ti 2p at 485.5 eV [17].

2.3. Photocatalytic reaction

Photocatalytic reactions were conducted in the same reactor as used previously, which was a 50 cm³ stainless steel autoclave with two quartz windows (diameter 1 cm) [18]. It was previously used for photocatalytic water splitting in the presence of pressurized CO₂. A weighed sample (20 mg) was suspended in a mixture of 10 cm³ water and 2 cm³ glycerol (Wako) in the reactor. The air remaining in the reactor was removed by purging with 1 MPa N₂ for five times. The reactor was placed on a heating plate and wrapped by a heating tape. The temperature was monitored by a thermocouple embedded in the reactor wall. The reactor was heated while stirring the reaction mixture by a magnetic stirrer. The reaction mixture was illuminated using a 500 W high-pressure Hg lamp (Ushio USH-500SC) at 50 °C for 4 h. The lamp emits predominantly the light of wavelengths at 365 nm, 405 nm, and 436 nm. After the reaction, the gaseous products evolved were collected in a gas trap. The amount of H₂ was determined by a gas chromatograph (Shimadzu GC-8A, molecular sieve 5A packed column, TCD detector, N₂ carrier) and those of CO, CO₂, and CH₄ by another gas chromatograph (Shimadzu

GC-8A, Porapak Q packed column, FID detector, N₂ carrier) with a methanizer converting those gases into CH₄.

3. Results and discussion

In the present work, 10 wt% NiO_x/TiO₂ catalysts calcined at different temperatures were used for the photocatalytic H₂ production from aqueous glycerol solution. The 10 wt% NiO loading approximately corresponds to monolayer coverage of NiO species over the surface of TiO₂ used that has a BET surface area of 50 m² g⁻¹. The state of NiO_x dispersion (namely, the state of NiO_x - TiO₂ junction/contact) was varied by changing the calcination temperature.

3.1. Catalytic performance

First, the performance of NiO_x-unloaded TiO₂ samples calcined at different temperatures was examined for photocatalytic H₂ production from a mixture of glycerol and water at 50 °C. Fig. 1 shows the rates of evolution of H₂ and other gaseous products of CO₂ and CO in photocatalytic reforming of glycerol at 50 °C. The evolution of CH₄ was not detected. When the calcination temperature was raised, the rate of H₂ evolution increased, had a maximum at 450 °C, and then decreased. The maximum H₂ evolution was 320 μmol g⁻¹ h⁻¹ under the conditions used. The amount of CO₂ evolved did not change so much but that of CO increased with the temperature. The evolution of H₂ was larger than that of CO₂ and CO for the catalysts calcined at 450 °C or below but smaller for the one at 650 °C. In addition, blank experiments were conducted in the absence of light and/or catalyst under the same reaction conditions. No H₂ production was detected in these blank reactions, indicating that both the light and the TiO₂ catalyst are required for the photocatalytic H₂ production from glycerol and water.

Figure 1

Then, the catalytic performance of NiO_x-loaded TiO₂ samples was tested and the results obtained are also shown in Fig. 1. The rate of H₂ evolution changed with the calcination temperature in a similar manner as observed with the NiO_x-unloaded samples. The maximum H₂ evolution appeared at the same temperature of 450 °C, being 900 μmol g⁻¹ h⁻¹. It was about three times larger compared to the maximum with the NiO_x-unloaded sample calcined at 450 °C. Thus, the loading of NiO_x to TiO₂ can

improve its photocatalytic performance. The total amount of CO₂ and CO formed was comparable to that of H₂ evolved for either 250 °C or 450 °C calcined NiO_x/TiO₂ catalyst. However, the ratio of CO₂ against CO is different, being 1.8 and 5.4 for the former and latter catalysts, respectively. CH₄ was also detected to form for the 650 °C calcined sample.

In addition, the performance of NiO alone was tested under the same reaction conditions. The NiO powder was prepared by calcining Ni(NO₃)₂ at 450 °C in an air stream of 50 cm³ min⁻¹ for 3 h and grinding in a mortar. This treatment changed Ni(NO₃)₂ to NiO, which was confirmed by XRD (not shown). It was found that H₂, CO, and CH₄ were evolved at rates of 91, 2124, and 917 μmol g⁻¹ h⁻¹, respectively. That is, compared to the above-mentioned NiO_x/TiO₂ sample calcined at the same temperature, the amount of H₂ was even smaller while those of CO and CH₄ were even larger. Hence, reactions with NiO alone are different from those with NiO_x/TiO₂ catalysts and so NiO is not effective for our target H₂ production from aqueous glycerol solution, for which the significance of NiO_x - TiO₂ junction/contact is again illustrated.

