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Titanium-Indium Oxy(nitride) with and without RuO₂ loading as Photocatalysts for Hydrogen Production under Visible Light from Water

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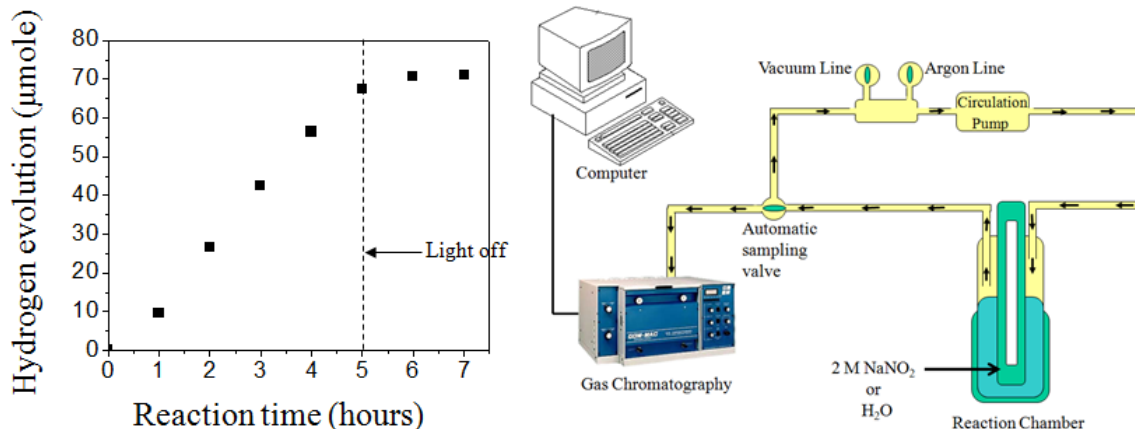
Abstract

Titanium-indium (oxy)nitride composite materials with and without RuO_2 loadings were produced by treating $\text{TiO}_2\text{-In}_2\text{O}_3$ mixed powders with ammonia at high temperature (700-850 °C) (Elemental analysis indicated an empirical formula of $\text{TiIn}_{0.029}\text{O}_{0.63}\text{N}_{1.4}$).

We have found that ammonolysis of TiO_2 to form Ti (oxy)nitride or In_2O_3 to form In (oxy)nitride do not give composites active toward methanol-water under visible light, but TiO_2 and In_2O_3 mixed together do give composites active toward methanol-water under visible light. Ti-In (oxy)nitride powders modified by surface loading with RuO_2 nanoparticles at 3 wt % achieves the highest H_2 evolution activity under visible light irradiation. The composite material did not react in the dark, but upon irradiation with visible light, the hydrogen production rate under illumination goes way up to $30 \mu\text{mole}\cdot\text{h}^{-1}$ and the turnover number shows that this is a photocatalytic reaction.

Graphical abstract

Photocatalytic H_2 evolution test



Highlights

► Titanium-Indium Oxy(nitride) with and without RuO₂ loading as Photocatalysts were investigated. ► 3 wt% RuO₂-loaded Ti-In oxy(nitride) composites showed higher catalytic performance than the other photocatalysts. ► The XPS data shows Ti⁴⁺ could be reduced to 3+ and 2+ upon ammonia treatment with In₂O₃ presence. ► It was found that the treatment temperature increased from 750 to 850 °C, the composites began to aggregate because of growth of the TiO₂ (anatase).

Keywords: H₂ evolution; Photocatalysts; Ru co-catalyst; Titanium Dioxide; Indium Oxide

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1. Introduction

Osterloh[1] has recently reviewed inorganic materials for photochemical water splitting. Over 130 inorganic materials/composites are mentioned. Metal nitrides and metal-oxynitride composites have also received some study, such as β - Ge_3N_4 and GaN:ZnO solid solution prepared from commercially available GeO_2 powder or a mixture of Ga_2O_3 and ZnO by nitridation under atmospheric NH_3 flow, respectively, and loaded with RuO_2 as co-catalyst.[2, 3] These studies revealed that the photocatalytic activity for water splitting depends on the crystallinity and composition of the material. Moreover, evidence shows that using nitrogen to replace Oxygen in TiO_2 to form $\text{TiO}_{2-x}\text{N}_x$ can enhance photocatalytic activities under visible light.[4, 5]

Additionally, Poznyak and co-workers have investigated the photoelectrochemical properties of nanocrystalline $\text{TiO}_2/\text{In}_2\text{O}_3$ composite solids.[6] It was shown that $\text{TiO}_2/\text{In}_2\text{O}_3$ composites allow efficient separation of photogenerated charge carriers occurring in interconnected TiO_2 and In_2O_3 particles, owing to the favorable energetics of the conduction bands of these oxides. Another report shows that nitrogen-doped In_2O_3 thin film electrodes are effective for photocatalytic water splitting.[7] Therefore, it may be possible to combine the TiO_2 property of formation of electrons and holes by absorbing light and then using the interconnection between TiO_2 and In_2O_3 to transfer the holes to In_2O_3 . Moreover, the nitrided treatment of a mixture of titanium oxide and indium oxide may be effective to enhance absorption of visible light. In our research, optimal preparation conditions were investigated in order to achieve the best hydrogen production under visible light. Reported herein are our results with methanol-water solutions.

2. Experimental

2.1. Preparation of Ti-In nitride composites with and without RuO₂

Composite powders were prepared by heating a mixture of 0.92 g (1.2×10^{-2} mol) anatase TiO₂ powder (Sigma-Aldrich, anatase, nanopowder, <25nm, 99.7%) and 3.2 g (1.2×10^{-2} mol) In₂O₃ powder (Sigma-Aldrich, nanopowder, <100nm, 99.9%) at different temperatures under NH₃ flow (250 mL/min) for 20 hours as shown in Fig. 1 (The reaction chamber diameter is 4.5 cm). The mole ratio of Ti to In in the starting material (TiO₂ and In₂O₃) was 1/1, which should give a Ti:In ratio of 1:2 (although, in reality, much of the indium was lost during the ammonia treatment; see later discussion). After 20 hours of ammonolysis, the sample was cooled to room temperature under NH₃ flow.

