**Supporting Information**

CrOx-mediated Performance Enhancement of

Ni/NiO-Mg:SrTiO3 in Photocatalytic Water Splitting

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**Figure S1.** Stability measurement: Photocatalytic activity of CrOx-modified Ni/NiOx-Mg:SrTiO3 during three cycles mimicking day/night operation. Reaction conditions: 25 mg catalyst in 25 mL DI water. 365 nm LED-light was used as illumination source. Note that fluctuations at longer measurement times are due to instabilities in the GC-detection.

Chart

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**Figure S3**. Comparison of Ni/NiOx-SrTiO3 and (CrOx modified) Ni/NiOx-SrTiO3 under 365 nm LED light illumination.



**Figure S4.** Photocatalytic activity of CrOx-modified Ni/NiOx-Mg:SrTiO3 with introduction of 80 ppm of H2, O2 and N2 between 150 minutes and 300 minutes. Reaction conditions: 25 mg catalyst in 25 mL DI water. 365 nm LED-light was used as illumination source.

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**Figure S5.** Photocatalytic activity of Ni/NiOx-Mg:SrTiO3 (a,b) and CrOx-modified Ni/NiOx-Mg:SrTiO3 (c,d) at variable purge gas rates. (a,c) the measured concentration of H2 and O2 in ppm, (b,d) the corresponding rate. Reaction conditions: 25 mg catalyst in 25 mL DI water and 365 nm LED-light was used as illumination source.

**Characterization**

Structural characterization of different material compositions by XRD is shown in Figure **S5**. The X-ray diffraction patterns of Mg:SrTiO3 are consistent with the typical SrTiO3 cubic structure. After deposition of NiOx and CrOx on the surface, the cubic phase remains, illustrating that incorporation of NiOx or CrOx in the lattice is minimized. The Raman spectra of various composites are shown in Figure S**6**. Two typical SrTiO3 bands center in the 200-400 cm-1 and 600-800 cm-1 ranges17, indicative of SrTiO3, while features of NiOx and CrOx remain undetected.



**Figure S6.** XRD patterns of pristine Mg:SrTiO3, Ni/NiOx-Mg:SrTiO3 and CrOx-modified Ni/NiOx-Mg:SrTiO3 composite photocatalysts.

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**Figure S7.** Raman spectra of Ni/NiOx-Mg:SrTiO3 and CrOx-modified Ni/NiOx-Mg:SrTiO3 composite photocatalysts.

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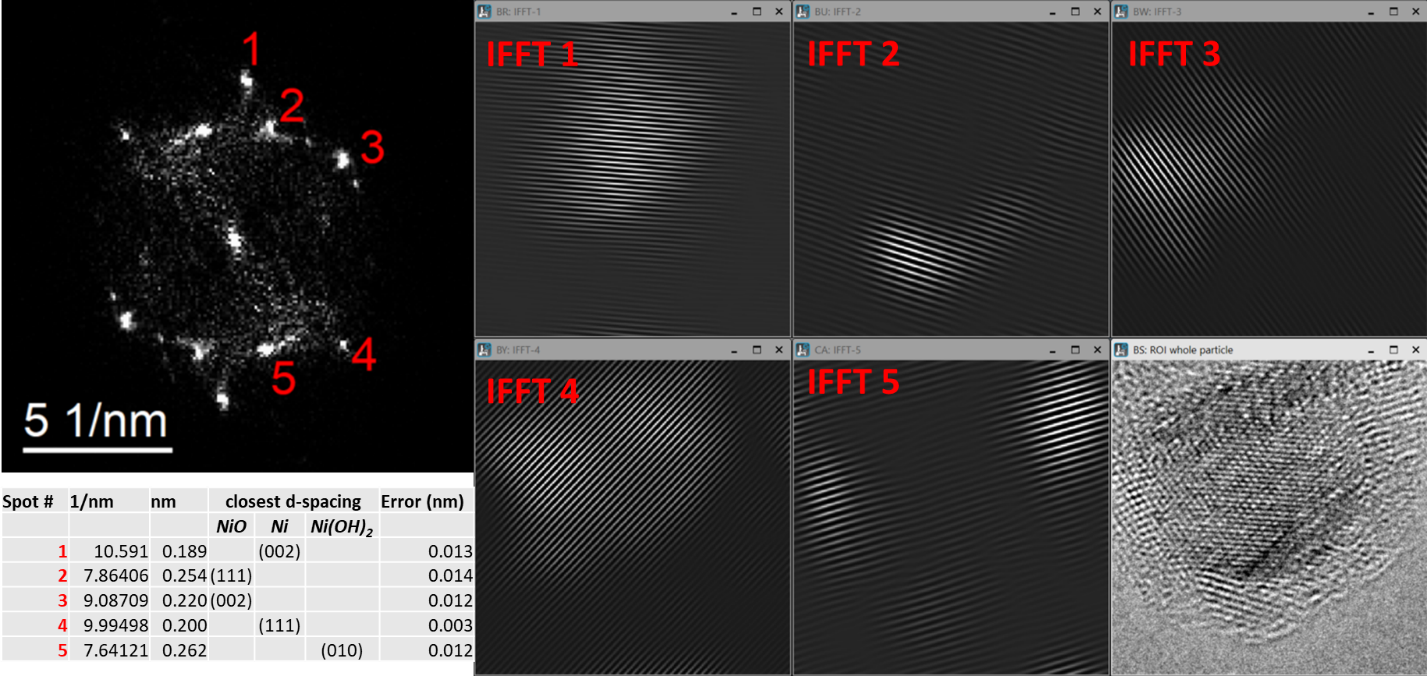
**Figure S8.** XPS spectra of the Ni2p3/2 signal of Ni/NiOx-Mg:SrTiO3 (a) and CrOx-modified Ni/NiOx-Mg:SrTiO3 (b): (both fresh and measured samples).

