Electrocatalytic and photocatalytic activity of sol-gel Pt/TiO_2 and $Pt/N/TiO_2$ films.

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Co-doping titania by N and Pt can be used as the photocatalysts for environmental purification, hydrogen production, carbon dioxide reduction, etc. under solar light. As known, the chemical nature of the doping agents can affect the efficiency and mechanism of catalytic or photocatalytic transformations. Herein, the different approaches of synthesis procedures were used to obtain mesoporous and non-porous Pt/TiO_2 and $Pt/N/TiO_2$ films to investigate the role of structural and surface peculiarities in environmentally important processes, such as electrocatalytic reduction of dissolved oxygen (EOR) and hydrogen evolution reaction (HER) as well as photocatalytic decomposition of atmospheric pollutant, nitrous oxide.

Synthesis procedure

The sol-gel method used for *mesoporous films* is based on the sol formation of titanium(IV) isopropoxide, platinum(II) acetylacetonate, a three-block copolymer Pluronic P123 as a template and acetylacetone as a stabilizing agent. The *nonporous films* are formed using the simpler and faster route based on the hydrolysis of titanium(IV) isopropoxide and platinum(II) acetylacetonate in ethanol medium. The platinum (II) acetylacetanate (1mol.%) and urea (5mol.%) were used as Pt and N sources. The three layered films were obtained by dip-coating procedure. The UV pretreatment of the film layers is performed to cause the formation of platinum nanoparticles ($Pt/(N)/TiO_{2UV}$). The thermal treatment of the sample was 450°C.

Electrocatalytic properties

Electrode	$E_{1/2}(O_2)$, V		$I(H_2)$, mA/cm^2 (E= - 1.0 V)
	1st cycle (before UV)	2nd cycle (after UV)	
TiO_2	-0.60	-	inactive
N/TiO_2	-0.58	-	inactive
Mesoporous films			
Pt/TiO_2	–0.55	–0.55	–1.35
$Pt/N/TiO_2$	–0.55	–0.55	–0.30
Pt/TiO_{2UV}	–0.55	–0.52	–1.59
$Pt/N/TiO_{2UV}$	–0.55	–0.49	–1.45
Non-porous films			
Pt/TiO_2	–0.55	**–0.50**	**–1.94**
$Pt/N/TiO_2$	–0.55	–0.53	–0.92
Pt/TiO_{2UV}	–0,55	–0.55	–0.62
$Pt/N/TiO_{2UV}$	-	–0.54	–1.14

Tab. 1. Efficiency of the films in EOR and HER

Electrocatalytic HER at potentials from -0.8 V to -1.3 V takes place over all Pt and Pt/N doped TiO_2 electrodes while Pt free ones are inactive.

The most efficient electrode for both EOR and HER is non-porous Pt/TiO_2.

Correlation between activity of the films in HER and relative intensity (I_{rel}) of XPS Pt4f peaks clearly shows that the formation of Pt-O-Ti bonds (71.1-72.1 eV) has more significant effect rather than Pt^0 (69.6-71.4 eV). No influence of N doping on the efficiency of electrocatalytic reaction is observed.

Activity of doped films in EOR at potentials from -0.5 V to -0.8 V is enhanced compared to TiO_2 and N/TiO_2 ones. The 2nd cycle of this reaction after additional UV exposure of the electrodes showed an increase of $E_{1/2}$ values pointing on the more effective EOR over some electrodes. It is suggested that UV exposure leads to the formation of Pt^0 that can improve the electrocatalytic reaction.

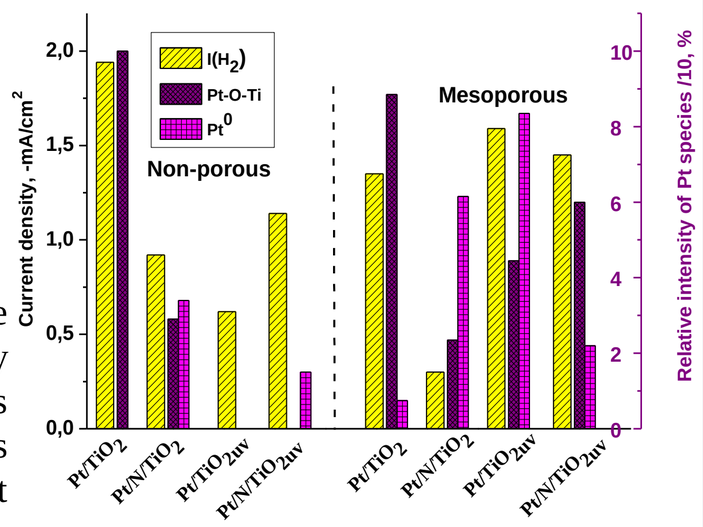

Fig. 3. Correlation between efficiency of HER and I_{rel} of some Pt species obtained from XPS data .

