Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Understanding synergetic effects of Zn and Rh-Cr promotion to wide-bandgap Ga, Ta and Ti oxides in photocatalytic water splitting

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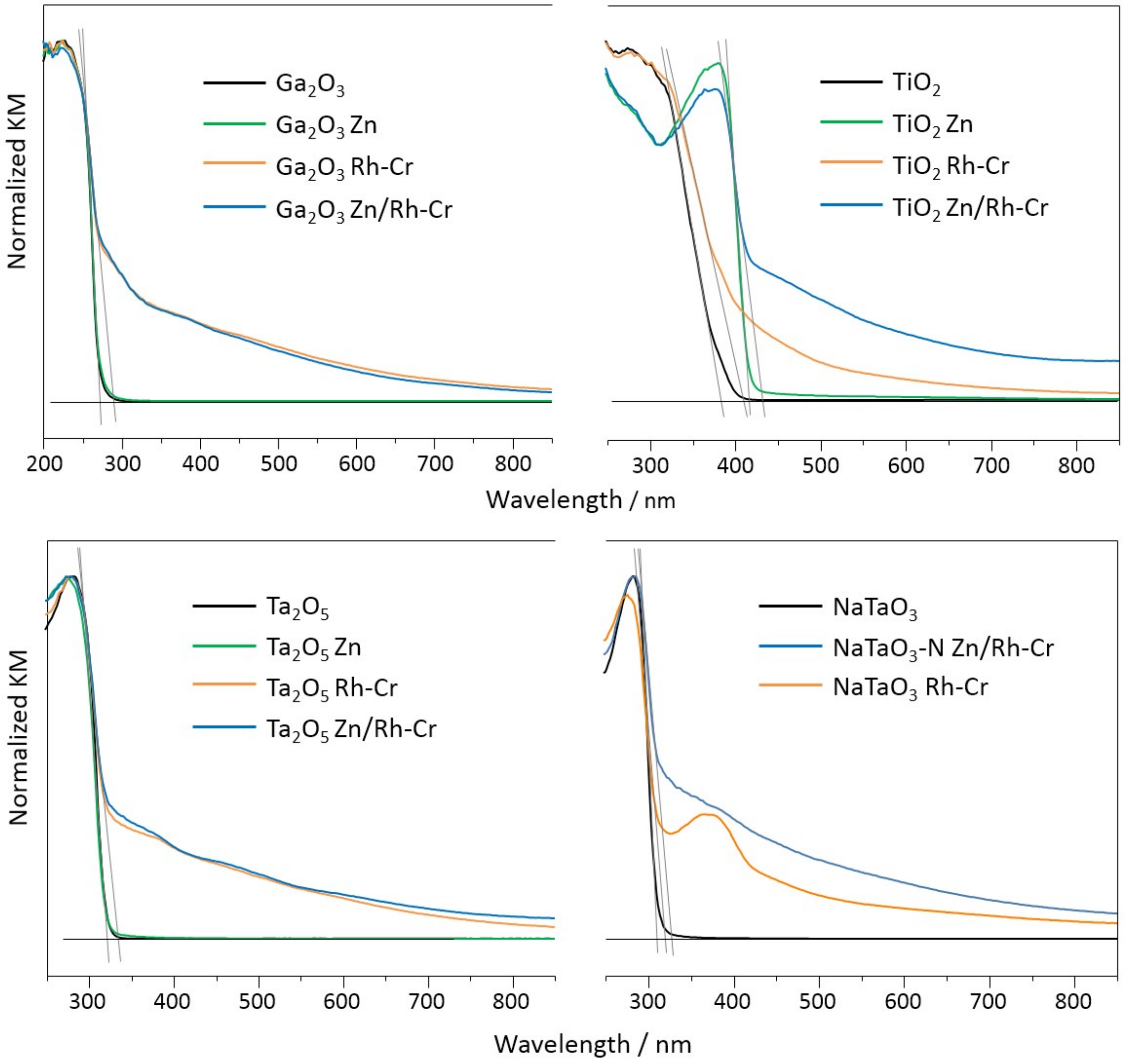
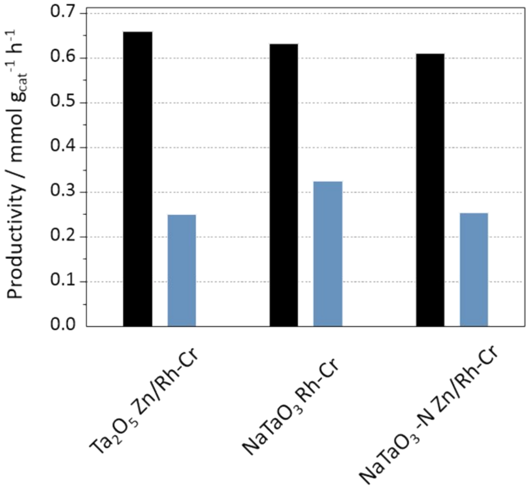


Figure S1. Diffuse reflectance KM plots of the used photocatalysts. Tauc plot intersecting lines are visualized in grey.

Table S1. KM plot derived λ_{onset} and corresponding Eg values (by the formula Eg = $1240/\lambda_{onset}$).