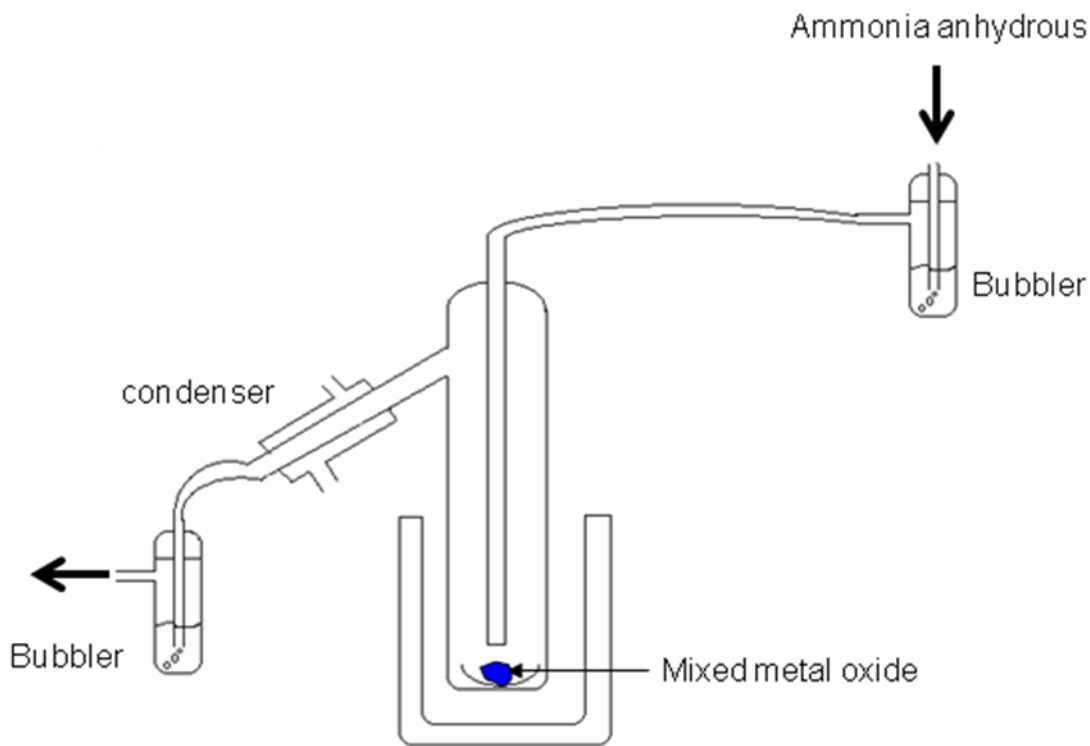


Fig. 1. Experimental setup for nitridation of TiO₂/In₂O₃ mixture.

RuO₂ was loaded onto the as-prepared Ti-In nitride powders as a co-catalyst by immersing the Ti-In nitride composite powders in a tetrahydrofuran (THF) solution containing dissolved ruthenium(III) acetylacetonate (purity, ≥97.0% (CH), Fluka) and stirring. The solution was then dried under air by heating in air at 80 °C to remove THF. The obtained powders were finally annealed in air at 400 °C for 4 h.

2.2 Photocatalytic activity

The reactions were carried out in a glass-enclosed reaction chamber connected to a gas circulation and evacuation system with a quartz inner irradiation-type reaction vessel.[8] The apparatus contained 345 ml 10 vol% methanol-water solution with 0.13 g sulfuric acid and 0.30 g of the composite RuO₂-loaded Ti-In (oxy)nitride. The reactant solution was evacuated and filled with argon three times to remove air completely, followed by irradiation ($\lambda > 400$ nm) under a 450 W high-pressure Hg lamp via a quartz tube that was air filled for full spectrum UV-vis studies, or filled with 2 M NaNO₂ aqueous solution for visible light studies.[3] The reaction temperature was controlled between 20 to 25 °C. H₂ production was monitored during the reaction with an online GC system (GOMAC model) employing a Supelco molecular 80/100 sieve 5A column with Ar as the carrier gas and a thermal conductivity detector (TCD).

2.3. Characterization of composites

The prepared samples were studied by powder X-ray diffraction (XRD; Bruker D8 X-ray diffractometer with Cu K α radiation), scanning electron microscopy (SEM; Hitachi S-3500 N), UV-visible diffuse reflectance spectroscopy (DRS; Varian Cary 500 Scan).

The Brunauer, Emmett, Teller (BET) surface area was measured with a Quantachrome NOVA-1200 instrument at liquid nitrogen temperature. X-ray photoelectron spectroscopy (XPS) was conducted using a SPECS Sage100 spectrometer operating in the fixed analyzer transmission mode using achromatic Mg K α (1253.6 eV) radiation at 240 W (12 kV and 20 mA) using a water-cooled X-ray gun cap and evacuated with turbomolecular pumping. The base pressure of the chamber was about 2×10^{-8} Torr, and the energy scales were calibrated using copper and the separation between photoelectron peaks generated by Mg and Al K α X-rays. Survey spectra were collected with a pass energy of 30 eV; a pass energy of 15 eV was used for both core and valence band spectra. Many of the spectra were calibrated by taking the C 1s peak due to residual hydrocarbon as being at 284.4 eV.

3. Results and Discussion

3.1. Characterization of Ti-In oxy(nitride) composites

Fig. 2 shows XRD patterns from samples obtained by nitridding a mixture of TiO₂ and In₂O₃ at several ammonolysis temperatures. TiO₂, In₂O₃ and TiN data are shown for comparison. All composites' patterns are similar to TiN and the peak assignments are based on the ICSD database. None of the diffraction peaks of starting materials were observed, indicating that the obtained samples were not physical mixtures of TiO₂ and In₂O₃. The peak around 34° corresponds to both InN and In metal. The XRD data demonstrate that an ammonolysis temperature above 850 °C, caused an increase of In metal formation (which was generally lost due to the volatility). It is known that In₂O₃ is

