Supporting Information

Transient behavior of Ni@NiO$_x$ Functionalized SrTiO$_3$ in Overall Water Splitting

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EXPERIMENTAL METHODS

Preparation of Ni@NiO$_x$ on SrTiO$_3$. SrTiO$_3$ was fabricated *via* a high temperature solid state process.[1,2] Briefly, stoichiometric amounts of SrCO$_3$ (99.995 % Sigma-Aldrich) and Rutile TiO$_2$ (99.995% Sigma-Aldrich) were mixed and calcined at two different temperatures, namely 1000 °C and 1100°C (heating rate 10 K/min), for 10 h. These powders will be referred to as BSTO-1000 and BSTO-1100. Deposition of core-shell Ni@NiO$_x$ particles on the surface of SrTiO$_3$ was achieved by a wet impregnation method,[1] applying a loading amount of 3 wt-% NiO. Briefly, 0.2 g SrTiO$_3$ powder was dispersed in 20 mL of an aqueous solution of 3.95 mM Ni(NO$_3$)$_2$. The obtained mixture was stirred for 2 h. Then, the solution was evaporated till dryness at 80 °C overnight, and calcined for 30 min at 400 ^{0}C (heating at 10 K/min) in flowing air (30 mL/min) in a tube furnace. The air above the solid was flushed with N$_2$ during cooling down to room temperature and then replaced by 5% H$_2$/N$_2$ (30 ml/min), followed by reheating the sample to 500 ^{0}C (at 10 K/min), and maintaining that temperature for 5 h. The final product was obtained by cooling down in nitrogen flow to 130 ^{0}C, and a treatment of 1 h in flowing air (30 ml/min) at this temperature. The Ni@NiO$_x$ containing samples are labeled BSTO1000-NiO$_x$ and BSTO1100-NiO$_x$, respectively.

Sample characterization

XRD measurements were performed on a Bruker D2 (Cu kα source) diffractometer. A Nova 600-nanolab HR-SEM (FEI instruments) was used for SEM experiments. TEM imaging of the deposited Ni/NiO$_x$ particles was performed using a Philips CM300ST-FEG microscope equipped with a Kevex EDX detector. Samples for TEM analysis were prepared by dispersion in ethanol, and deposition onto a carbon coated TEM grid. The X-ray Photoelectron spectroscopy (XPS) measurements were performed on a Quantera SXM (Physical Electronics) instrument, equipped with an Al Kα X-ray source (1486.6 eV). The binding energies were referenced to the Ti 2p3/2 core level peak at 457.7 eV, since surface carbon quantities were low before and after the photocatalytic experiments.

Reference NiO and NiOOH samples were used to determine the peak positions of the different Ni species in the composite material. Commercial NiOnano-powder from Sigma-Aldrich, (<50 nm particle size, 99.8% trace metals basis) was used. NiOOH was prepared as a thin film on ITO/glass,using a three-step electrochemical method previously reported by Chang et al.[3]

The Ni concentration on samples before and after photocatalytic measurement was determined by Inductively coupled plasma optical emission spectroscopy (ICP-OES), using a Perkin Elmer 8300dv instrument. Ni was dissolved out of various specimens in 4.5 mL of 7M nitric acid. The Ni loading was determined using results from the isotope with the lowest detection limit.

Photocatalytic activity experiments.

The photocatalytic activity of the compounds in pure water was measured using a continuously stirred tank reactor connected to a highly sensitive gas chromatograph (CompactGCInterscience). The GC was equipped with a Pulsed Discharge Detector. The pH of the suspension was measured to be 9 initially, and hardly changed during the experiments.By a constant helium (7N) purge (10 mL/min), the gas to be analyzed was transferred to the GC. In the GC, a 50 μL sample loop inserted a sample onto a Q-bond column to remove H_2O, and a Molsieve 5A, to separate the gaseous components present in the sample, being H_2, O_2 and N_2. The optical glass reactor (402.013-OG, Hellma) was illuminated by a 1.5 AM solar simulator (ABET technologies model 10500 low cost solar simulator, 5 cm^2 beam area), which is representative of the intensity profile of solar radiation. The intensity incident on the reactor window from 300-900 nm amounted to 59 mW/cm^2, and from 300-400 nm to 0.9 mW/cm^2. The measurements were performed using 25 mg catalyst in 25 mL of purified water. The apparent quantum efficiency of selected samples was calculated as reported elsewhere.[5]