Chart, histogram

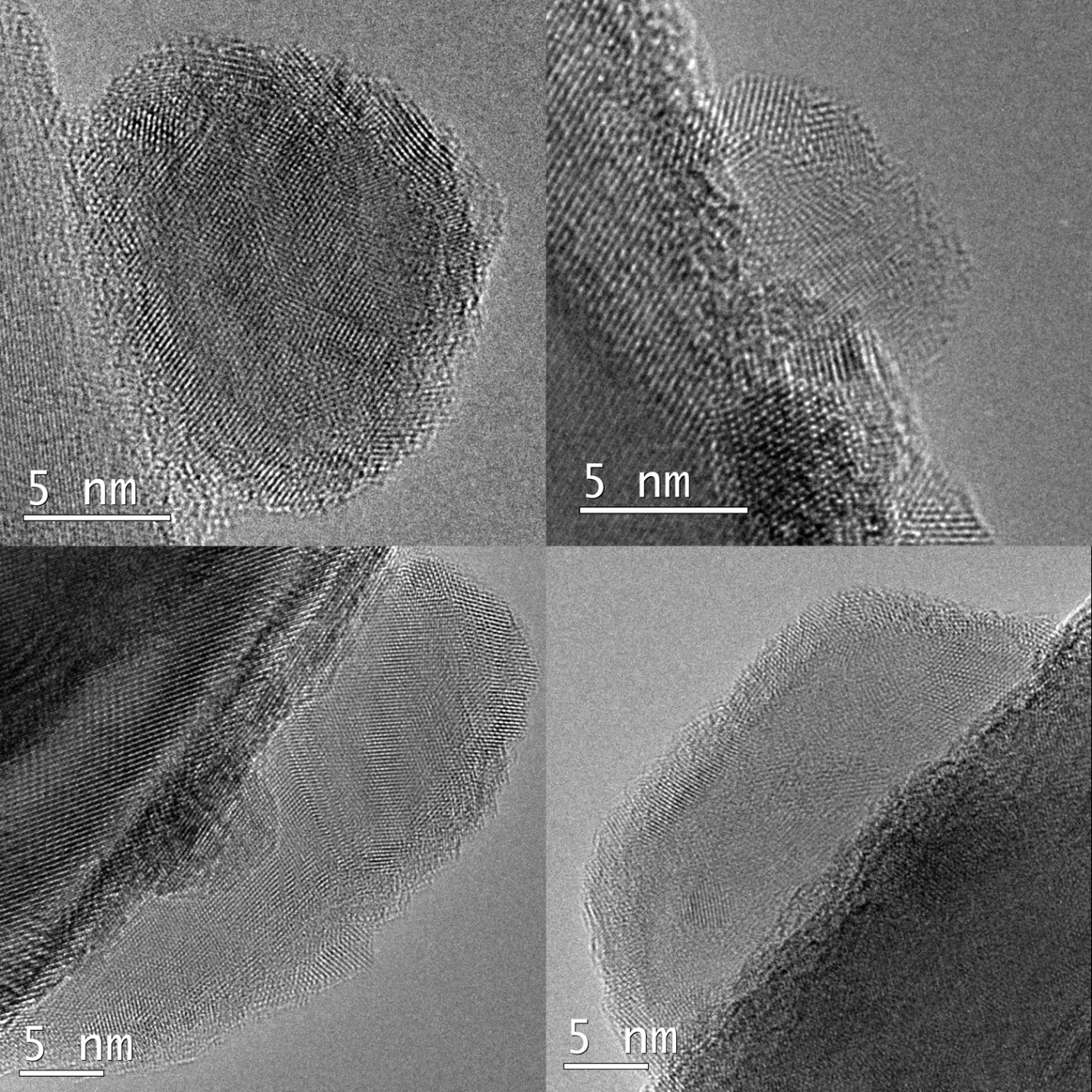
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**Figure S9.** XPS spectra in the O1s region of both fresh and measured samples of Ni/NiOx-Mg:SrTiO3 (a) and CrOx-modified Ni/NiOx-Mg:SrTiO3 (b).