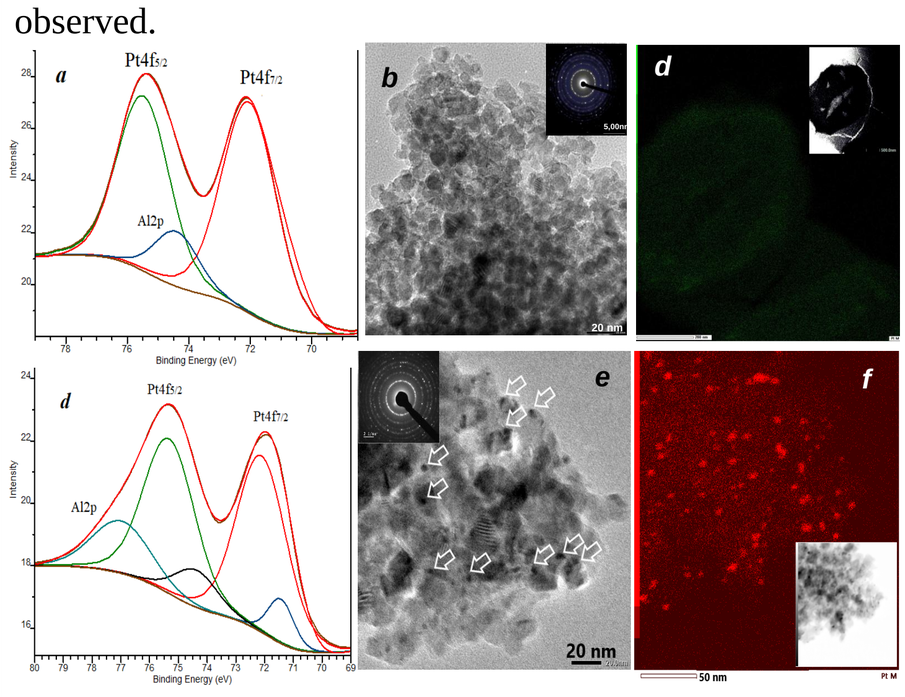

Fig. 4. XPS Pt4f spectra, TEM images and electron diffraction patterns (inserts), EDS mappings with corresponding TEM images (inserts) of non-porous (a, b, c) and mesoporous (d, e, f) Pt/TiO_2 films.

TEM images and EDS mapping confirm the absence of Pt^0 in the structure of non-porous Pt/TiO_2 while it is observed for mesoporous one.

The mean sizes of TiO_2 and Pt^0 obtained from TEM images point on the nanoparticle formation in the range of 9-14 nm and 3-4 nm, respectively.

The values of d-spacing is corresponding to the anatase (101) polymorph of TiO_2.

Photocatalytic activity

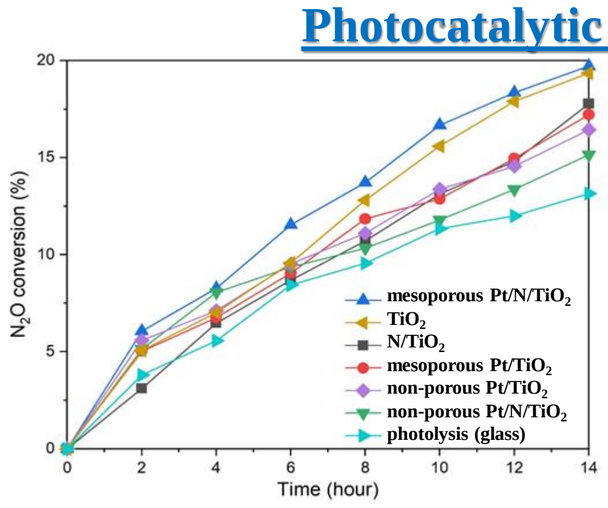

Fig. 1. Photocatalytic decomposition of N_2O under UV light over TiO_2 and doped TiO_2 films

Comparing the photocatalytic performance of mesoporous $Pt/N/TiO_2$ and Pt/TiO_2 films, one can be noted that N doping is responsible for more efficient separation of an electron-hole pair formed after UV exposure on TiO_2.