reduced to metallic Indium upon ammonolysis of Indium oxide by anhydrous ammonia

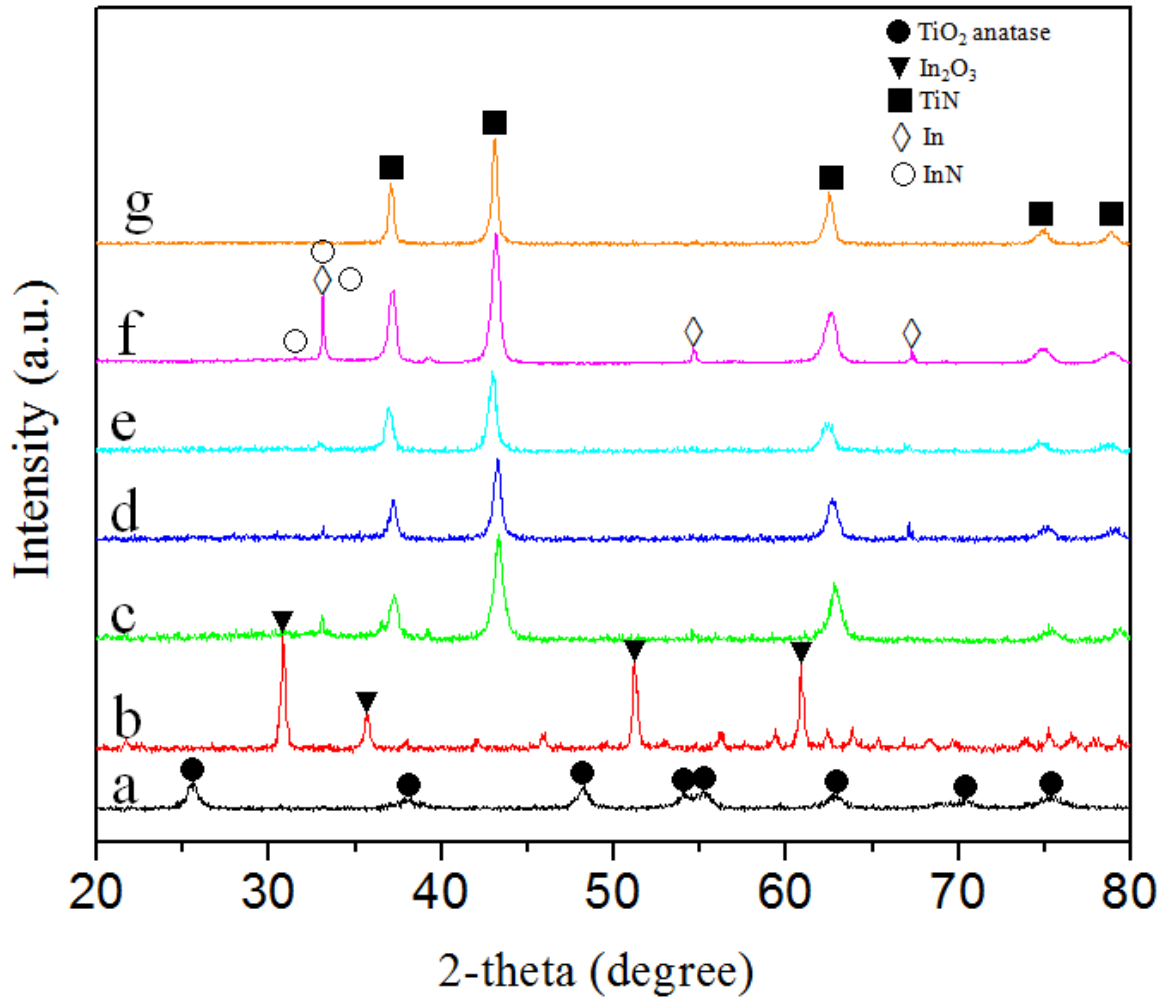


Fig. 2. Powder XRD patterns of Ti-In oxy(nitride) composites obtained by different ammonolysis temperatures samples. (c) 700 °C (d) 750 °C (e) 800 °C (f) 850 °C.

*(a) TiO₂ anatase (b) In₂O₃ (g) TiN for comparison.

above 650 °C.[9] Indeed, we found that starting with only In₂O₃ and then nitridation, indium metal was produced under the action of hot NH₃. The high ammonolysis temperature not only reduced In³⁺ into In, but also could cause InN decomposition. Decomposition temperatures reported for InN range from 500 °C for thin films[10, 11] to 710 °C. In our research, even when the ammonolysis temperature was above 700 °C,

some InN persisted when TiO₂ was also present as a co-reactant. Therefore, combining TiO₂ and In₂O₃ not only created H₂ production activity, but also helped to stabilize InN.

We have examined four areas of the XPS spectra for several samples : the Ti 2p region (466-453 eV), In 3d region (450-454 eV), the O 1s region (525-537 eV), and the N 1s region (394-400 eV). The survey spectra of all the Ti-In (oxy)nitride powders confirmed the presence of Ti, In, O, N and C. The binding energies (BEs) were calibrated using the C 1s energy of 284.4 eV as an internal calibration.

The Ti 2p_{3/2} has three peaks (Fig. 3A), 458.5 eV, 457 eV and 455.6 eV. Ti 2p_{5/2} has three peaks, 463.9 eV, 462.5 eV and 461.3 eV. They are in agreement with the values reported in the literature for Ti⁴⁺, Ti³⁺ and Ti²⁺, respectively.[9, 12] The XPS data show that the ammonolysis process can reduce Ti⁴⁺ to lower oxidation states. Moreover, the low ammonolysis temperature samples have a higher ratio of Ti⁴⁺, which shows the higher ammonia treatment temperature causes more reduction of Ti⁴⁺ into Ti³⁺ or Ti²⁺. One interesting finding was that there was no Ti³⁺ and Ti²⁺ formation when only TiO₂ was nitrated by hot NH₃. This again, suggests that there is an important synergistic interaction between In and Ti during the nitridation.

As shown in Fig. 3B, The In core spin orbit split to the 3d_{5/2} peak at 444.5 eV. These results are close to the reported values for bulk InN (444.3 eV). [7, 13] Therefore, XPS further confirms the formation of InN.

Regarding the XPS spectra after photocatalytic reaction, In 3d_{3/2} XPS spectra (Fig. 3) shows loss of intensity for low ammonolysis temperature samples, which suggests that the lower temperatures yield less stable nitrides. But if the ammonolysis temperature exceeds 850° C, most of the In was sublimed and lost, and only TiN remained. The

