Supporting information

Material preparation

The metal modified catalysts were prepared as follows. First, the laser pyrolysis-derived titania nanopowder (typically 0.5 g for one batch) was dispersed in 45 ml of distilled water using o rotovibrator stainless steel rod for 10 minutes. Then, 5 ml of aqueous solution containing the dissolved noble metal precursor (~0.025 g $AgNO_3$,~0.025 g $H_2PtCl6\ nH_2O$ (~38wt.% metallic Pt) or ~0.022 g $KAuCl_4$) was slowly added to TiO_2 suspended previously in water. The final step of metal-reduction was carried out by slowly injecting in TiO2 suspension with noble metal precursor, 5 ml of aqueous solution containing 0.04 g of freshly dissolved $NaBH_4$. The solid material was recovered by filtration, washed with pure water, dried at 70°C for 8 h and finally homogenized with an agate mortar.

Elemental composition determined by EDAX analysis

The elemental analysis data derived from EDAX measurements are presented in Table S1.

Table S1 Elemental composition obtained from EDAX analysis of simple and metal - modified TiO_2

Catalyst	Metal / at%	Ti / at%	O / at%	C / at%	Imp.
TiO_2	0	31.30	67.20	0.80	0.7
Ag/TiO_2	0.04	31.75	64.31	0.40	3.5
Au/TiO_2	0.01	30.82	65.53	0.44	3.2
Pt/TiO_2	0.01	22.79	72.60	0.50	4.1

XPS analysis

Table S2 XPS survey of elemental composition of simple and noble metal-modified TiO_2

Sample	**C** / at%	**O** / at%	**Ti** / at %	**Cl** / at %	**Na** / at %	**Au** / at %	**Ag** / at %	**Pt** / at %
TiO_2	19.20	56.70	22.34	1.76	-	-	-	-
Ag/TiO_2	13.60	52.9	20.34	0.52	12.60	-	0.04	-
Au/TiO_2	25.58	46.40	28.0	-	-	0.02	-	-
Pt/TiO_2	14.50	48.87	17.80	5.10	13.71	-	-	0.02

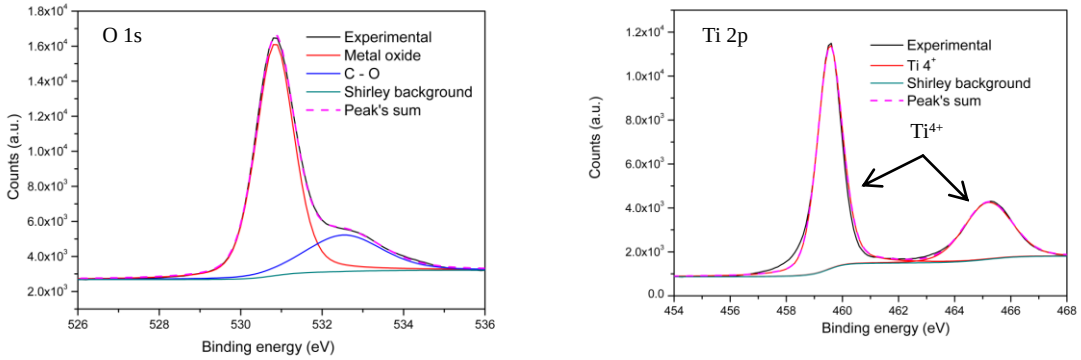


Fig. S1 High resolution XPS spectra of TiO_2 in O1s and Ti2p binding energy regions.

Figures S1 shows the high resolution XPS spectra of O 1s and Ti 2p core levels of TiO_2 sample. The maxima in O 1s binding energy region is characteristic to O^{-2} of TiO_2. The doublet $Ti2p_{3/2}$ (binding energy 459 eV) and Ti $2p_{1/2}$ (binding energy 465 eV) arise from spin orbit splitting. These peaks are consistent with Ti $^{4+}$ in TiO_2 lattice.