Characterization of $SrTiO_3$

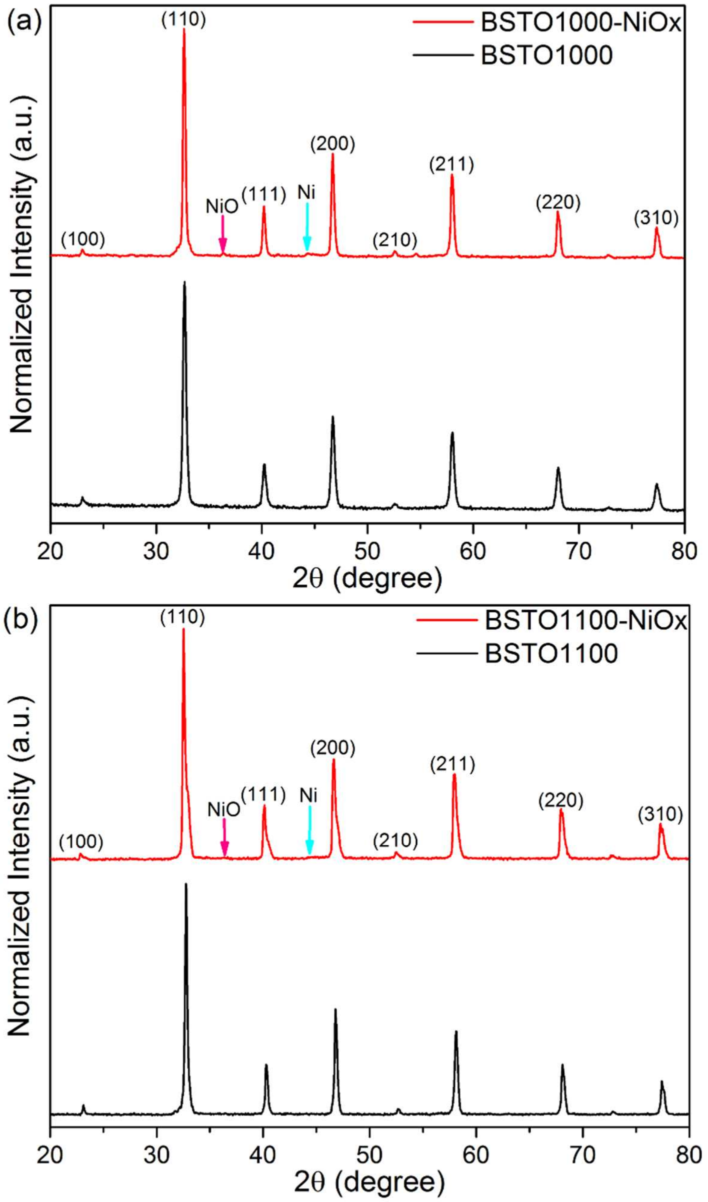

Fig. S1 XRD patterns of $SrTiO_3$ prepared at 1000°C and 1100°C before and after functionalization with Ni@NiO_x core-shell particles.