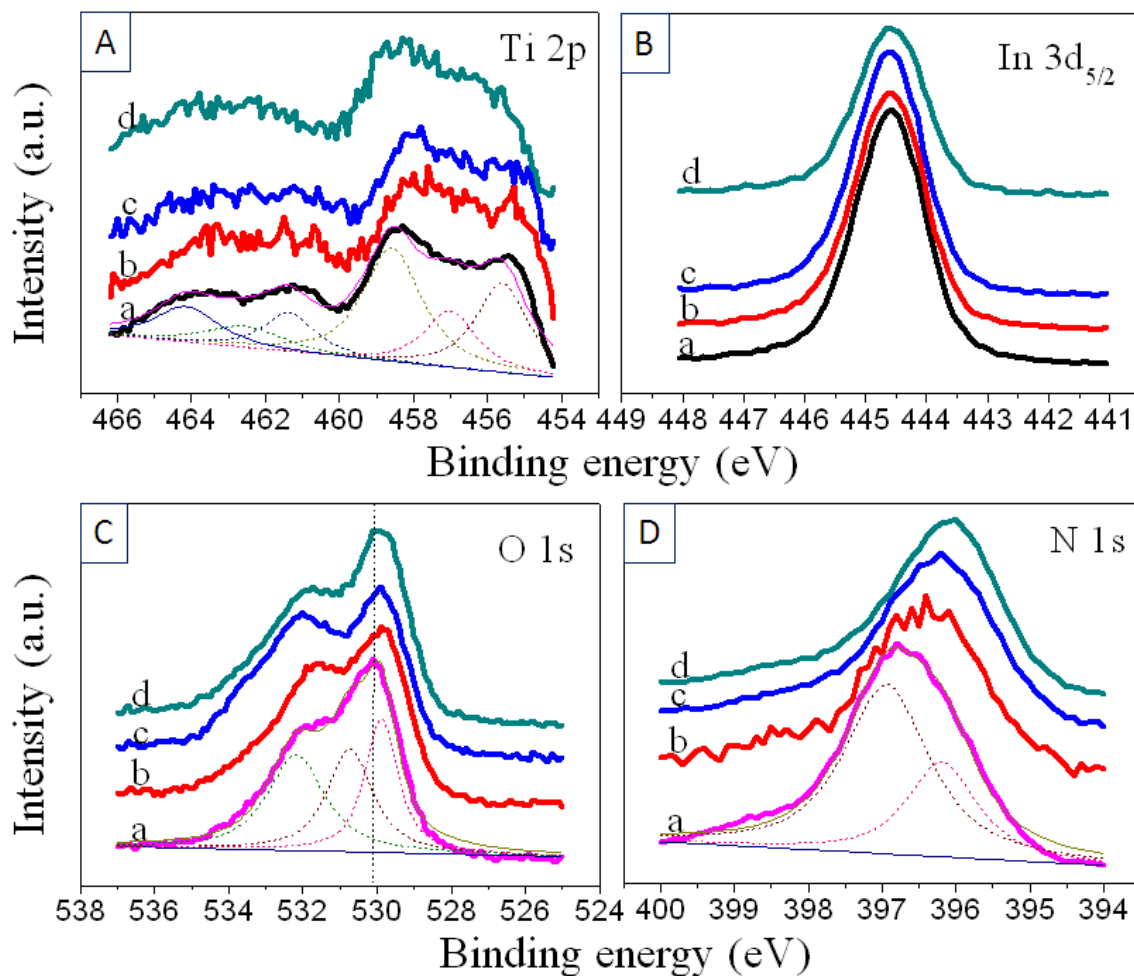


Fig. 3. XPS spectra of Ti-In oxy(nitride) composites obtained by different ammonolysis temperatures. (a) 850 °C (b) 800 °C (c) 750 °C (d) 700 °C.

resulting sample had poor H_2 production activity. Therefore, a suitable ammonolysis temperature is very important, which has to be high enough to allow N doping, but not too high to further reduce In^{3+} into In metal. All $In\ 3d_{3/2}$ XPS spectra (Fig. 3) show the shifting to higher BE after the reaction, which indicates that some of the doped nitrogen was replaced by oxygen.

Fig. 3C shows that the O 1s core level is composed of at least three components. The peak positions and intensities are reliably determined by a standard curve fitting procedure using XPSPEAKS software. The O 1s signal at 529.8 eV is assigned to In_2O_3

and TiO₂ according to the literature,[14] while the signal at 530.8 eV is probably due to oxygen in surface adsorbed hydroxyl groups[15] and the signal at 532.1 eV is from the surface adsorbed H₂O. Low ammonolysis temperature samples show a small shift to lower energy (529.0 eV) for the O 1s peak that is assigned to In₂O₃ and TiO₂. This shift is similar to results found for substitutional N-doped TiO₂ samples, in which the P25 TiO₂ sample shows an O 1s peak at 530.8 eV, versus a shift to 530.0 eV that is observed for the nitrogen-doped TiO₂ samples.[16]

The N 1s XPS spectrum in Fig. 3D has two components: 396.9 eV and 396.2 eV. The N 1s XPS data confirms the N is substitutional instead of interstitial. [4, 5, 17] The 396.9 eV peak could be assigned to Ti-N, and In-N is at 396.2 eV because Ti has a higher electronegativity than In. The XPS high-resolution spectra of N 1s show the 850 °C ammonolysis sample's peak at 396.7 eV with a slight shift to 396.1 eV for the 700 °C sample (Fig. 3D). The difference of 0.6 eV between these two N 1s peaks correlates with InN formation for the N 1s state in substitutional sites. Therefore, the data (Fig. 3D) shows more formation of N in substitutional sites under higher ammonolysis temperature conditions.

3.2. Photocatalytic activity of Ti-In oxy(nitride) composites

Fig. 4 shows the hydrogen production activity of a Ti-In oxy(nitride) composite (ammonolysis at 700 °C) in 10 vol% methanol-water solution under visible light. In the dark, there was no activity observed. However, after the light was on, the reaction can be driven by visible light, producing ~0.5 μmole·h⁻¹ H₂ gas. The activity stabilized, and

continued to produce H₂ gas for over 200 hours. H₂SO₄ was added to adjust solution pH to acidic condition, the photocatalytic activity was not enhanced.