Hydrogen could be produced through the two reactions in which one is photo-splitting of water and the other is photo-reforming of glycerol with water (Scheme 1). To examine the significance of the two reactions, the NiO_x/TiO₂ samples calcined at 250 °C, 450 °C, and 650 °C were also tested for the photocatalytic H₂ production from water in the absence of glycerol. The maximum H₂ production was observed to occur for the 450 °C calcined sample. However, it was only 6.6 μmol g⁻¹ h⁻¹, which was smaller by two orders of magnitude than that in the presence of glycerol. Hence, for a mixture of glycerol and water, the H₂ was evolved through photocatalytic reaction between the two.

The most active 450 °C calcined catalyst was further tested for longer reaction periods of time. Fig. 2 indicates the time profile obtained, showing that the H₂ production continued to occur at an almost fixed rate during the reaction up to 12 h and so the catalyst did not change in its activity.

Figure 2

In our reaction runs, gas chromatograph analysis was tried to detect possible liquid products of CH₃OH, HCOOH, CH₃OH, and C₂H₅OH. We failed to detect such products, which may be ascribed to low conversion of glycerol (< 0.05 % estimated

rough from the initial amount of glycerol used and the total amount of H₂ evolved in 4 h with the most active catalyst) and/or these should easily be changed to gaseous products by action of NiO.

The photocatalytic production of H₂ from aqueous glycol solution was recently studied over TiO₂ catalysts in the absence of costly noble metals [10-12]. Fornasiero et al. prepared several types of CuO_x/TiO₂ catalysts by different methods and showed that Cu nanoparticle embedded TiO₂ catalysts prepared by a water-in-oil microemulsion method have superior performance compared to conventional Cu/TiO₂ catalysts prepared by impregnation [10, 11]. The performance of our NiO_x/TiO₂ catalysts prepared by conventional impregnation is comparable to their Cu/TiO₂ catalysts. Lalitha et al. also studied the performance of CuO_x/TiO₂ catalysts prepared by impregnation and calcination at 350 °C and 450 °C [12]. The photocatalysts of Fornasiero et al. and Lalitha et al. are visible light sensitive. (Our NiO_x/TiO₂ catalysts have not been tested under visible light conditions due to the limitation of experimental setup.)

3.2. Catalyst characterization

The properties of NiO_x-loaded and unloaded TiO₂ samples calcined at different temperatures were examined by different methods. Table 1 shows the results of N₂ adsorption. The 650 °C calcined sample had a markedly decreased surface area of 14 m² g⁻¹. In contrast, the surface area of NiO_x-unloaded TiO₂ was observed to decrease to 43 m² g⁻¹, indicating that the significant decrease in the surface area of NiO_x-loaded TiO₂ by the calcination at 650 °C is induced by the doping of NiO_x. Fig. 3 gives XRD patterns and the bulk phase composition and other parameters determined thereof. The anatase/rutile ratio was 83/17 and the size of TiO₂ was 21 nm for NiO_x-unloaded mother TiO₂ sample. These structural parameters did not change by the NiO_x-loading and the following calcination at 250 °C and 450 °C. After the calcination at 650 °C, however, the phase composition changed drastically to an anatase/rutile ratio of 9/91. The phase composition also changed by the calcination for NiO_x-unloaded TiO₂ but less markedly; the anatase/rutile ratio decreased to 59/41 by the calcination at 650 °C. Thus, the phase transformation of TiO₂ during the calcination was assisted by the presence of NiO_x species. The average TiO₂ crystallite size increased with the temperature but marginally. For the NiO_x-loaded samples calcined at 250 °C and 450 °C, NiO was detected, the size being 4 - 6 nm; NiO was highly dispersed on the surface of TiO₂. On calcination at 650 °C, the NiO changed to NiTiO₃ with an average size of 51 nm and the BET surface

decreased significantly to $14 \text{ m}^2 \text{ g}^{-1}$.