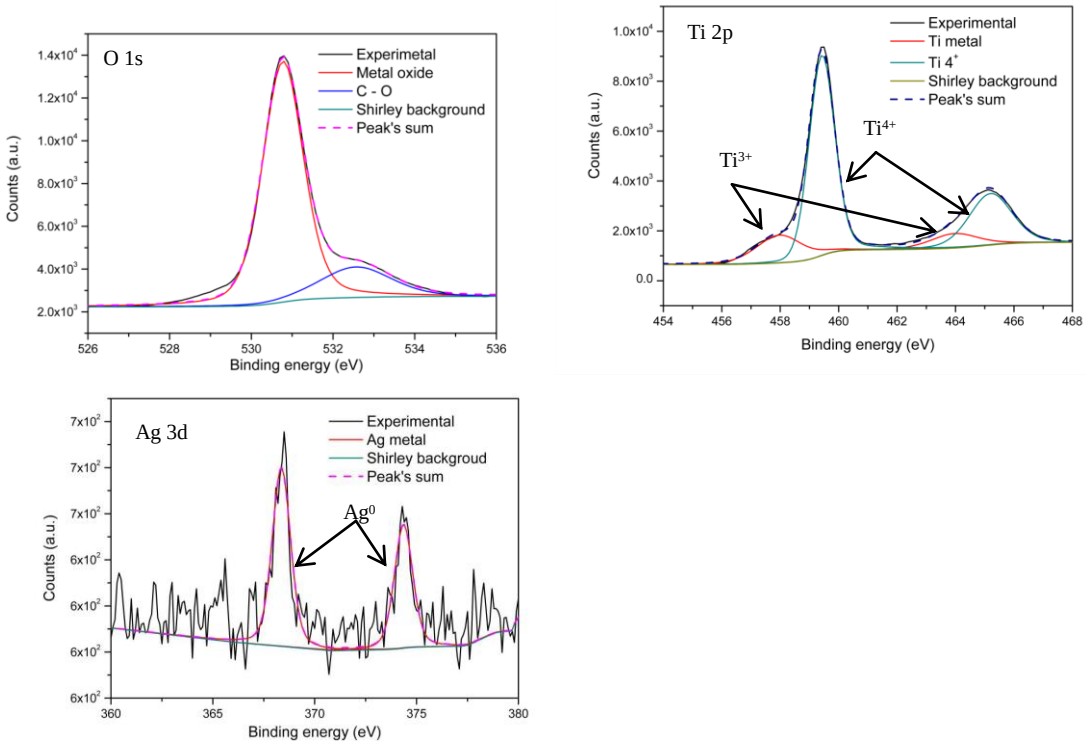


Fig. S2 High resolution XPS spectra of Ag/TiO_2 in O 1s, Ti 2p and Ag 3d binding energy regions.

From O 1s XPS spectrum of Ag/TiO_2 in Fig. S2 it comes out that, the oxygen is in form of O^{2-}. The shoulder $Ti2p_{1/2}$ at binding energy 457 eV, observable in all metal-modified samples, corresponds to Ti^{3+} species. The concentration of Ti^{3+} (at.%) of all investigated samples is given in Table S6. The Ag 3d region in XPS spectrum shows two narrow peaks centred at ~ 366.94 eV ($3d_{5/2}$) and ~ 372.94 eV ($3d_{3/2}$).The literature data points out that the binding energies of Ag+ and Ag^0 are very close each other, being difficult to discriminate between the metallic and oxidized state [1, 2]. However, from corroboration of TEM and XPS data we can assume that the metallic relative large sillver nanoparticles visible in TEM micrographs are in metallic state but their surface is likely to be covered by a thin oxide layer.