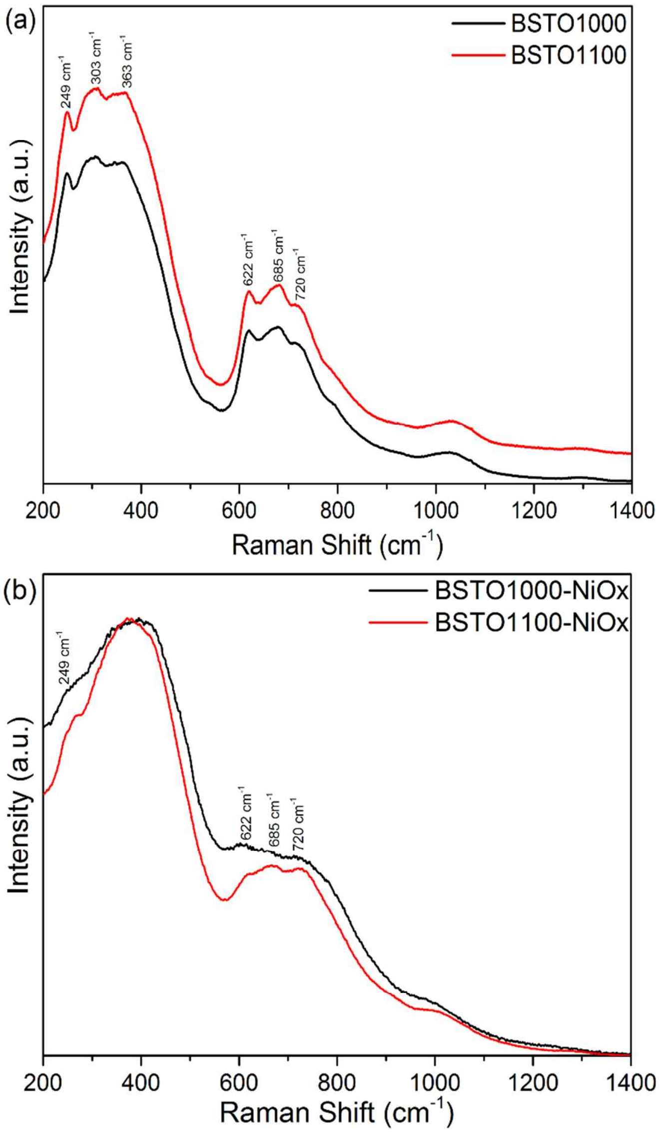

Fig. S2 Raman spectra of a) $SrTiO_3$and b) Ni@NiO_xon $SrTiO_3$prepared at 1000°C and 1100°C, respectively.