Table 1, Figure 3

Fig. 4 shows UV/Vis spectra of those NiO_x -loaded and unloaded TiO_2 samples. The loading of 10 wt% NiO_x was found to have a significant impact on the absorption at wavelength $> 350 \text{ nm}$. The NiO_x loading strengthened the absorption in this range of wavelength, depending on the calcination temperature used. These data were reformed to a plot of $(\text{Absorbance} \cdot \text{Energy})^{1/2}$ against Energy in Fig. 4(b). For NiO_x -unloaded TiO_2 , the band gap was estimated to be 2.75 eV; while, for the NiO_x -loaded samples calcined at 250 °C and 450 °C, it was lowered to 2.17 eV. The difference was 0.58 eV. The decrease in the band gap energy may be one of factors responsible for the enhanced H_2 production rate observed with the 250 °C and 450 °C calcined $\text{NiO}_x/\text{TiO}_2$ catalysts (Fig. 1). The band gap of TiO_2 depends on its structure, being 3.2-3.3 eV for anatase TiO_2 [19, 21] and 3.0-3.1 eV for rutile TiO_2 [20, 21]. In our samples, the phase composition did not change by the loading of NiO_x and the calcination at temperatures of 250 °C and 450 °C (Table 1). Therefore, the decrease in the band gap observed should result from the formation of NiO_x and TiO_2 junction. This desirable N - P junction was likely to be destroyed after the calcination at a higher temperature of 650 °C, at which NiO_x changed to NiTiO_3 (Fig. 3).

Figure 4

The catalysts were further characterized by XPS measurements. Fig. 5 shows Ni_{2p} , Ti_{2p} , and O_{1s} XPS spectra collected with the NiO_x unloaded and loaded TiO_2 samples calcined at different temperatures. For the unmodified TiO_2 , the binding energy (BE) values of $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ were 458.5 eV and 464.5 eV, respectively, the difference being 6 eV. These peaks may come from anatase TiO_2 species and a shoulder peak at 457 eV from rutile TiO_2 species. The loading of NiO_x and the following calcination caused significant changes: the 650 °C calcined sample had a peak at a BE of 464 eV but no other peaks were detected, in which the surface Ti species should be in a structure different from anatase and rutile TiO_2 species. The 450 °C calcined sample also had a peak at a similar BE along with a small peak at about 457 eV. The latter peak indicated that a small amount of Ti species of rutile structure remained on its surface. The 250 °C calcined may be on a way of changing from a mixture of anatase and rutile Ti species to other structures. A similar significant change was observed for O 1s. The NiO_x -unloaded TiO_2 sample had a peak at 529.5 eV while the 450 °C and 650 °C

calcined ones had a peak at a larger BE of 535 eV. According to the literature, the BE values of NiO and Ni₂O₃ are 529.7 eV and 531.5 eV, respectively. The spectra of Ni 2p were a little noisy but the peaks were detected at 860 eV and 865 eV. The BE values of Ni 2p_{3/2} of metallic Ni, NiO, NiAl₂O₃, and NiWO₄ are 852.3 eV, 853.3 eV, 857.2 eV, and 857.6 eV, respectively, [17], which are smaller compared to the peaks observed with the NiO_x-loaded calcined TiO₂ samples. At present, unfortunately, it is difficult to determine the surface Ni-Ti-O structure but it may be assumed that the above-mentioned NiO_x - TiO₂ junction was formed for the calcined NiO_x/TiO₂ samples. Very recently Iwaszaki et al. investigated the performance of NiO_x-loaded TiO₂ catalysts for the photocatalytic degradation of 2-naphthol and *p*-cresol and discussed their high performance after considering their structural features estimated theoretically by density functional theory simulations [16]. It is assumed that NiO clusters have a strong interaction with the surfaces of anatase and rutile TiO₂ through Ni-O-Ti bonds and additional Ni-Ti bonds for rutile TiO₂. These structural changes caused by NiO loading can reduce the band gap energy.

Figure 5

Hence, it can be said that the loading of NiO_x onto TiO₂ and the following calcination cause the band gap energy to lower by 2.5 eV and this is one of factors responsible for the enhancement of the photocatalytic activity in H₂ production from glycerol and water. The maximum H₂ evolution is obtained with 450 °C calcined NiO_x/TiO₂ sample. However, when the calcination temperature is raised to 650 °C, the surface properties (XPS and UV/Vis) are similar to those of the 450 °C calcined sample but the BET surface area is markedly lowered and so this results in a lower activity.

