Immobilization of Co, Mn, Ni and Fe oxide co-catalysts on TiO₂ for photocatalytic water splitting reactions

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Figure S1. On the top: ATR-FTIR spectra of the obtained composites along with the original salts, reference TiO$_2$, photocatalyst powder before calcination (M(acac)$_x$-TiO$_2$, with M corresponding to Co, Mn, Fe and Ni) and after calcination (MO$_x$-TiO$_2$). The reference M(acac)$_x$ salts show the characteristic C=O band (1572.5 cm$^{-1}$ for Fe(acac)$_3$, 1589.2 cm$^{-1}$ for Co(acac)$_3$, 1598.8 cm$^{-1}$ for Mn(acac)$_2$ and 1594.0 cm$^{-1}$ for Ni(acac)$_2$) and the fingerprint region from 1700 cm$^{-1}$ to 500 cm$^{-1}$ of the organic ligand. The presence of the acetylacetonate is also visible in the M(acac)$_x$-TiO$_2$ composites between 1700 cm$^{-1}$ and 1120 cm$^{-1}$. The band at 3412.7 cm$^{-1}$ for Ni(acac)$_2$ and 3409.5 cm$^{-1}$ for Co(acac)$_3$ correspond to the presence of crystalline water. After calcination at 350 °C, the absence of acetylacetonate signals can be assigned to its complete oxidation. On the bottom: photographs of the TiO$_2$ composites after impregnation with the different metal precursors before calcination.
Figure S2. Complete data sets of the in situ XRD experiments performed for pure acetylacetonate precursors (Mn(acac)₂, Co(acac)₃, Ni(acac)₂ and Fe(acac)₃). The data was recorded at air with a 5°C/min heating rate and temperature range from 25 °C to 800 °C. Legend: a: Mn₃O₄, NiO, b: Mn₂O₃, Ni.
Figure S3. Quasi in situ ATR-FTIR spectra showing the thermal decomposition of the original salt precursors (Mn(acac)₂, Co(acac)₃, Ni(acac)₂ and Fe(acac)₃) calcined at a temperature range from 25 °C to 600 °C.

Figure S4. SEM of the FeOₓ·TiO₂ sample representative for the rest of the composites. The images reveal the presence of nanoparticle aggregates corresponding to typical TiO₂ nanopowder. Image (c) shows individual TiO₂ nanoparticles with expected dimensions (20-50 nm). No foreign particles has been generated upon the composite formation.
Figure S5. EDX mapping of the CoOx-TiO2 (a), NiOx-TiO2 (b), MnOx-TiO2 (c), and FeOx-TiO2 (d) nanocomposites along with the Co (e), Ni (f), Mn (g) and Fe (i) EDX signals acquired for pure reference TiO2 powder. The images on the bottom are not related to the actual presence of these elements in TiO2, but rather originate from the data acquisition process and "non-zero" background signal of the EDX scans.

Figure S6. Electron diffraction (ED) pattern of the MOx-TiO2 composite. (a) Pure TiO2, (b) NiOx-TiO2, (c) MnOx-TiO2, (d) FeOx-TiO2 and (e) CoOx-TiO2 revealing that all samples show the corresponding d values of the TiO2 anatase phase (red) and rutile (yellow). The anatase phase is much more intense in all samples indicating a much higher concentration in the sample, while the rutile phase is present in a much lower amount, as can be seen by the much less intense signal.
Discussion of Raman data

In TiO\textsubscript{2} reference spectrum, peaks present at around 144, 198, 397, 517 and 640 cm\textsuperscript{-1} can be assigned to the \(E_g\), \(E_g\), \(B_1\), \(A_{1g}+B_{1g}\) and \(E_g\) modes of anatase phase, respectively (Figure S7), while the peak present at 448 cm\textsuperscript{-1} can be attributed to the \(E_g\) mode of rutile phase, in line with TiO\textsubscript{2} composition. Table S1 presents a summary of the peak positions and peak full-width at half-maxima (FWHM) of the strongest anatase \(E_g\) band of the TiO\textsubscript{2} reference as well as the rest of the MO\textsubscript{x}-TiO\textsubscript{2} composites:

<table>
<thead>
<tr>
<th></th>
<th>I ((E_g))</th>
<th>II ((E_g))</th>
<th>III ((B_1))</th>
<th>IV ((A_{1g}+B_{1g}))</th>
<th>V ((E_g))</th>
<th>VI FWHM of peak I ((E_g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2}</td>
<td>144</td>
<td>198</td>
<td>397</td>
<td>517</td>
<td>640</td>
<td>9.5</td>
</tr>
<tr>
<td>MnO\textsubscript{x}-TiO\textsubscript{2}</td>
<td>153</td>
<td>203</td>
<td>397</td>
<td>512</td>
<td>636</td>
<td>22.3</td>
</tr>
<tr>
<td>FeO\textsubscript{x}-TiO\textsubscript{2}</td>
<td>150</td>
<td>202</td>
<td>398</td>
<td>515</td>
<td>637</td>
<td>17.3</td>
</tr>
<tr>
<td>CoO\textsubscript{x}-TiO\textsubscript{2}</td>
<td>152</td>
<td>204</td>
<td>396</td>
<td>512</td>
<td>631 673</td>
<td>22.3</td>
</tr>
<tr>
<td>NiO\textsubscript{x}-TiO\textsubscript{2}</td>
<td>144</td>
<td>198</td>
<td>398</td>
<td>517</td>
<td>639</td>
<td>10.5</td>
</tr>
</tbody>
</table>

It can be seen from Table S1 that, compared with TiO\textsubscript{2}, all MO\textsubscript{x}-TiO\textsubscript{2} samples demonstrate substantial peak shifts (blue-shifts for peak ‘I’ and ‘II’, red-shifts for peak ‘IV’ and peak ‘V’), except for NiO\textsubscript{x}-TiO\textsubscript{2} sample. As an example, the shift of the most intense \(E_g\) band (I) can be considered.

It is known that the peak shift in Raman can be caused by different reasons, including the crystallite size\textsuperscript{1}, crystal strain\textsuperscript{2}, non-stoichiometry/doping\textsuperscript{3}, surface adsorbed species\textsuperscript{1}, etc. It is also known that the FWHM of the anatase \(E_g\) mode (~ 146 cm\textsuperscript{-1}) reflects the stoichiometric ratio of O/Ti\textsuperscript{4}. In the oxidation annealing experiment of TiO\textsubscript{2-x} performed by Parker and Siegel\textsuperscript{4}, the authors have discovered that the FWHM above 13 cm\textsuperscript{-1} indicates that the oxide is oxygen deficient (\(x > 0\)); and the higher the FWHM value is, the higher does the oxygen deficiency (\(x\)) get. The substantially larger FWHM values of MO\textsubscript{x}-TiO\textsubscript{2} (for Mn, Fe, Co) therefore suggest that the samples may have oxygen deficiency.

Overall, considering our composite systems, the data for MnO\textsubscript{x}-TiO\textsubscript{2}, CoO\textsubscript{x}-TiO\textsubscript{2} and FeO\textsubscript{x}-TiO\textsubscript{2} may suggest the presence of additional (apart from those observed in TEM) surface-adsorbed species on TiO\textsubscript{2}, creation of O vacancies or bulk doping with M ions.
More specifically for each of the composites (see Figure S7):

**MnO$_x$-TiO$_2$:**

The observed broadening/shoulder of the peak IV at 512 cm$^{-1}$ and peak V at 640 cm$^{-1}$ can be assigned to newly formed MnO$_x$ species decorating TiO$_2$ surface. These bands may be caused by various MnO$_x$ phases incl. manganite, pyrolusite or todorokite. However, given the similarity in the band position of different MnO$_x$ species, especially in light of the amorphous nature of the MnO$_x$ clusters in our composites, it seems incorrect to make any assumption about the possible phase or even oxidation state of Mn species. Besides this, MnO$_x$ have low Raman activity and are known for their high sensitivity to the laser-induced heating, which can easily cause shifts and broadening of the Raman peaks and thus unreliable interpretation of the Raman data.

**FeO$_x$-TiO$_2$:**

Compared with the Raman spectra of TiO$_2$, no additional band corresponding to FeO$_x$ have been detected. On the other hand, the observed peak broadenings of TiO$_2$ bands is also unlikely caused by the potential Raman bands of FeO$_x$ due to the position mismatch. No further conclusions can be made.