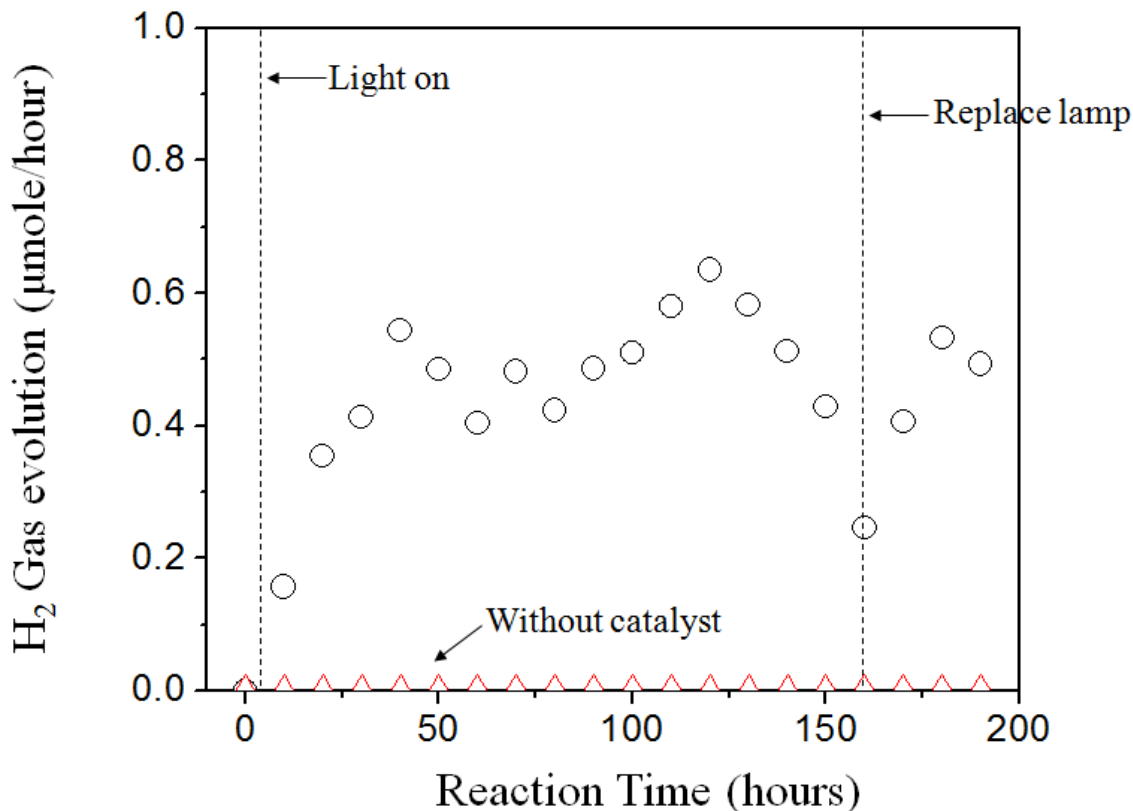


Fig. 4. Dependence of visible light hydrogen production activity of a Ti-In oxy(nitride) composite (ammonolysis at 700 °C) without RuO₂. Catalyst (0.3g), an 10 vol% methanol-water solution; light source, high-pressure mercury lamp (450 W) with 2M NaNO₂ solution as a filtration. Inner irradiation-type reaction vessel. Reaction temperature was controlled between 20 to 25 °C.

3.3. Photocatalytic activity of RuO₂-loaded Ti-In oxy(nitride) composites

Ti-In oxy(nitride) composites alone exhibited only small photocatalytic activity for hydrogen evolution. However, when loaded with RuO₂, the material became much more photocatalytically active. Fig. 5 shows the dependence of visible light activity of different ammonolysis temperatures RuO₂-loaded (1 wt%) Ti-In (oxy)nitride samples in pH adjusted (sulfuric acid) 10 vol% methanol-water solution. (In this work, methanol is used

as a sacrificial agent so that the best condition for the hydrogen evolution step can be ascertained.[18]) The hydrogen production activity was observed at a higher rate. The light source was turned off after 5 h (Fig. 5), and no hydrogen evolution activity was

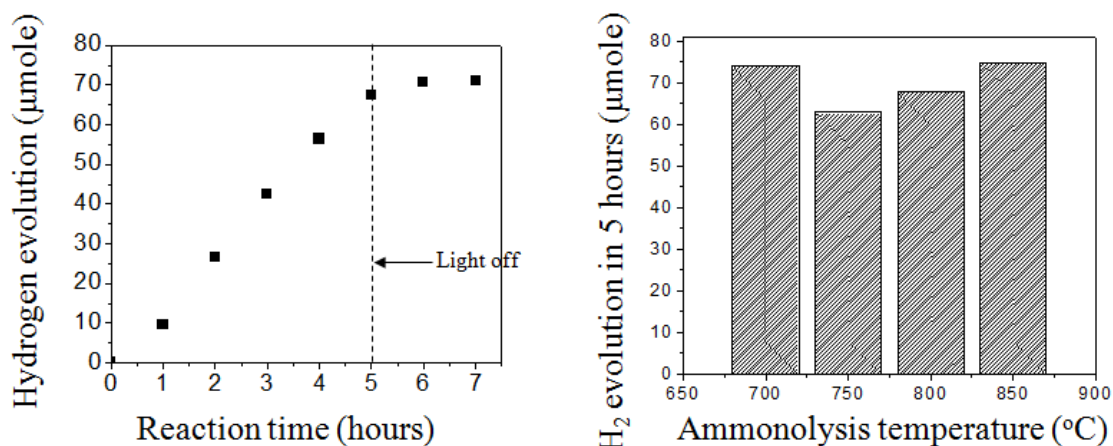


Fig. 5. Dependence of visible light hydrogen production activity of RuO₂-loaded (1 wt %) Ti-In oxy(nitride) composites obtained by different ammonolysis temperatures samples. Catalyst (0.3g), an methanol-water solution (10 vol %); light source, high-pressure mercury lamp (450 W) with 2M NaNO₂ solution as a UV light filter. Inner irradiation-type reaction vessel. Reaction temperature was controlled between 20 to 25 °C.

noted, indicating that this is a photo-driven reaction. Moreover, the maximum rate of H₂ evolution was 14 μmole·h⁻¹. The amount of the RuO₂-loaded Ti-In oxy(nitride) photocatalyst used contained 22 μmol of RuO₂. The number of electrons consumed was estimated to be 516 μmol judging from the amount of evolved H₂. The electron turnover number to amounts of loaded RuO₂ reached 23, respectively, after 45 h of irradiation. Therefore, by this measure it can be concluded that H₂ evolution photocatalytically proceeded.