Under the reaction conditions used, the conversion of glycerol was so small that it was difficult to determine its conversion and detect liquid products. These pieces of information may be necessary to make a discussion on reaction mechanisms over NiO_x/TiO₂ catalysts. A few authors discuss the mechanisms of photocatalytic reforming of glycerol over Pt/TiO₂ [5] and CuO_x/TiO₂ [12]. Daskalaki and Kondarides assume that hydroxyl radicals and other oxidants are photogenerated from water and these oxidize and change organic compounds towards lower molecular weight compounds, eventually to CO₂. The photocatalytic reforming of glycerol producing H₂ should occur through those reaction processes. Lalitha et al also assume several processes for the photocatalytic production of H₂ from glycerol over CuO_x/TiO₂ catalysts [12].

4. Conclusions

NiO_x-loaded TiO₂ catalysts are active for the photocatalytic production of H₂ from aqueous glycerol solution at 50 °C. The activity can remain unchanged in a long time of 12 h at least. The catalytic performance of NiO_x/TiO₂ depends significantly on calcination temperature. The maximum activity can be achieved after the calcination at 450 °C. The calcination temperature would influence the formation of n-type (NiO_x) and p-type (TiO₂) junction. The calcination at 450 °C decreased the band gap energy by 0.58 eV with respect to the mother TiO₂ material, which was responsible for the improved H₂ production. The calcination at a higher temperature of 650 °C caused a significant decrease in the surface area, reducing the catalytic performance.

Acknowledgements

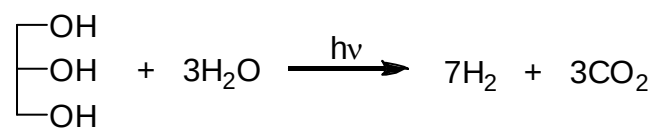
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Scheme, Figures, Table in the order of appearance:



Scheme 1 Photocatalytic reaction between glycerol and water

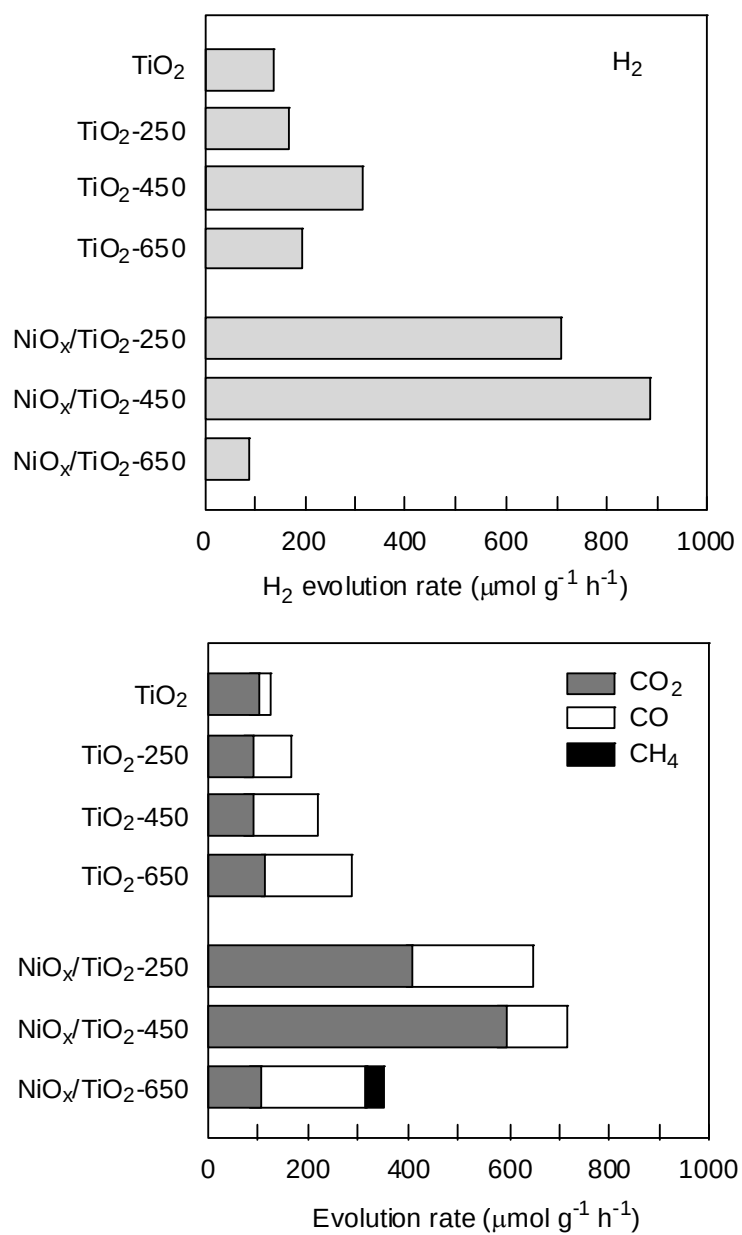


Fig. 1 Evolution of H₂ (upper) and other gaseous products (bottom) in photocatalytic reaction at 50 °C between glycerol and water with NiO_x-unloaded and loaded TiO₂ samples uncalcined and calcined at 250 °C, 450 °C, and 650 °C.

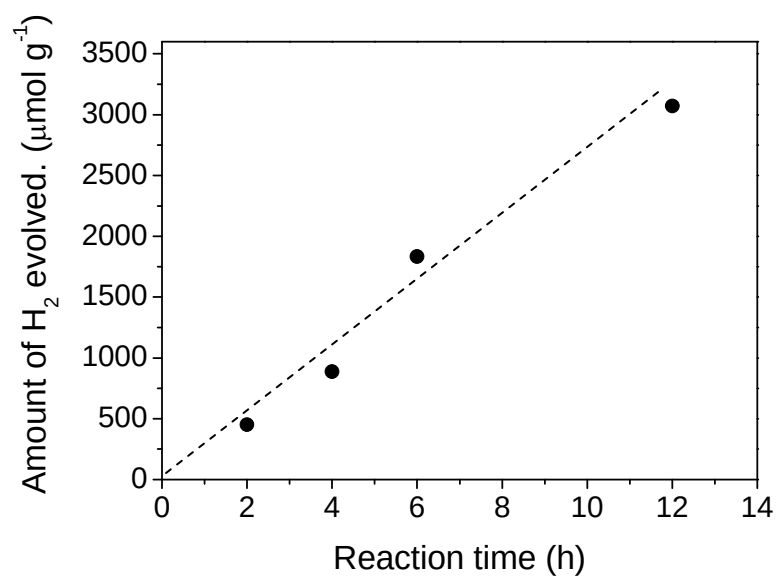


Fig. 2 Time profile of the H₂ evolution in photocatalytic reaction between glycerol and water at 50 °C with NiO_x/TiO₂ catalyst calcined at 450 °C

Table 1 Structural properties of NiO_x/TiO₂ catalysts determined by N₂ adsorption and XRD measurements

Catalyst	Anatase/rutile ratio	Crystallite size ^a (nm)			Surface area (m ² g ⁻¹)
		TiO ₂	NiO	NiTiO ₃	
TiO ₂	83/17	21	–	–	50
NiO _x /TiO ₂ 250 °C ^b	80/20	22	4	–	54
NiO _x /TiO ₂ 450 °C ^b	80/20	23	6	–	50
NiO _x /TiO ₂ 650 °C ^b	9/91	27	–	51	14

a. The average crystallite size of TiO₂ was calculated by following equation: $D_{ave} = D_a * [I_a / (I_a + I_r)] + D_r * [I_r / (I_a + I_r)]$, where D_{ave} is average crystallite size and D_a and D_r are crystallite size of anatase d(101) and rutile d(110), respectively. I_a and I_r are the peak intensity of anatase d(101) and rutile d(110), respectively. The ratio of anatase and rutile was determined by the equation $W_r = 1 / [1 + 0.8 * (I_a / I_r)]$ and $W_a = 1 - W_r$, where W_a and W_r are the mole ratio of anatase and rutile. The average crystallite size of NiO and NiTiO₃ were calculated by the Scherrer's formula, $D = 0.9 * \lambda / (\beta_{1/2} * \cos\theta)$, λ is the wavelength (0.15418 nm Cu K α radiation) of the X-ray, $\beta_{1/2}$ line-width at medium height of anatase d(101), rutile d(110), NiO d(200) and NiTiO₃ d(104), and θ the diffraction angle. For these calculation procedures, see Refs. [22-24].

b. Calcination temperature.

