Photocatalytic hydrogen production from methanol over Nd/TiO_2

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Introduction

The question of renewable energy is becoming more and more frequent these days. Not only because the fossil fuels are becoming to be scarce but also due to increasing environment pollution caused by combustion of fossil fuels. Besides utilizing the elements like wind, sun or water, a new more reliable way of clean energy production is being seek out. One of such possibility is the photocatalytic oxidation of low alcohols, for example methanol. Not only, this reaction is environmentally friendly, but also is a promising way, how to replace obsolete fossil fuel combustion. This work is focused on a modification of titanium dioxide by neodymium. Lanthanides possess 4f electron configuration, which can significantly improve photocatalytic activity of TiO_2. The partly filled 4f electrons in rare earth ions can form a new energy level between the TiO_2 valence and conduction bands resulting in narrowed band gap [1,2].

The presented and even more the future work is introducing not very common modification of TiO_2 by neodymium prepared by unconventional method; the high pressure processing by hot water.

Photocatalytic experiment

The homemade stirred batch photoreactor (Fig. 1) was used for the photocatalytic oxidation of methanol. 8W Hg UV lamp with the peak intensity at 254 or 365 nm was used as a source of irradiation. The UV lamp was placed on top of the reactor over a visor from quartz glass. 0.1 g of photocatalyst was suspended in 100 ml of 3% methanol aqueous solution and kept under vigorous stirring. Gas samples were discontinuously taken by gas tight syringe and immediately analyzed on GC/BID. The photocatalytic activity of prepared neodymium modified titanium dioxide photocatalysts was evaluated based on the production of hydrogen.

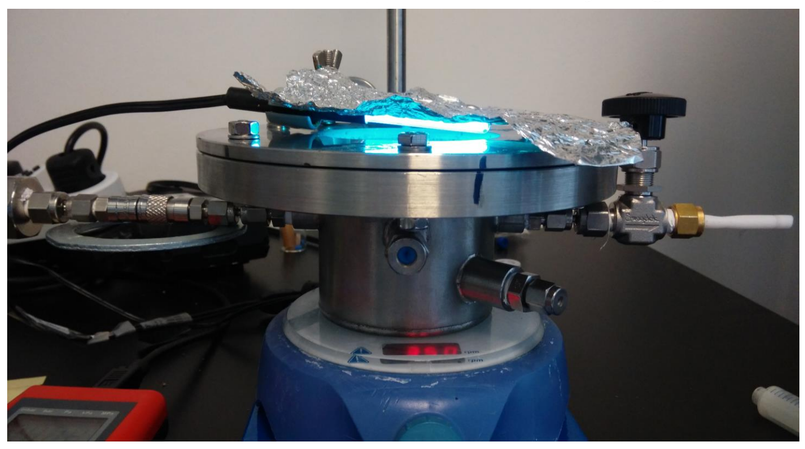

Fig. 1: Photoreactor used for the photocatalytic hydrogen production from methanol.

Photocatalysts preparation method

The parent TiO_2 and a set of neodymium doped TiO_2 photocatalysts (with 0.2 to 1.5 wt.% of Nd_2O_3) were prepared via sol–gel processing controlled within reverse micelles of nonionic surfactant Triton X-114 in cyclohexane in combination with calcination. Titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$, purity >97%,Aldrich) and neodymium(III) nitrate hexahydrate ($Nd(NO_3)_3.6H_2O$, purity >99%, Aldrich) were used as metal cations sources. For TiO_2 and Nd-doped TiO_2 synthesis the molar ratio of cyclohexane: Triton X-114: H_2O: $Ti(OCH(CH_3)_2)_4$ was kept 11: 1: 1: 1, changing the Nd:Ti molar ratio particularly. The prepared sols were poured in a thin layer into a Petri's dishes and left for 24 h on air at ambient temperature and pressure for gelation. The sols converted to rigid yellowish transparent gels. The titania and neodymium doped titania gels were thermally treated at 450 °C for 4 h with heating rate 5 °C/min in order to produce powder photocatalysts. All prepared solids were sieved to particle size < 0.160.

Characterization results

All prepared photocatalysts were characterized by UV-Vis DRS, XRD, N_2 physisorption and spectroelectrochemical and photoelectrochemical measurements.

XRD analysis confirmed only anatase phase in all samples (Fig. 2). Also there are no noticeable significant structural differences after addition of neodymium.

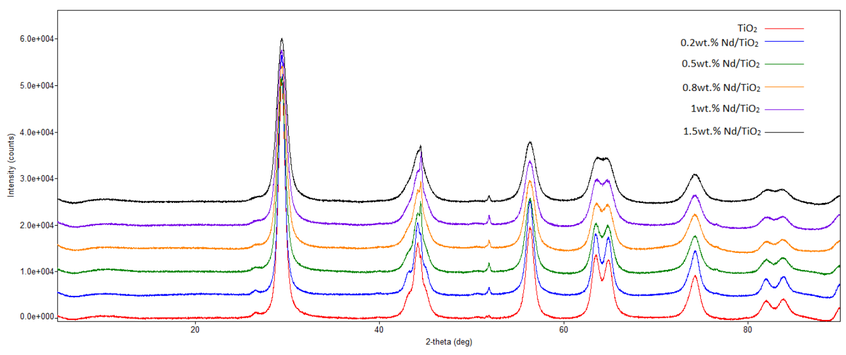

Fig. 2: XRD patterns of Nd/TiO_2 photocatalysts.