**CoO$_x$-TiO$_2$:**

Additional shoulder and peak arising at 470 cm$^{-1}$ and 673 cm$^{-1}$, respectively, can be assigned to the Co$_3$O$_4$ in line with our expectations. Compared with the standard position of the A$_{1g}$ band of crystalline Co$_3$O$_4$ expected at 680 cm$^{-1}$, the shifted vibrational band at 673 cm$^{-1}$ of our CoO$_x$-TiO$_2$ may indicate for the highly defective structure, in line with the amorphous nature, surface distribution and mixed composition of our CoO$_x$ clusters. In addition, referring to XPS data, Co$^{2+}$ could be present as dopant in the TiO$_2$ lattice. Due to the larger ionic radius of Co$^{2+}$ (0.885Å), substitutional Co$^{2+}$ dopants would tend to distribute on the surface of TiO$_2$, which would further lead to the formation of surface oxygen vacancies and surface disorder reflected in the shift of the TiO$_2$ E$_g$ band in the Raman spectra. Surface Co$^{2+}$ species could also take part in the observed OER.

**NiO$_x$-TiO$_2$:**

Especially interesting result was observed for NiO$_x$-TiO$_2$ composites whose Raman spectra did not resemble the behaviour observed for the rest of the composites (i.e. peak shifts and broadening of main TiO$_2$ bands), but looked rather identical to the reference TiO$_2$ powder.

Typically, signal broadening, decreased intensity and the peak shifts of TiO$_2$ bands may be indicative of the presence of doping, oxygen vacancies and other structural defects and disorders as well as crystal strain and surface adsorbed species. As mentioned before, some of these effects can take place in our MO$_x$-TiO$_2$ composites, but, surprisingly, there is no indication of these for the NiO$_x$-TiO$_2$ sample. Why does not this particular samples exhibit this kind of behaviours that could be expected for surface-immobilized amorphous MO$_x$ species?

According to our TEM results, NiO$_x$-TiO$_2$ sample features extremely small, but well defined NPs with the size of about 1 to 2 nm. Such homogeneity of the particle size and their fine distribution may indicate that the formed NiO$_x$ NPs are thermodynamically stable and have reached a certain optimal size during the precursor decomposition, followed by nucleation and growth of the NiO$_x$. If this process is energetically favourable, all Ni species would be consumed to form these NPs and one could expect neither Ni incorporation into the TiO$_2$ matrix (doping) nor presence of atomic Ni-based species over the TiO$_2$ surface, thus explaining no shifts or peak broadenings of the substrate TiO$_2$. Further investigation is required to understand this exceptional behaviour.
Figure S8. Steady-state photoluminescence (PL) spectra of the FeO$_x$-TiO$_2$, CoO$_x$-TiO$_2$ and NiO$_x$-TiO$_2$ composites along with the TiO$_2$ reference.
**Discussion about the crystallinity of the obtained MOx species**

To elucidate a possible reason why the resulting composites feature amorphous MOx NPs, we have subjected the pure Ni(acac)2 salt precursor to the same synthetic procedure than the composites (but without TiO2 present) and analysed the dried product after solvent evaporation with XRD. The data in Figure S9b revealed that indeed the salt losses its crystalline structure after being recollected as a powder. This, in turn, can explain why the resulting oxides after calcination may be of amorphous nature. The amorphous nature was also confirmed by synthesised model composites - using Ni(acac)2-TiO2 - with an increased amount of Ni(acac)2 up to 24.4 wt. %. The x-ray diffractograms of these model systems showed only the presence of TiO2 (rutile and anatase, Figure S9b and c) for both thermal treated and untreated samples. Thus, with these model system investigations, it can be confirmed that the generated metal species in our composites are indeed amorphous.

![Figure S9.](image)

Figure S9. (a) XRD data of the MOx-TiO2 composites (prepared at 350 °C) and the TiO2 reference to demonstrate the incapability of XRD to detect the newly deposited species. (b) Pure TiO2 as reference material and the corresponding Ni(acac)2-TiO2 as well as NiOx-TiO2 composites after calcination demonstrating that even higher precursor loadings do not yield XRD signals that can be attributed to NiOx species. The diffractogram on the bottom corresponds to the Ni(acac)2 salt after dissolution in ethanol showing that the originally crystalline salt loses its crystal structure after being recollected. (c) In situ XRD data of the Ni(acac)2-TiO2 composite with 24.4 wt. % Ni(acac)2 content (heating rate 5°C/min at air) from 20 °C to 800 °C: only signals corresponding to TiO2 (anatase and rutile) are visible in the spectra. Importantly, XRD profile starts changing (new peaks appear) above roughly 500 °C, which is exclusively related to gradual anatase-to-rutile conversion.
Figure S10. Survey XPS spectra of the (a) NiOx-TiO2, (b) MnOx-TiO2, (c) FeOx-TiO2 and (d) CoOx-TiO2 composites.