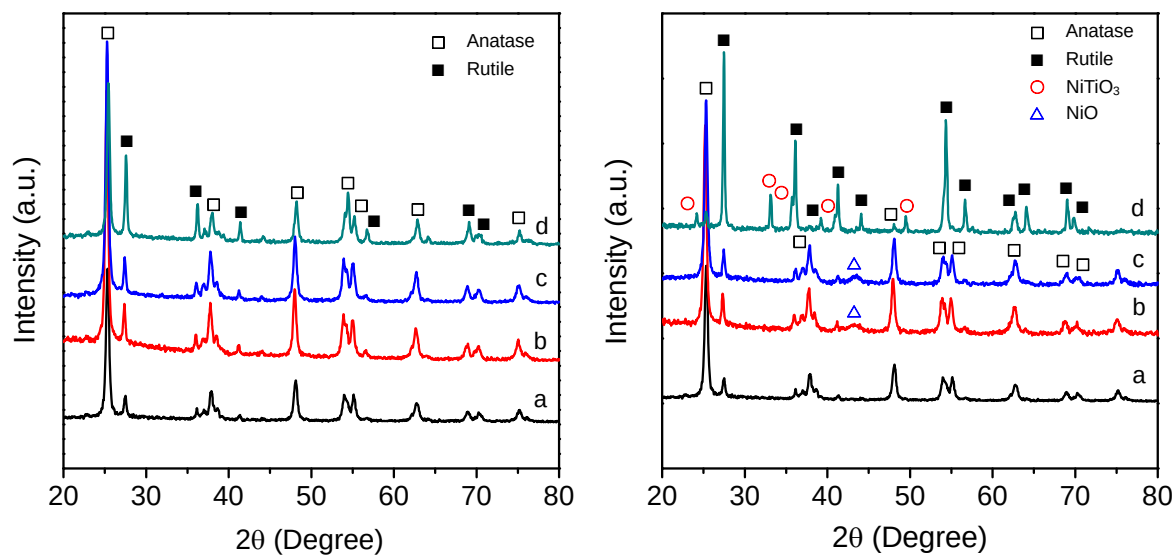


Fig. 3 XRD patterns (left) for NiO_x-unloaded TiO₂ samples untreated (a) and calcined at 250 °C (b), 450 °C (c), and 650 °C (d) and (right) for NiO_x-unloaded (a) and loaded TiO₂ samples calcined at 250 °C (b), 450 °C (c), and 650 °C (d)