Material	λ_{onset} /nm	E_g / eV	Material	λ_{onset} / nm	E_g / eV
TiO_2	382	3.25	Ta_2O_5	321	3.86
TiO_2 Zn	416	2.98	Ta_2O_5 Zn	321	3.86
TiO_2 Rh-Cr	409	3.03	Ta_2O_5 Rh-Cr	334	3.71
TiO_2 Zn/Rh-Cr	432	2.87	Ta_2O_5 Zn/Rh-Cr	334	3.71
Ga_2O_3	270	4.59	$NaTaO_3$-N	310	4.01
Ga_2O_3 Zn	270	4.59	$NaTaO_3$-N Zn/Rh-Cr	327	3.79
Ga_2O_3 Rh-Cr	290	4.28	$NaTaO_3$ Rh-Cr	319	3.89
Ga_2O_3 Zn/Rh-Cr	290	4.28			



Catalyst	H_2	O_2
Ta_2O_5 Zn-Rh/Cr	0.66	0.25
$NaTaO_3$ Rh-Cr	0.63	0.32
$NaTaO_3$-N Zn/RhCr	0.61	0.27

Figure S2. Comparison of H_2 and O_2 steady-state productivity of Ta_2O_5 Zn/Rh-Cr, $NaTaO_3$ Rh-Cr and $NaTaO_3$-N Zn/Rh-Cr catalysts in slurry reactor (left), and correspondent H_2 and O_2 productivity (mmol·g^{-1}·h^{-1}) values (right).

During the course of our investigations, many tantalum based materials in the general form $MTaO_3$ (where M = Na or K) have been synthesized as promising candidates for overall water splitting. As further variety, different doping and co-catalyst impregnation have been attempted. La and N doping but also Cu, Fe, and Ti doping, using a hydrothermal synthesis approach. Ni, Pt, and Ru based co-catalyst impregnation on different tantalate substrate were also performed and these materials were tested for water splitting activity. $NaTaO_3$ materials were synthesized by urea combustion[1], and hydrothermal [2] techniques. Urea combustion $NaTaO_3$ samples were prepared from Ta_2O_5, Na_2CO_3, and $CO(NH_3)_2$ (molar ratio 1 : 1 : 4), mixed in a thick water slurry, dried at 353 K and crushed in a mortar. The urea blended precursors were then slowly heated (2 K/min) up to 573 K and subsequently brought to 873 K (5 K/min, 4 h).

Hydrothermal N-doped $NaTaO_3$ nanocubes were prepared in a Teflon lined autoclave. A Ta_2O_5, NaOH and NH_4OH (molar ratio 1 : 33 : 7.5) solution-suspension in water was prepared and heated at 453 K for 12 h under hydrothermal conditions. The solid product was then washed by centrifugation and dried at 353 K.

Contrarily to our expectation, no one of these materials was capable of overall water splitting activity or oxygen production in either slurry or gas phase. Hydrogen evolution productivity was in most case present, but at level in the range of bare Ta_2O_5, i.e. more than one order of magnitude inferior to data reported in literature for tantalate materials.

Remarkably different behaviour was observed for $NaTaO_3$-N Zn/Rh-Cr and $NaTaO_3$ Rh-Cr loaded catalysts. They exhibited excellent quasi-stoichiometric H_2 and O_2 evolution in slurry under UV irradiation.

The two Rh-Cr modified tantalum oxide display very similar catalytic activity. Especially, Zn doping does not seem to have any relevant (or even slightly negative) effect on the productivity. Even more importantly, the productivity is equivalent to what observed for Ta_2O_5 Zn/Rh-Cr, with a possible slight improvement in oxygen evolution (which gets closer to the desired stoichiometry). These findings showed that crystal structure only played a marginal role in determining the activity of Rh-Cr impregnated tantalum based materials, supporting a non-semiconductor-based mechanism. Other parameters, such as the presence of specific Ta-O surface active units, and their interaction with the Rh-Cr co-catalyst, could be better explaining the similar catalytic activity observed for the Ta_2O_5 and $MTaO_4$ materials.

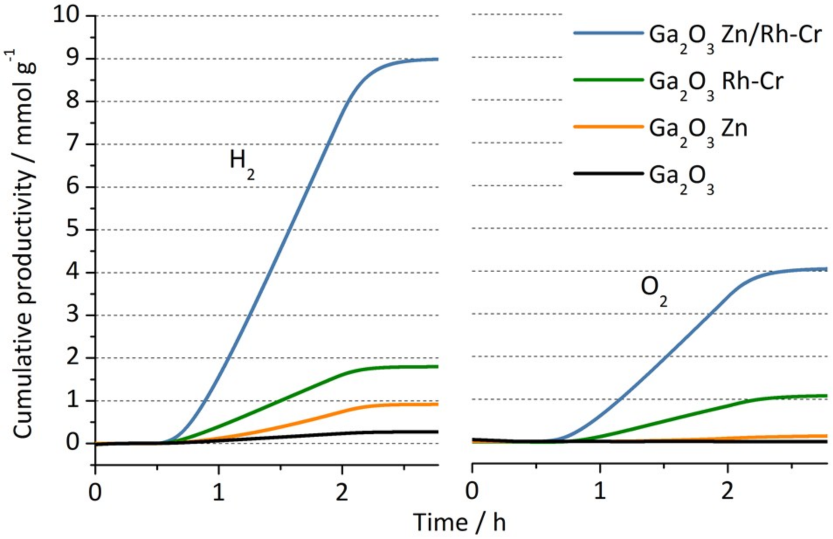


Figure S3. H_2 and O_2 cumulative productivity profiles with the unpromoted and promoted Ga_2O_3 catalysts in the continuous flow slurry reactor under 1.5 h UV (high pressure Hg lamp) irradiation (ON at 0.5 h, OFF at 2 h), calculated from the concentration profiles shown in **Fig. 3.**

1. J. Xu, Y. He, J. Zhang, J. Qian, D. Xu, X. He and D. Yang, *Micro & Nano Lett*, **2012**, *7*, 72-75.
2. H. Fu, S. Zhang, L. Zhang and Y. Zhu, *Mater. Res. Bull.*, **2008**, *43*, 864-872.