The absorption edge energy is one of the key aspects in photocatalysis. The absorption edge energies of prepared samples were subtracted from UV-Vis DRS spectra (Fig. 3). It is clear that the addition of neodymium had barely any effect on absorption edge energy. On the other hand, it seems the sample with the highest amount of neodymium have the largest absorption edge energy indicating high amounts of neodymium have negative effect on absorption edge energy of photocatalyst.

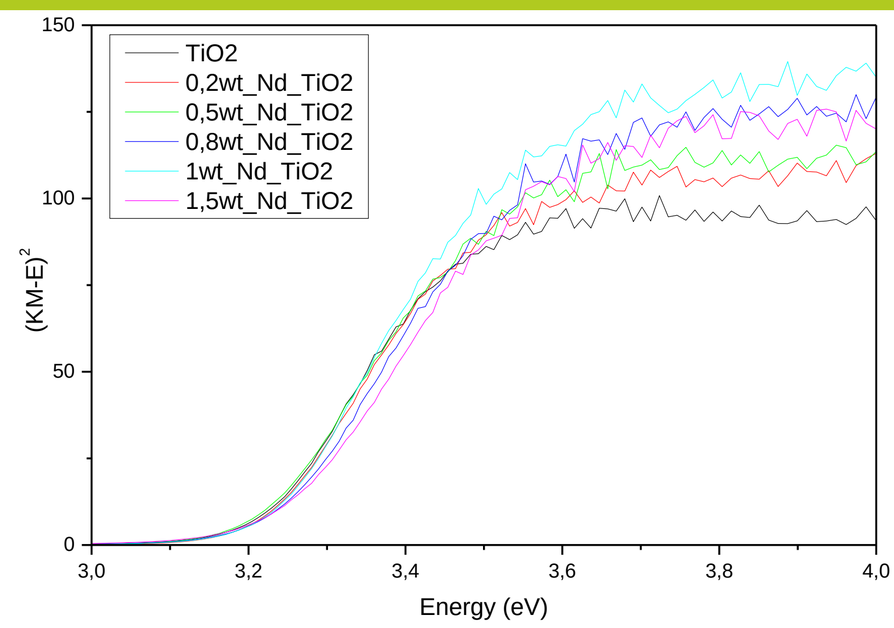

Fig. 3: UV-Vis DRS spectra of Nd/TiO_2 photocatalysts.

The photocurrent measurements were conducted to predict the photocatalytic activity of the prepared photocatalysts (Fig. 4). It is evident all the Nd/TiO_2 photocatalysts generate several times higher current than pure TiO_2. This implies higher amount of generated electron-hole pairs. The slope of current drop after the shutter is closed is indicating how fast the recombination of electrons and holes is.

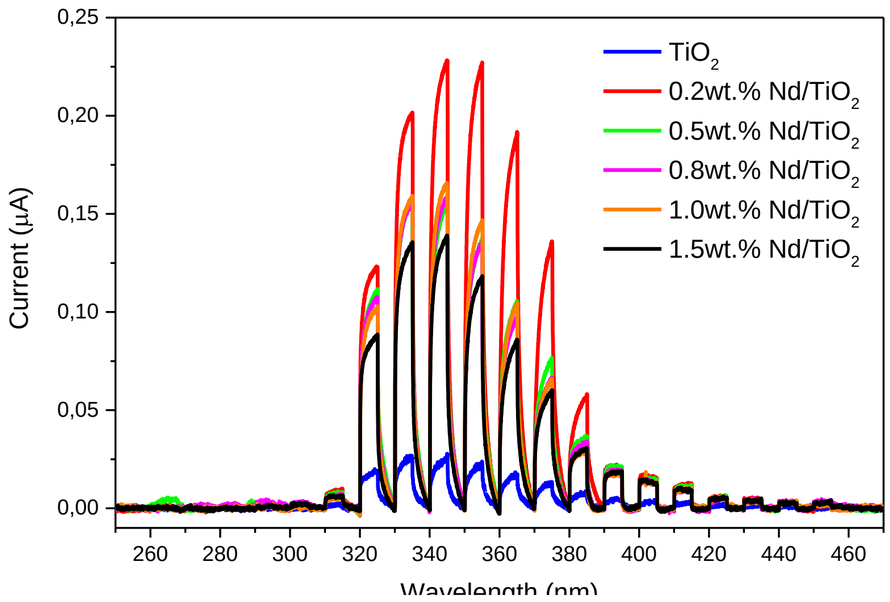

Fig. 4: Photocurrent generation at electrode made from Nd/TiO_2 photocatalysts.

Conclusion

A series of titanium dioxide photocatalysts doped by various amounts of neodymium were successfully prepared by sol-gel method followed by thermal treatment.

All the photocatalysts were characterized by a number of methods, such as XRD, UV-Vis DRS, N_2 physisorption, spectroelectrochemical and photoelectrochemical measurements.

The photocatalytic hydrogen production from methanol was carried out in stirred batch reactor under 254 nm or 365 nm irradiation.

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