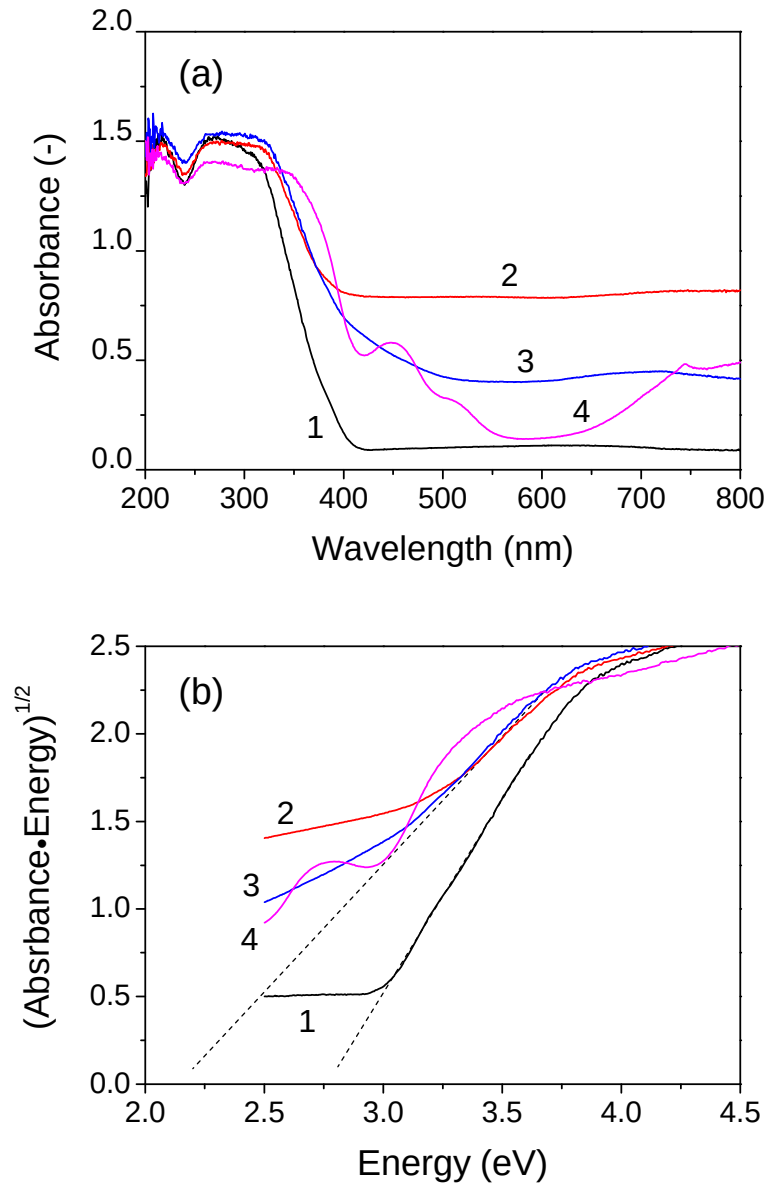


Fig. 4 (a) UV/Vis spectra measured for NiO_x-unloaded (1) and loaded TiO₂ samples calcined at different temperatures of 250 °C (2), 450 °C (3), and 650 °C (4). (b) Plot of $(\text{Absorbance} \cdot \text{Energy})^{1/2}$ against Energy obtained from the data (a).

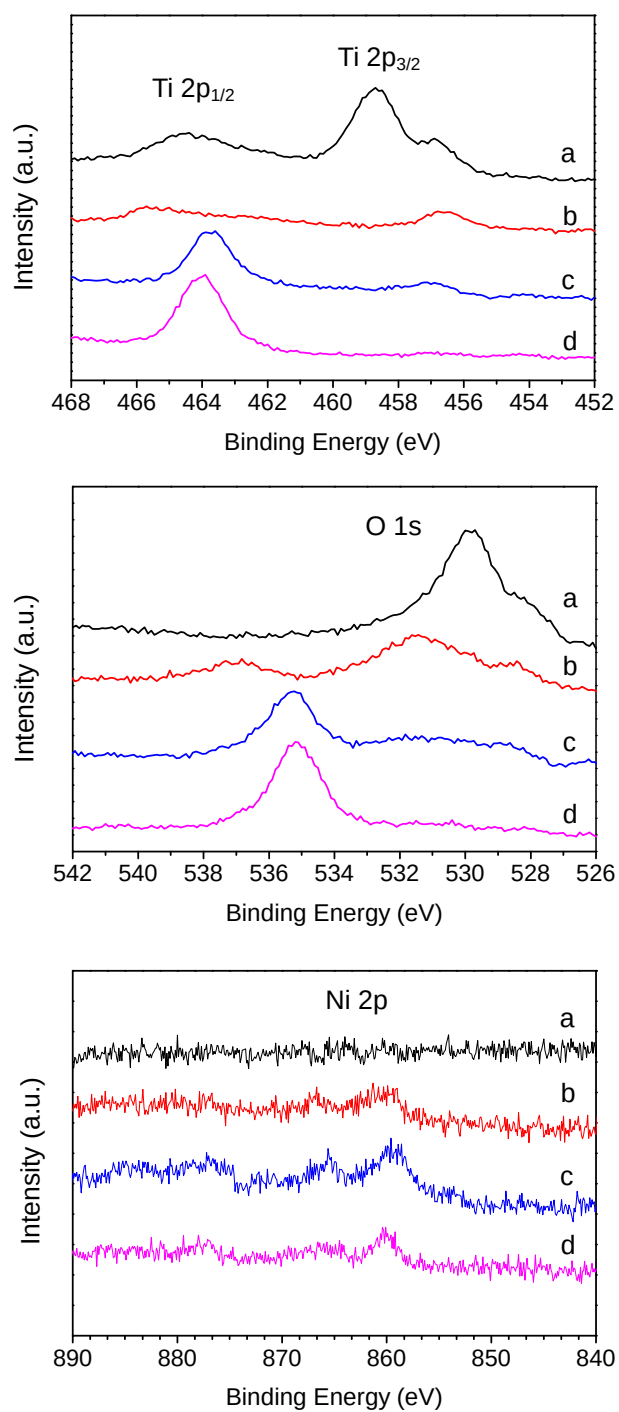


Fig. 5 XPS spectra of Ti 2p, O 1s, and Ni 2p for the NiO_x-unloaded (a) and loaded TiO₂ samples calcined at 250 °C (b), 450 °C (c), and 650 °C (d)