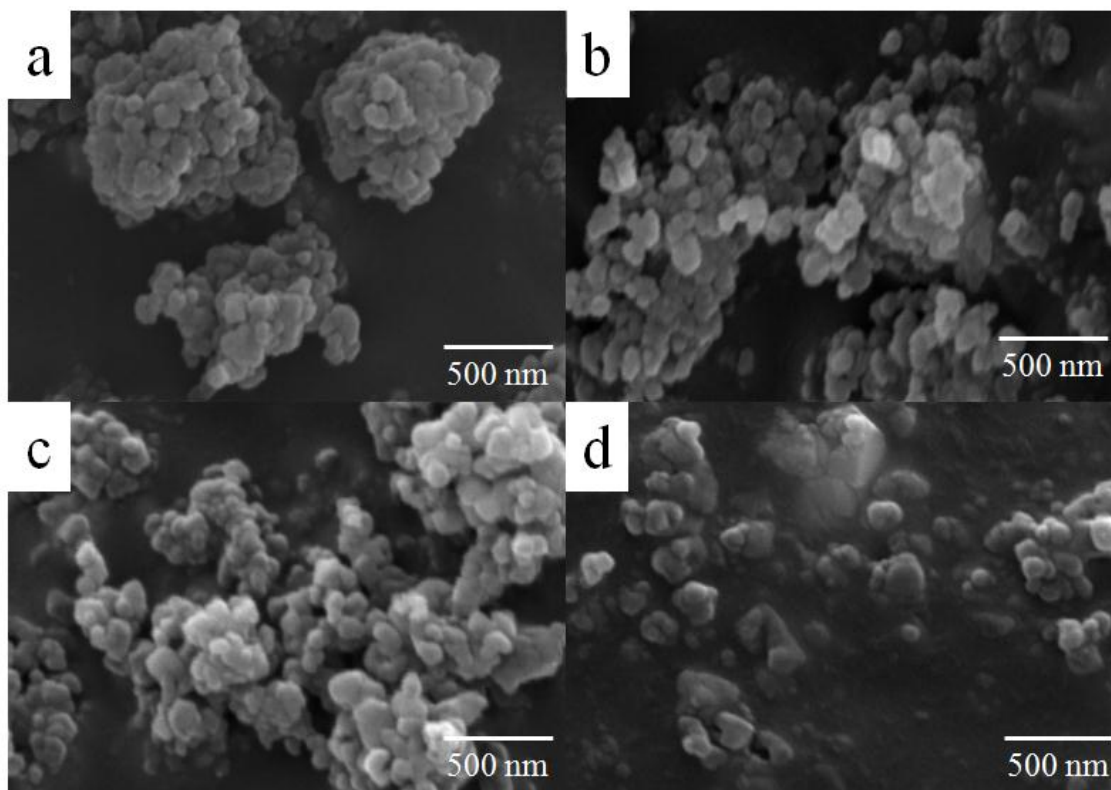


Fig. 6. SEM images of RuO₂-loaded (1 wt %) Ti-In oxy(nitride) composites obtained by different ammonolysis temperatures. (a) 700 °C (b) 750 °C (c) 800 °C (d) 850 °C.

The surface morphologies of RuO₂-loaded Ti-In oxy(nitride) composites are presented in Fig. 6. The average particle size of the individual units of the sample treated at 700 °C was about 20 nm (Fig. 7). However, as the treatment temperature increased from 750 to 850 °C, the units began to aggregate and the boundaries between them became increasingly unclear because of growth of the TiO₂ (anatase) (Fig. 8, inset).

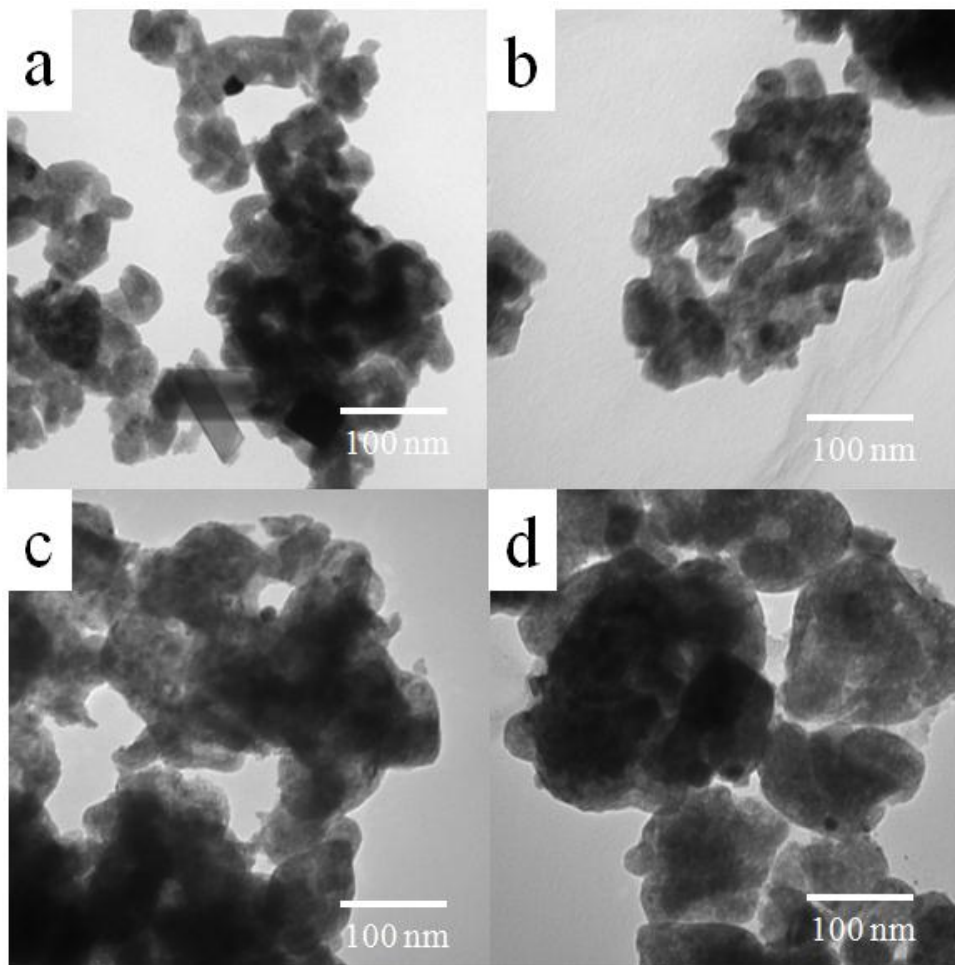


Fig. 7. TEM images of RuO₂-loaded (1 wt %) Ti-In oxy(nitride) composites obtained by different ammonolysis temperatures. (a) 700 °C (b) 750 °C (c) 800 °C (d) 850 °C