XPS data points on the formation of substitutional N (3,5%), fragments C-N-C (74.2 %) and O-N-O (22.3 %) with binding energy at 395.6, 399.7 and 402.0 eV, respectively.

The most active catalyst for N_2O decomposition process is found to be mesoporous $Pt/N/TiO_2$ film. The lower activity of non-porous $Pt/N/TiO_2$ and $1\%Pt/TiO_2$ films can be explained by lower adsorption degree of N_2O molecules leading to the lower efficiency of photocatalytic process.

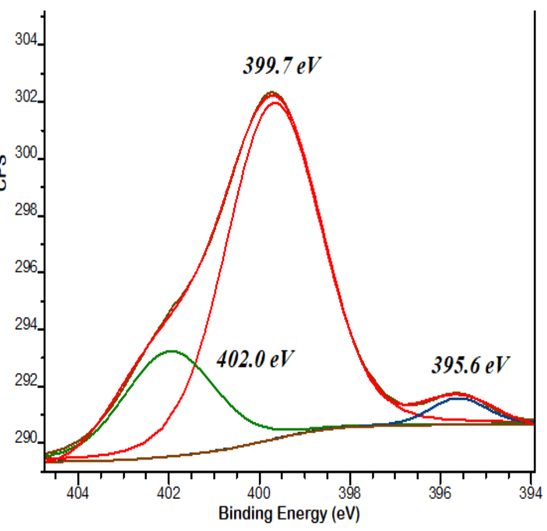

Fig. 2. XPS N1s spectrum of mesoporous $Pt/N/TiO_2$ film

Photoelectrochemical investigation

Quantum yield (QY) efficiency is drastically increased for all Pt containing films compared to TiO_2 and N/TiO_2 at both 430 and 380 nm. The bandgap is narrowed to 3.1-2.9 eV depending on the synthesis conditions and flat band potential (E_{fb}) is anodically shifted for all Pt modified samples and is situated at near -0.4 V. The change in the electronic structure of TiO_2 due to Pt ions doping is noted. It also proves the XPS results where the formation of common bonds between Ti and Pt ions (Ti-O-Pt) was detected.

Electrode	$QY\times10^3$ 430 nm	$QY\times10^3$ 380 nm	E_{BG}, eV	E_{fb}, V	E_{VB}, V
TiO_2	0.13	6.3	3.2	-0.51	+2.69
N/TiO_2	0.18	3.4	3.1	-0.44	+2.66
mesoporous					
Pt/TiO_2	3.86	14.39	3.1	-0.39	+2.71
$Pt/N/TiO_2$	2.42	34.54	3.0	-0.37	+2.63
Pt/TiO_{2UV}	3.86	71.96	3.0	-0.35	+2.65
$Pt/N/TiO_{2UV}$	1.21	27.63	3.0	-0.31	+2.69
non-porous					
Pt/TiO_2	4.65	34.54	2.9	-0.35	+2.55
$Pt/N/TiO_2$	3.88	31.66	2.9	-0.38	+2.52
Pt/TiO_{2UV}	2.05	25.33	2.9	-0.38	+2.52
$Pt/N/TiO_{2UV}$	2.33	25.91	2.9	-0.44	+2.46

Tab. 2. Photoelectrochemical characteristics of synthesized electrodes.

Conclusions

Electrocatalytic activity of the obtained electrodes is mainly dependent on the oxidation state of Pt on the surface where the formed Pt^0 and Ti-O-Pt fragments can be responsible for enhanced EOR and HER, respectively.

The mesoporous surface and N doping improve the photocatalytic N_2O decomposition under UV light compare to other films.

Photoelectrochemical results point on the change of the electronic structure of titania due to the doping with Pt ions.

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