TEM analysis

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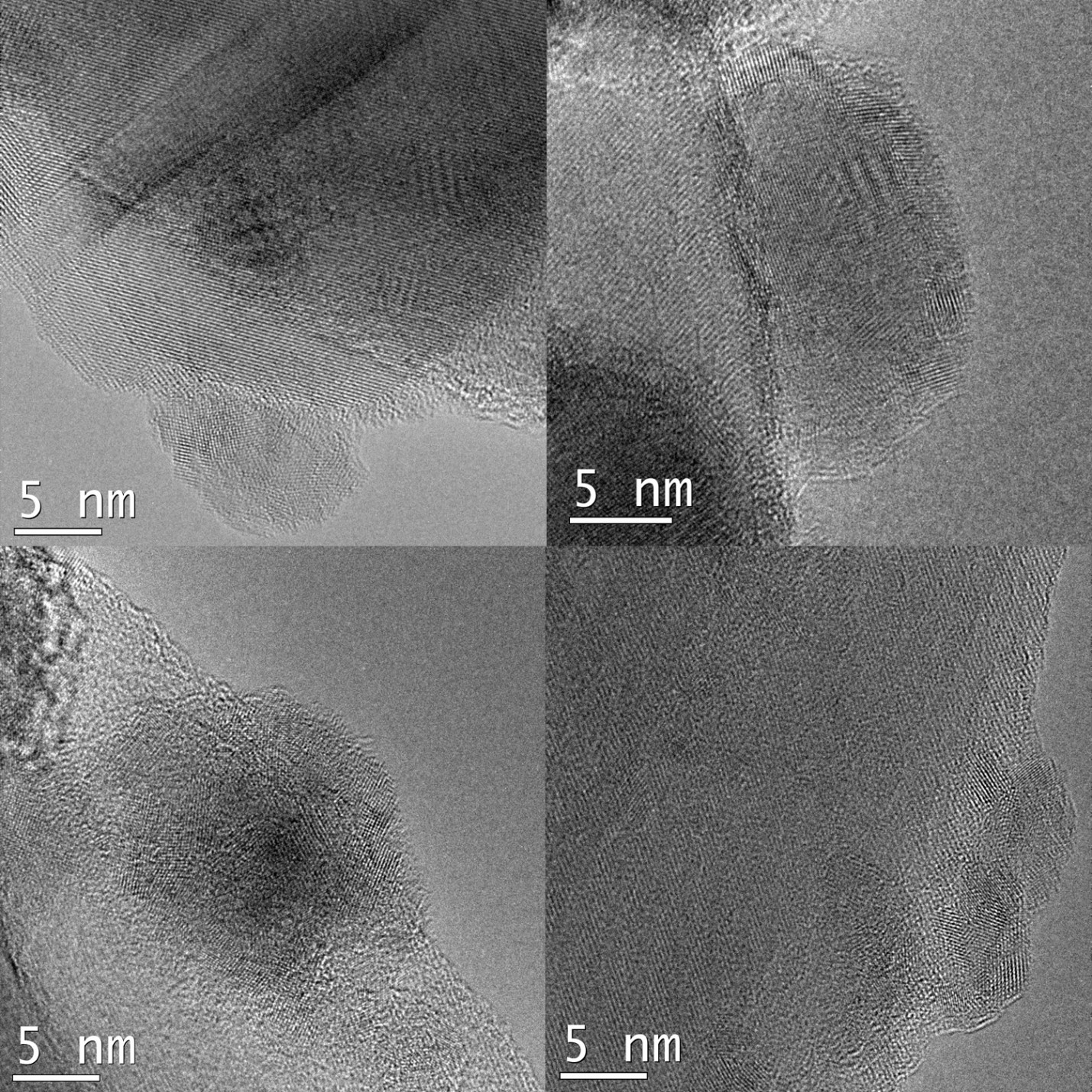
**Figure S10.** Inverse FFT analysis and phase identification applied to a NiOx particle from CrOx-modified Ni/NiOx-Mg:SrTiO3 (fresh).