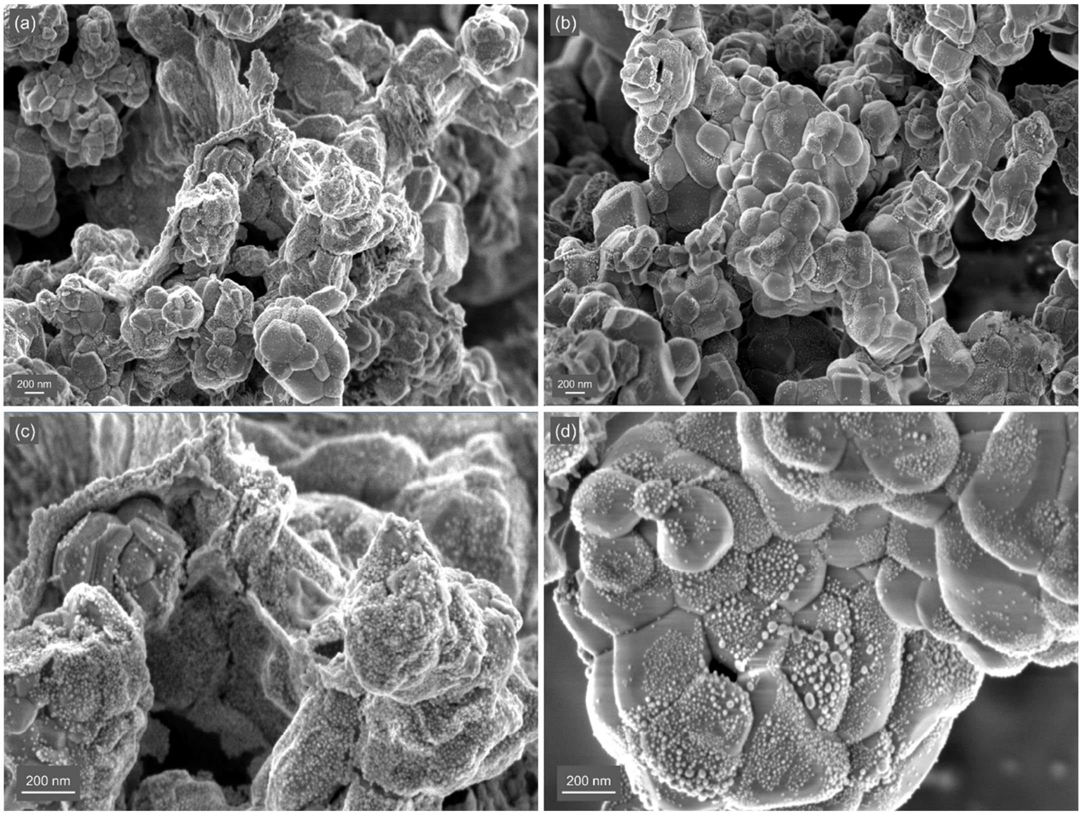

Fig. S3 High-resolution SEM images of $SrTiO_3$ prepared at (a,c) 1000°C and (b,d) 1100°C before and after functionalization with $Ni@NiO_x$ core-shell particles.

Representative high-resolution SEM (HRSEM) images of BSTO1000-NiO_x and BSTO1100-NiO_x catalysts are shown in Fig. S3. Well-crystallized $SrTiO_3$ particles with multiple facets can clearly be observed, in particular for the sample prepared at 1100°C. On the surfaces of $SrTiO_3$ crystallites (most obvious in Fig S3d), $Ni@NiO_x$ particles of variable sizes can be observed. Several $Ni@NiO_x$ particles are significantly smaller than 10 nm, whereas others are present in the size range of 10-30 nm. The spatial distribution of the particles forBSTO1100-$NiO_x$is not as homogeneous as forBSTO1000-NiO_x(compare FigsS3(c) and S3(d)). Some facets appear almost void of particles, whereas others are densely covered, typically containing the $Ni@NiO_x$ particles of the largest sizes.

Overall water-splitting

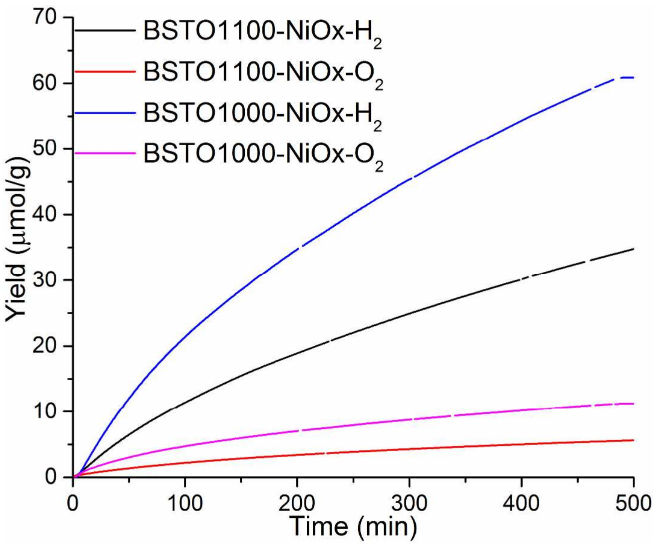

Fig. S4 Integrated H_2 and O_2yields obtained forNi@NiO$_x$ core-shell particlesdeposited on SrTiO$_3$ prepared at 1000°C and 1100°C, respectively.

To evaluate the photocatalytic activity of the Ni@NiO$_x$ core-shell functionalized SrTiO$_3$ materials prepared at different temperatures, solar water splitting under 1.5 AM solar light illumination was performed. As shown in Fig. S4, H_2 and O_2evolved simultaneously. BSTO1000-NiO$_x$ outperforms BSTO1100-NiO$_x$. Thus, for further experiments BSTO1000-NiO$_x$ was used.

Using a measuredhydrogen production rate of 0.1 µmolg^{-1} min^{-1} (i.e.6 µmolg^{-1}h^{-1}), and the determined light intensity of 0.9 mW/cm^2 in the range of 300-400 nm, the apparent quantum efficiency can be calculated to be 0.6%. Taking the different reaction conditions applied by Osterlohet al.[4]into account (in particular the higher light intensity applied), the activity and yield are of the same order of magnitude as reported previously.