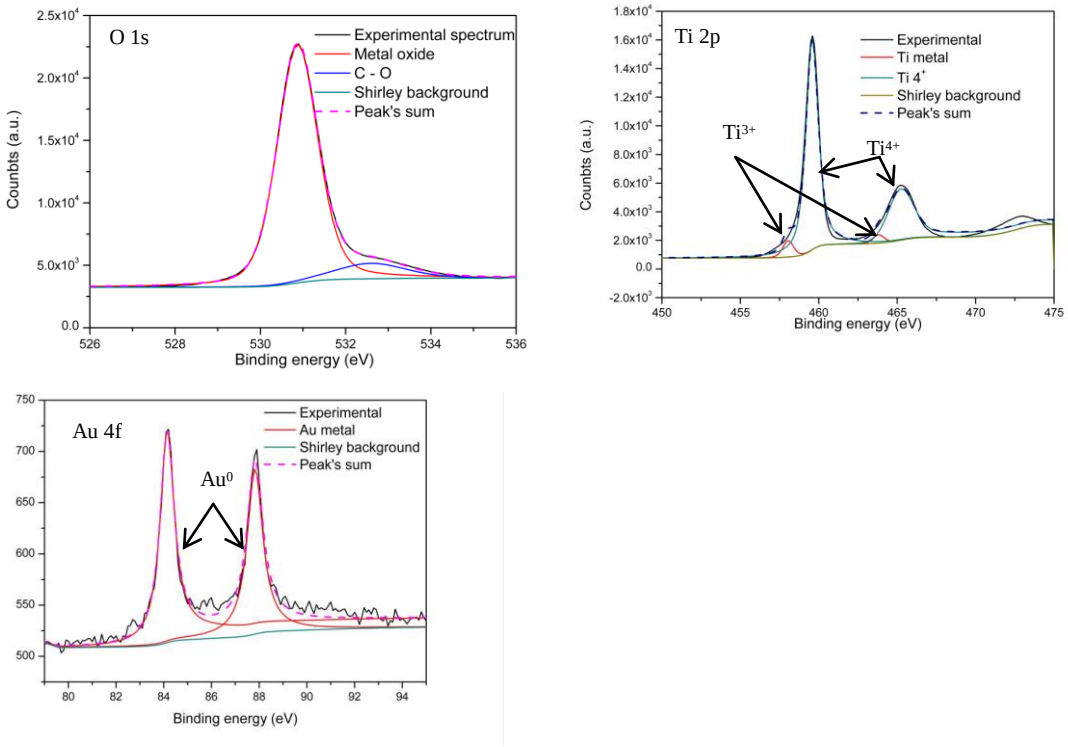
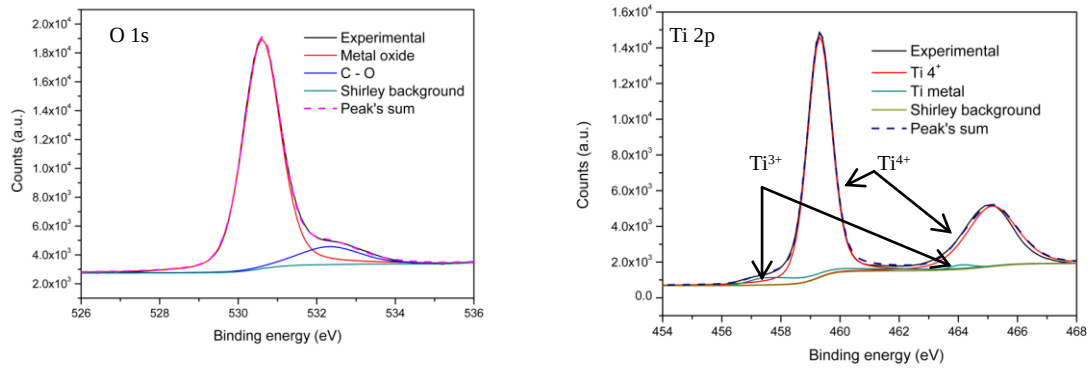


Fig. S3 High resolution XPS spectra of Au/TiO_2 in O 1s, Ti 2p and Au 4f binding energy regions.