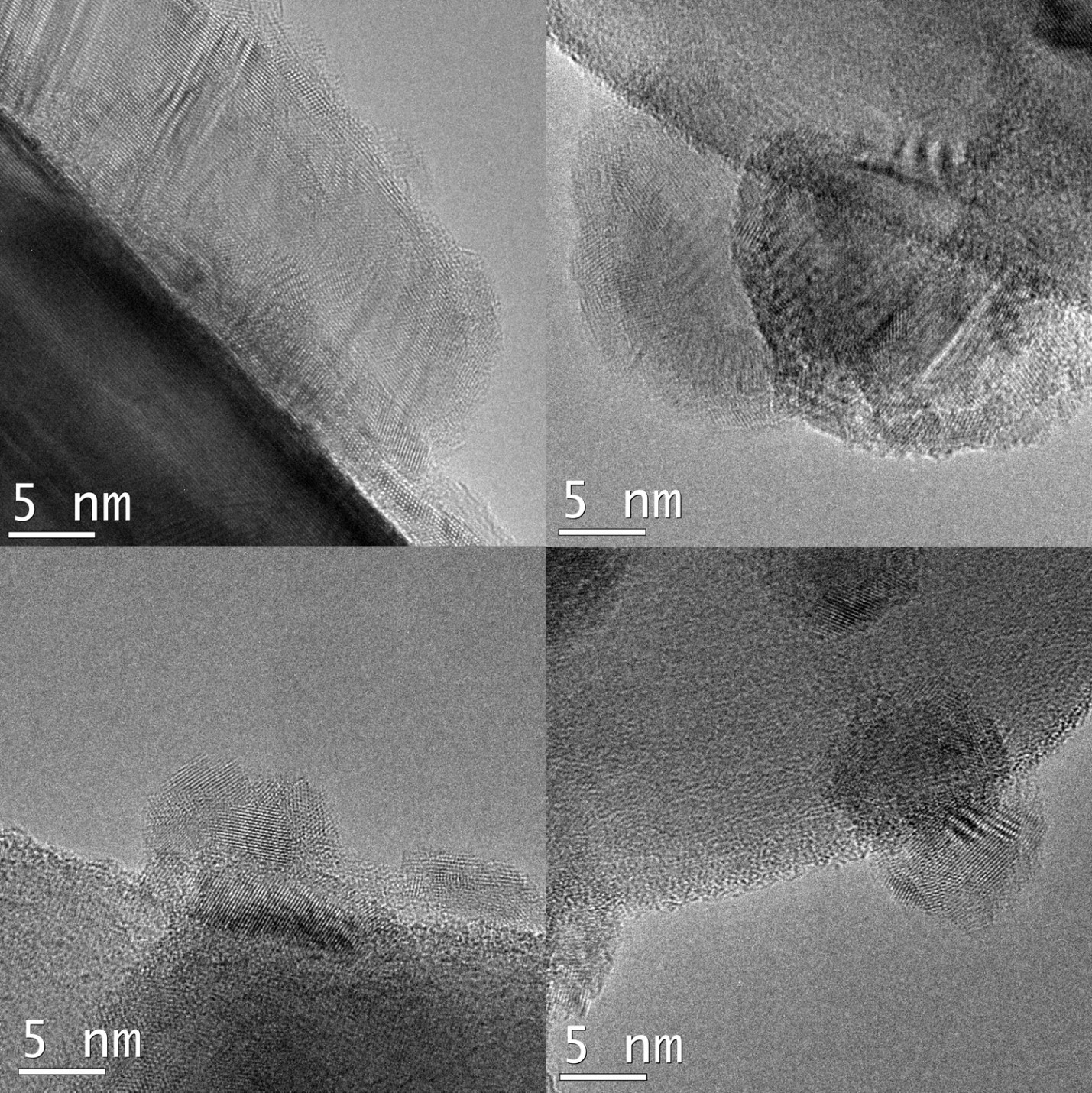
**Figure S11.** Additional HRTEM images of NiOx particles on CrOx-modified Ni/NiOx-Mg:SrTiO3 (fresh).