Figure S11. XPS spectra with the corresponding fits. a) and b) 2p Mn from the MnOx-TiO2 composite. c) Ni 2p spectra of NiOx-TiO2 composite.
Figure S12. Experimental setup for the hydrogen evolution reaction (HER) experiments that were performed in flow-mode (see Methods). The oxygen evolution reactions (OER) experiments were performed in the same reactor, but without any gas flow. The oxygen sensor was introduced through septum.
Discussion of the XPS data for the samples after OER

Figure S13. XPS spectra of the (a) FeOx-TiO2, (b) CoOx-TiO2 and (c) NiOx-TiO2 composites before (upper raw) and after OER (lower raw).

XPS spectrum of the FeOx-TiO2 after photocatalytic reaction (**Figure S13a**) clearly indicates the increase of the signals corresponding to Fe$^{3+}$ species as can be seen from the appearing of the characteristic satellites at 719 and 737 eV. The spectrum after OER shows that Fe$^{2+}$ is still present in the composite as one of the main components, but we can clearly suggest that some of the initial Fe$^{2+}$ species oxidized during the photocatalytic process (the samples prepared for these XPS measurements were exposed to 1h-long illumination under OER conditions).

XPS spectrum of the CoOx-TiO2 after reaction (**Figure S13b**) also indicates that oxidation of the initially present Co species takes place. As such, we do not anymore observe the shoulder at 778 eV (corresponding to small amount of metallic Co potentially present in the as-prepared composite), while the satellite at 786 eV gets effectively reduced implying that some of the Co$^{2+}$ species (e.g. the suggested Co(OH)$_2$) turn into Co$^{3+}$ during the photocatalytic OER.

XPS spectrum of the NiOx-TiO2 after OER (**Figure S13c**) marks strong differences to the other samples investigated after reaction: no signal characteristic for NiO/Ni species can be observed anymore. This cannot be related to composite instability or potential leaching of the Ni species into the solution under photocatalytic conditions as the XPS data after HER experiment clearly shows that Ni signal is preserved even after 14 hour light illumination run. We believe that this specialty of the NiOx-TiO2 is related to the role of NiO$_x$ species in OER and associated with the electron reduction of Ag$^+$ that was used as sacrificial agent. Given that XPS is a surface sensitive technique, we suggest that metallic Ag – being the product of Ag$^+$ reduction, as also confirmed by XPS – gets deposited onto NiO$_x$ sites that act as electron acceptor and release centres. This Ag shell effectively blocks the Ni sites not allowing for any XPS analyses.

This result highlights the differences between NiO$_x$ and the other two co-catalysts active for OER in terms of their role in charge extraction and separation, however, would require an extended investigation to elaborate on this in light of the rest of the data.
Table S2. XPS fitting parameters

<table>
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<tr>
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<th>MnO</th>
<th>Co metal*</th>
<th>Co(OH)₂</th>
<th>Co₂O₄</th>
<th>FeO</th>
<th>Ni metal†</th>
<th>NiO</th>
<th>Ni(OH)₂</th>
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<td>24.23</td>
<td>3.32</td>
<td>4.80</td>
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</tr>
<tr>
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<td>Co³⁺</td>
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<td>Ni(OH)₂</td>
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<td>855.3</td>
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Table S3. XPS quantification data of the best fits: Ni, NiO and Ni(OH)₂. Ni 2p composition in atomic % before HER, after HER (still wet from the reaction) and after HER dried overnight.

<table>
<thead>
<tr>
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<th>before</th>
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<th>after(dry)</th>
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<tbody>
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<td>Ni</td>
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<td>9.2</td>
</tr>
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<td>NiO</td>
<td>33.6</td>
<td>0.0</td>
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<tr>
<td>Ni(OH)₂</td>
<td>63.0</td>
<td>83.3</td>
<td>59.5</td>
</tr>
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</table>

*line shape LA(1.2,5,5)
†line shape LA(1.1,2.2,29)
References