The XPS analysis of Au/TiO_2 sample evidenced the presence of O^{2-}, Ti^{3+}, Ti^{4+} and Au^0 species (see Fig. S3).



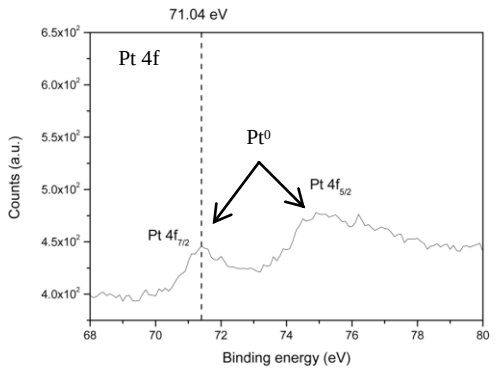


Fig. S4 High resolution XPS spectra of Pt/TiO_2 in O 1s, Ti 2p and Pt 4f binding energy regions.

The XPS survey of Pt/TiO_2 sample reveals the appearance of O^{2-}, Ti^{3+}, Ti^{4+} and Pt^0 (see Fig. S4). The metals of all investigated samples are in zero oxidation state (see Table S3).

Table S3 Chemical state of titanium in the investigated materials

Sample	**Ti^{3+}** / at. %	**Ti^{4+}** / at. %
TiO_2	0	100
Ag/TiO_2	22.9	77.1
Au/TiO_2	10.9	89.1
Pt/TiO_2	8.8	91.2

From data depicted in Table S4, it comes out that the amount of titanium in its reduced form (Ti^{3+}) is variable, depending on the supported metal.

XRD analysis

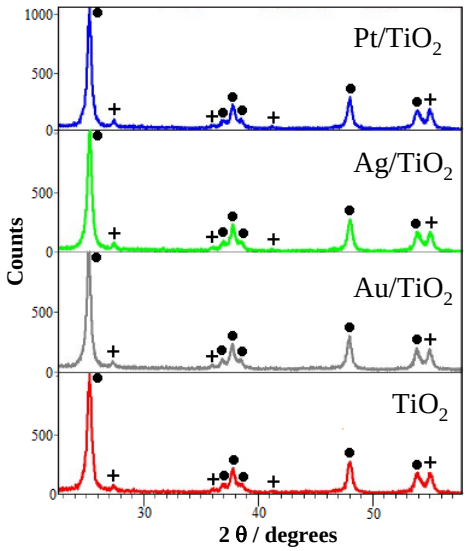


Fig. S5 Comparative XRD difraction patterns of simple and metal-modified TiO_2. •-anatase, +-rutile.

Table S4 Crystalline phase composition and average crystallite size of simple and metal-modified TiO_2.

Catalyst	Anatase/ at%	Rutile / at%	[a] D(XRD) / nm
TiO_2	94.4	5.6	18.8
Au/TiO_2	95.3	4.7	19.3
Ag/TiO_2	93.4	6.6	19.8
Pt/TiO_2	95.1	4.9	20.6

[a]-average crystallite size calculated from the characteristic reflection line of anatase (101) plane ($2\Theta \approx 25^o$) using Debye – Scherrer equation.

References

1. X. Wang, S. Li, H. Yu, Jiaguo Yu, S. Liu, "Ag_2O as a new visible-light photocatalyst: self-stability and high photocatalytic activity", Chem. Eur. J. 17 (2011) 7777 – 7780.

2. R. Kumar , R. M. El-Shishtawy, M. A. Barakat, "Synthesis and characterization of Ag-Ag_2O/TiO_2@polypyrrole heterojunction for enhanced photocatalytic degradation of methylene blue", Catalysts 6 (2016) 76 (11 pages).