**Figure S12.** HRTEM images of NiOx particles on Ni/NiOx-Mg:SrTiO3 (fresh).



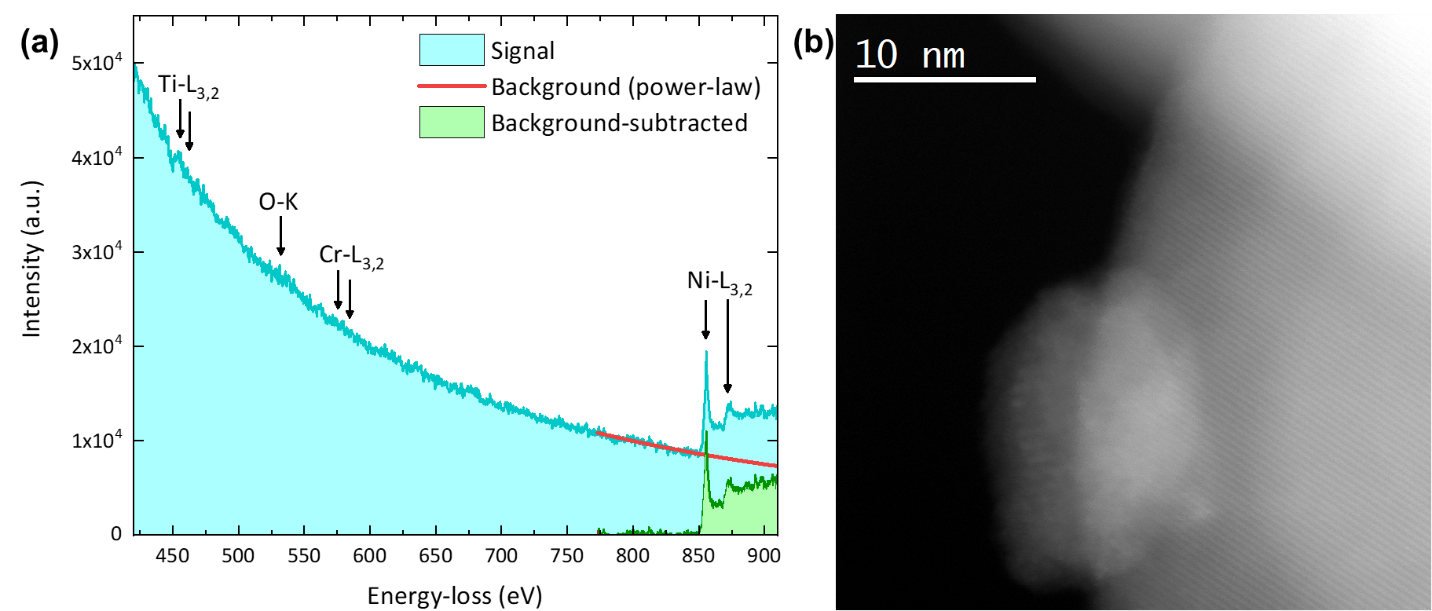
**Figure S13.** HRTEM images of NiOx particles on CrOx-modified Ni/NiOx Mg:SrTiO3-NiOx (used).

