A novel oxynitride photocatalyst system for water splitting: La2Zn1-xTi1+x(O,N)6

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The photocatalytic splitting of water under solar radiations is a challenging and promising domain of research to provide clean and renewable H_2 as an alternative energy resource. Current oxide photocatalysts (TiO_2, ZnO, $SrTiO_3$, $NaTaO_3$…) are wide-gap semiconductors for which UV-light is necessary to produce electron-hole pairs by photoexcitation. However, the UV light represents only a small fraction (5%) of the solar spectrum. So far the (oxy)nitride approach become attractive for the efficient utilization of solar energy. A consequence of the anionic N^{3-}/O^{2-} substitution results in an increase of the covalent character which is illustrated by a shift of the absorption edge towards higher wavelength values (band gap < 3 eV). However other requirements have to be considered to synthesize an efficient visible-light-driven photocatalyst such as the mobility of the photogenerated charge carriers, the crystal structure or the chemical stability. Here, we have investigated the monoclinic perovskite-type oxynitride system $La_2Zn_{1-x}Ti_{1+x}(O,N)_6$.

Synthesis

Citrate route 1000°C ***crystallized powders***

La_2ZnTiO_6 → NH$_3$ - 900°C - 10h → $La_2ZnTiO_{6-3x}N_{2x}$ with 0 < x < 0.129

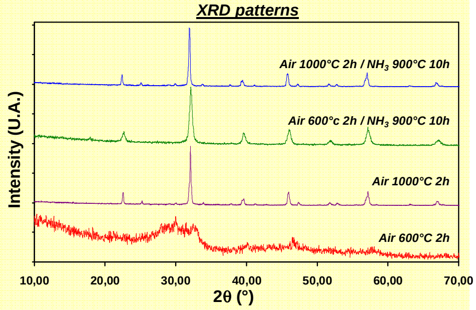
"La_2ZnTiO_6" - type structure - double perovskite

Citrate route 600°C ***"poorly crystallized" powders***

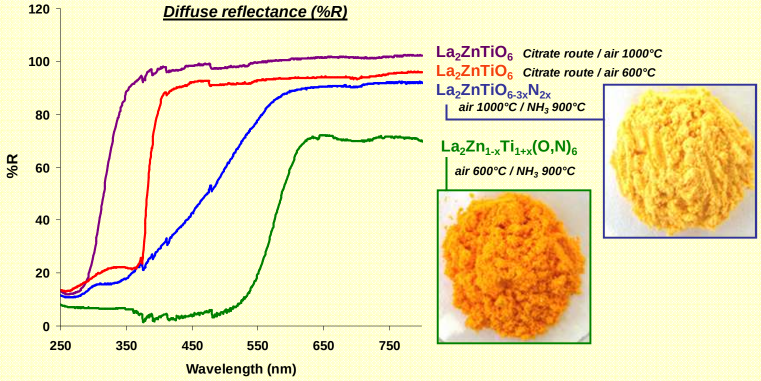
"La_2ZnTiO_6" → NH$_3$ - 900°C - 10h → $La_2Zn_{1-x}Ti_{1+x}(O,N)_6$ + La_2O_3 + "ZnO"

"$LaTiO_2N$" - type structure - simple perovskite

Note: La_2O_3 easily removed by washing with dilute HCl (0.1M)

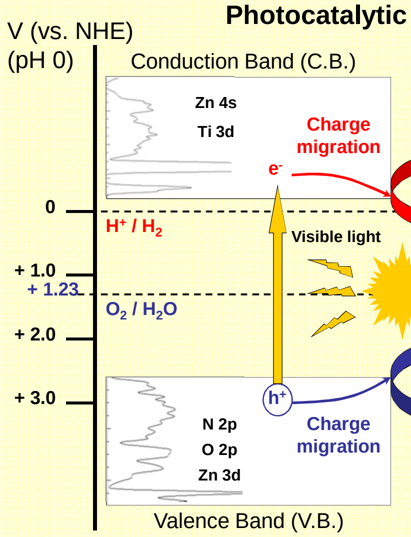


UV-Vis diffuse reflectance spectra



Samples	Temperature	%O	%N	S_g (m²/g)	Optical band gap (eV)	Color
$La_2Zn_{1-x}Ti_{1+x}(O,N)_6$	Calcination 600°C 2h NH$_3$ 900°C 10h	17.6	5.0	32 ± 1	2.35	orange
$La_2ZnTiO_{6-3x}N_{2x}$	Calcination 1000°C 2h NH$_3$ 900°C 10h	18.7	0.5	7 ± 1	3.18	yellow