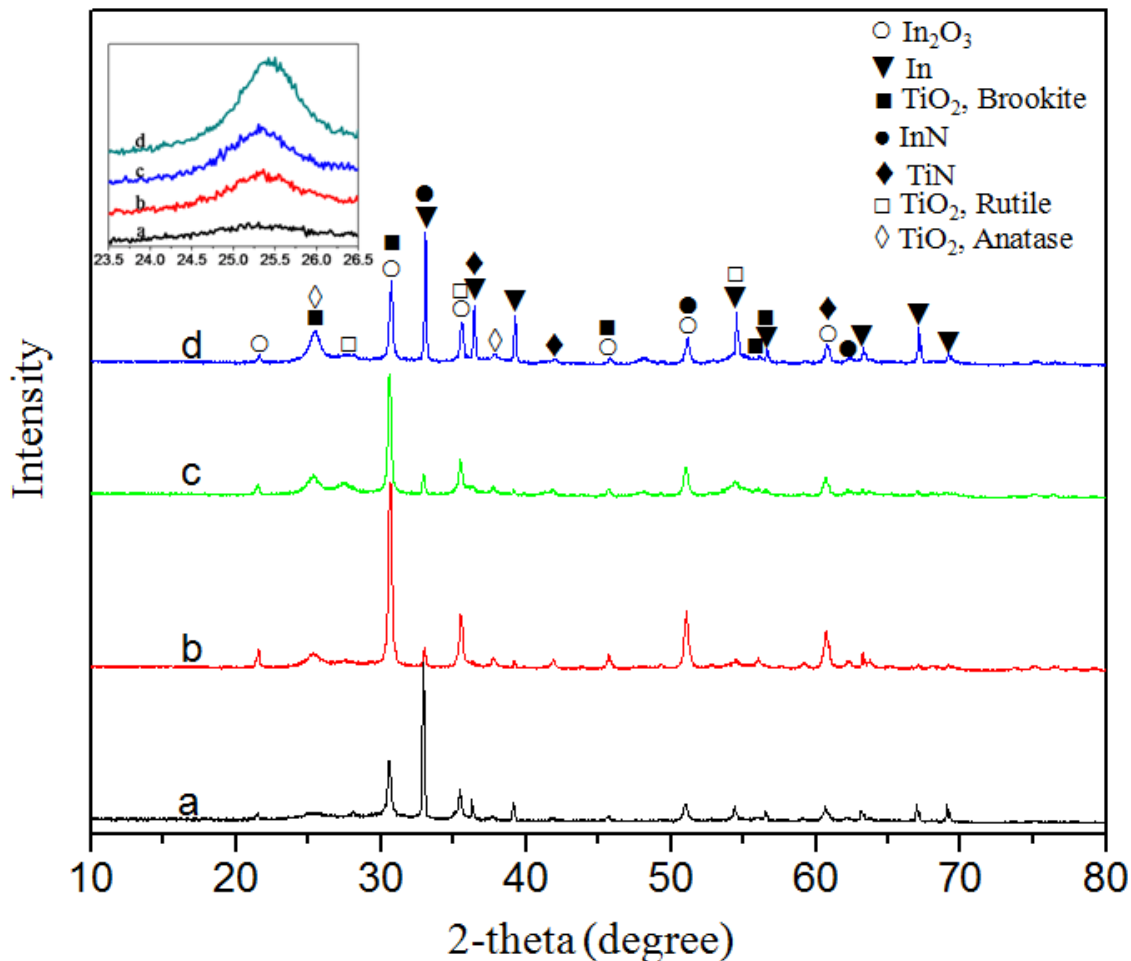


Fig. 8. Powder XRD patterns of RuO₂-loaded (1 wt %) Ti-In oxy(nitride) composites obtained by different ammonolysis temperatures. (a) 700 °C (b) 750 °C (c) 800 °C (d) 850 °C

Table 1 shows the hydrogen production activity of different RuO₂-loaded Ti-In oxy(nitride) (ammonolysis at 750 °C) composites in pH adjusted (sulfuric acid) water-methanol under visible light. The photocatalytic activity increased markedly with increasing RuO₂ content to a maximum at about 3 wt %, with the activity dropping at higher RuO₂ contents. Fig. 9 shows UV-Visible diffuse reflectance spectra for solid composites prepared with different RuO₂-loading amounts, and show an increase in

Table 1

Photocatalytic activity of different RuO₂-loaded Ti-In oxy(nitride) (ammonolysis at 750 °C) composites and Ti oxy(nitride) under visible light in methanol-water solution (10 vol%) .

Samples	RuO ₂ -loaded amount (wt%)	H ₂ evolution accumulated in 5 hours (μmole)
Ti oxy(nitride)	0	0
Ti-In oxy(nitride)	0	0.25
Ti-In oxy(nitride)	1	60
Ti-In oxy(nitride)	2	80
Ti-In oxy(nitride)	3	150
Ti-In oxy(nitride)	4	120

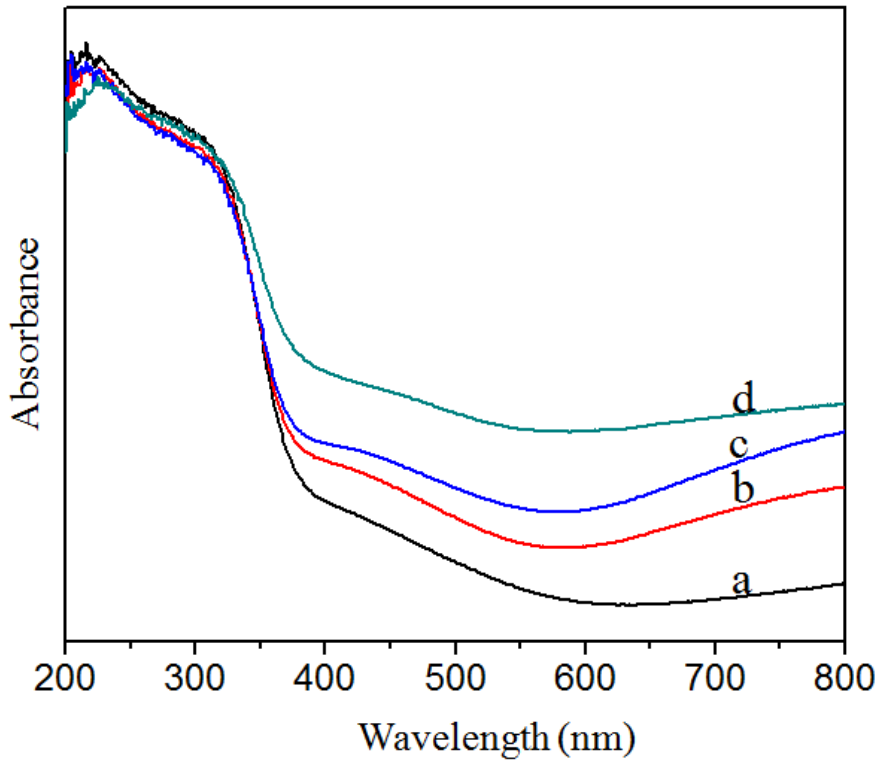


Fig. 9. Diffuse reflectance spectra of samples obtained by different RuO₂-loaded amount Ti-In oxy(nitride) (ammonolysis at 750 °C) composites. (a) 1 wt % RuO₂ (b) 2 wt % RuO₂ (c) 3 wt % RuO₂ (d) 4 wt % RuO₂.