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**Figure S14.** HRTEM images of NiOx particles on Ni/NiOx-Mg:SrTiO3 (used).

STEM-EELS

The surface of the as-prepared CrOx-modified Ni/NiOx-Mg:SrTiO3 was further investigated using STEM-EELS. A representative core-loss spectrum is show in **Figure S14**. Despite the higher scattering cross sections making Cr potentially easier to detect, no Cr-L2,3 peak is visible. One explanation for the lack of a Cr signal in the EELS analysis of individual particles is that particles with Cr may have a very small relative amount of Cr which is below the detectability limit of EELS, despite the higher scattering cross sections. The advantage of the EDX is that the background is very low allowing larger areas, containing many Ni/NiOx particles on the thick Mg:SrTiO3 support to be analyzed, which apparently enhanced the Cr signal enough to be detectable. Another explanation is that the electron dose rates required for creating sufficient signal in the EELS analysis of individual particles was high enough to drive Cr out of the surface due to radiation damage.



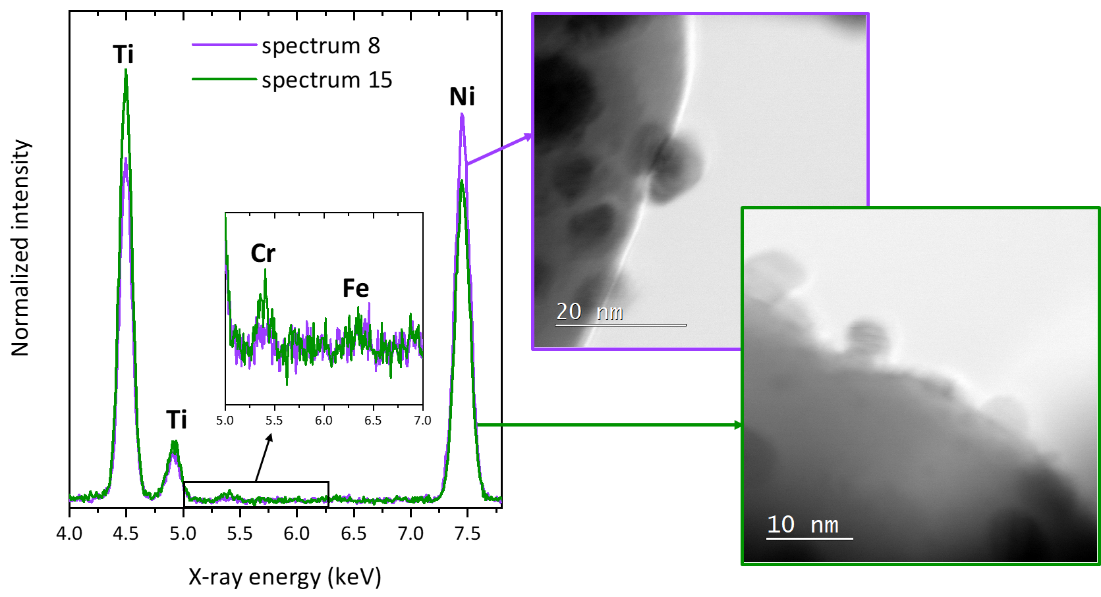
**Figure S15.** (a)Representative core-loss EELS spectrum from the fresh and Cr-treated Mg:SrTiO3-NiOx showing the presence of Ni and absence of Cr. The energy-loss spectra were obtained by scanning the beam over the NiOx particles only. (b) A typical STEM image, produced from the annular dark field detector, of a supported NiOx particle.