Photocatalytic water splitting

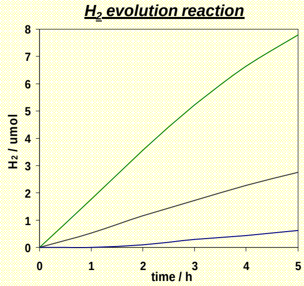


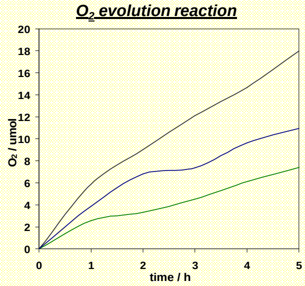
It is expected that the expanded nature of the Zn 4s band improves the mobility of the photogenerated carriers thus enhancing the photocatalytic activity of the material.

Absorption of solar energy, excitation, and creation of an electron / hole pair.

Efficient charge separation and fast transport of the carriers must be achieved in order to avoid recombination between electrons and holes.

Photocatalytic activity





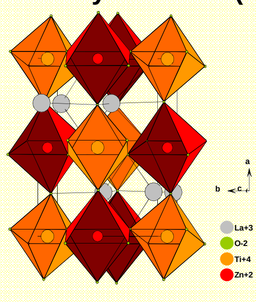
The performance of this new photocatalyst is compared to the reference material $LaTiO_2N$.

Activity / Time	$La_2Zn_{1-x}Ti_{1+x}(O,N)_6$		$La_2ZnTiO_{6-3x}N_{2x}$		$LaTiO_2N$	
	[a] H_2 (µmol.h^{-1})	[b] O_2 (µmol.h^{-1})	[a] H_2 (µmol.h^{-1})	[b] O_2 (µmol.h^{-1})	[a] H_2 (µmol.h^{-1})	[b] O_2 (µmol.h^{-1})
1 h	1.76	4.03	0	3.88	0.52	5.88
2 h	3.56	6.24	0.10	6.81	1.16	9.03
4 h	6.63	8.40	0.53	9.65	2.27	14.69

[a] conditions: catalyst (0.2g); 200ml 20% MeOH; 300 W Xe lamp (>420nm); 0.2 g La_2O_3

[b] conditions: catalyst (0.1g); 200mL 0.02 M $AgNO_3$; 300 W Xe lamp (>420nm); 0.2 g La_2O_3 ; 2% Co_3O_4

Density of States (DOS) from GGA calculations for La_2ZnTiO_6



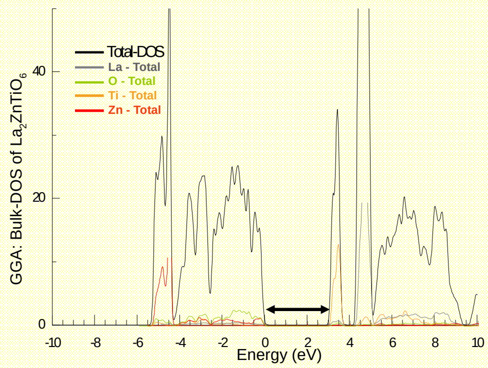
La_2ZnTiO_6

Structure used for calculation

Unit Cell parameters:
a = 7.895 Å
b = 5.5964 Å
c = 5.5809 Å
β= 90.03°

Space Group:
P1 21/n 1 (No: 14)
Monoclinic

Iwakura et al. , J. Nov. Carb. Res. Sciences, 3 (2011) 1-5



DFT: E_{gap}= 3.00 eV   DR US-VIS: E_{gap}≈ 4.00 eV

Note: complete ordering of Zn/Ti on B-site used for calculation calculation in progress on the oxynitride composition

Conclusion

The development of alternative routes for visible-light-photocatalysis represents a promising challenge where nitride-type compounds can play a major role. Within few years, several advances have been made in the number of phases tested for overall water splitting. With the example of La-Zn-Ti-O-N type phases, we have demonstrated that oxynitrides containing lanthanides, d^0-type, and d^{10}-type metal ions exhibit interesting photocatalytic behavior. The effect of the Zn/Ti ratio on the performance of the oxynitride will be investigated.

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