absorbance in the visible region along with the increase of RuO₂ loading. Based on UV-Visible spectra, the hydrogen production is affected by visible light absorbance: the higher the absorbance, the higher the activity. The decrease in photocatalytic activity with higher RuO₂ content indicates that loading with excess RuO₂ causes agglomeration and reduces the number density of photocatalytic active sites. Fig. 10 shows the SEM and

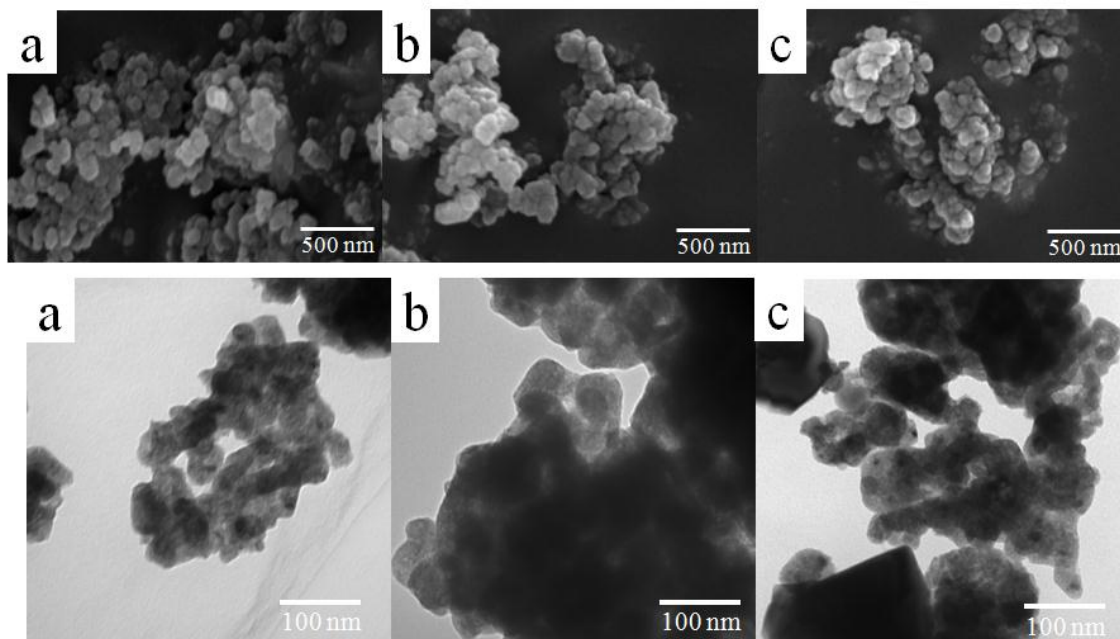


Fig. 10. SEM (up) and TEM (down) images of different RuO₂-loaded amount Ti-In oxy(nitride) (ammonolysis at 750 °C) composites. (a) 1 wt % RuO₂ (b) 2 wt % RuO₂ (c) 3 wt % RuO₂.

TEM images of the RuO₂-loaded Ti-In oxy(nitride) composites. The surface morphology shows no obvious change during the increase of loaded RuO₂. However, TEM images show more dark dots inside the particles due to the agglomeration of excess RuO₂. The same tendency has been reported for RuO₂-loaded (Ga_{1-x}Zn_x)(N_{1-x}O_x) solid solution[19] and (Zn_{1+x}Ge)(N₂O_x) Solid Solution[20]. Moreover, the decrease of surface area may due to the agglomeration (Table 2), when the RuO₂ loaded amount exceeds 3 wt%.

Table 2

Characteristic properties of different RuO₂-loaded Ti-In oxy(nitride) (ammonolysis at 750 °C) composites.

RuO ₂ -loaded amount (wt%)	Surface Area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)
1	10.4	0.22	14.5
2	13.5	0.29	14.6
3	18.1	0.42	14.5
4	10.7	0.23	14.5

During these experiments there was no O₂ evolution observed, even though the potential of generated holes might be thermodynamically high enough for oxidation of water to form O₂. However, there are no reaction centers for the four-electron oxidation for O₂ evolution. On the other hand, the standard redox potentials for HCHO/CH₃OH and H₂CO₃/CH₃OH are 0.232 and 0.044 V, so methanol oxidation is easy compared to oxidation of water coupled with O₂ evolution from water (1.23 V) from both thermodynamic and kinetic standpoints.[21] Moreover, it is well-known that O₂ evolution has a large overpotential (> 0.5 V).[21]

4. Conclusions

Novel RuO₂-loaded Ti-In (oxy)nitride composites were prepared by nitridation of TiO₂ and In₂O₃ under an NH₃ flow of 250 mL·min⁻¹ and loaded with RuO₂ by using Ruthenium(III) acetylacetonate as the precursor. The preparation of (oxy)nitride provides a new strategy to synthesize InN at high temperature (> 700 °C). And Ti⁴⁺ could be reduced to 3+ and 2+ upon ammonia treatment with In₂O₃ presence. The change in the

product with nitridation temperature was examined, and it was revealed that an active mixed nitride/oxide phase formed above 700 °C of nitridation. However, temperature above 900 °C caused Indium metal to form, which is volatile at 900 °C and was lost, resulting in mainly TiN formation, and these samples exhibited no photocatalytic activity. The XRD and XPS spectra confirmed that the prepared powders had nitrogen substituted at some of the oxygen sites in the TiO₂ and In₂O₃. The UV-Visible diffuse reflectance spectra absorbance in the visible light region varied with RuO₂ loaded amount from 1 to 4 wt%, which are directly reflected by different H₂ evolution activities, but excess RuO₂ may reduce the number density of photocatalytic active sites resulting a lower performance. The optimum preparation conditions for RuO₂-loaded Ti-In (oxy)nitride in order to achieve high hydrogen evolution are thus considered to be nitridation between 700 to 850 °C under NH₃ flow at 250 mL·min⁻¹ and loaded with 3 wt% RuO₂. The composite produced under these conditions minimizes Indium loss by reduction to Indium metal and subsequent volatilization, but some Indium is retained as InN that is stabilized in the structure, and is important in hydrogen production. And the 3 wt% RuO₂ loaded amount gave the optimum balance between reaction sites and aggregation.

Acknowledgments

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