STEM-EDX

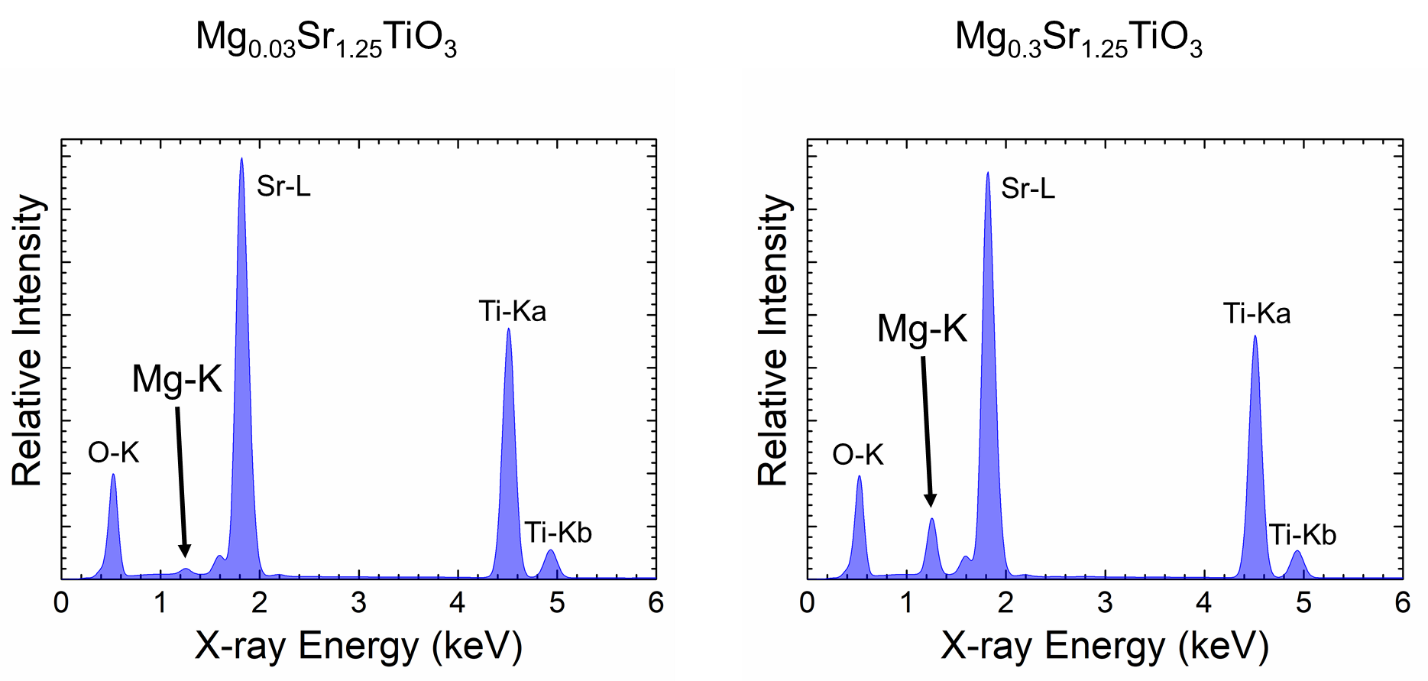
In the electron microscope, the pole piece (containing Cr and Fe) is constantly excited by X-rays emitted from the sample (resulting from ionization of the sample by fast electrons), therefore each spectrum will contain a baseline Cr and Fe signal. Thus, if Cr is present (and detectable) on the NiOx particles, the Cr/Fe ratio should increase in regions containing these particles. To assess whether the Cr signals present in regions containing Ni/NiOx were statistically significant above the pole piece contribution, the relative intensity of the Cr, Ni, and Fe peaks of each individual spectra were normalized to the Sr-Kα line at 14.14 keV, which suffers minimally from thickness-dependent absorption effects.



**Figure S16.** EDX signal analysis: Cr/Fe integrated peak intensity ratios found for each spectrum from the bulk (left graph), supported NiOx particles (middle graph), and the bare Mg:SrTiO3 surface (right graph). Similarly, the mean and average error (0.721 ± 0.309) associated with bulk (*i.e.*, pole piece contribution) is marked in maroon/light red.

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**Figure S17.** Comparison of EDX spectra 8 and 15 from regions containing NiOx particles. Both spectra exhibit high Ni content but only one (spectrum 15) shows significant Cr signal above the pole piece contribution.



**Figure S18.** Simulated EDX spectra of Mg0.03Sr1.25TiO3 (left) and Mg0.3Sr1.25TiO3 (right) produced using NIST’s DTSA-II software.

**Stability: ICP studies**

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**Figure S19.** Experimental dissolution data obtained for the photocatalysts examined. Dissolution is measured constantly over time for Sr (a), Ni (b), Mg (c).

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**Figure S20.** Accumulated amounts during the first 10 minutes of contacting with the aqueous flow.