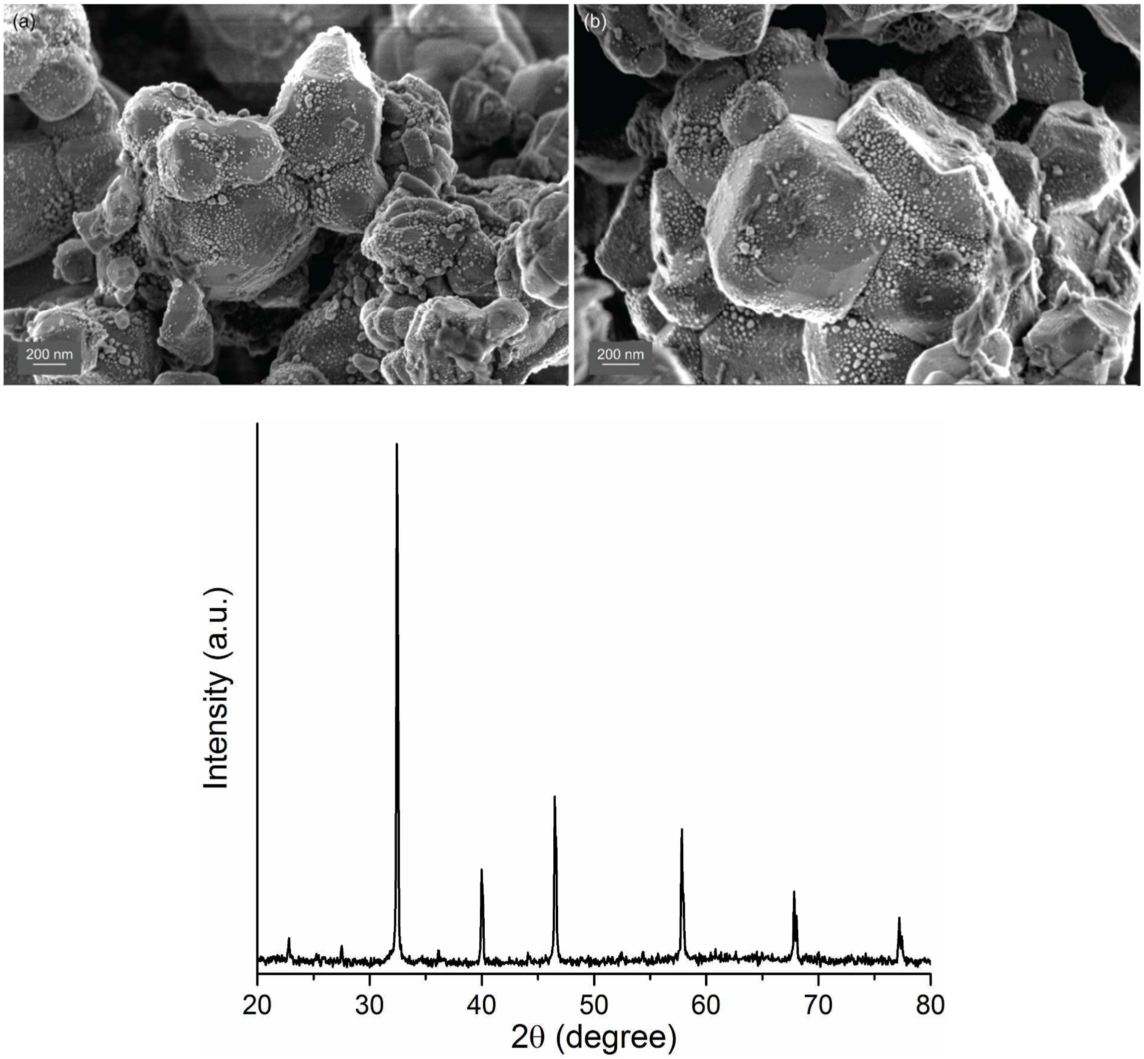

Fig. S5 HRSEM images and XRD pattern of $SrTiO_3$ after photocatalytic water splitting.

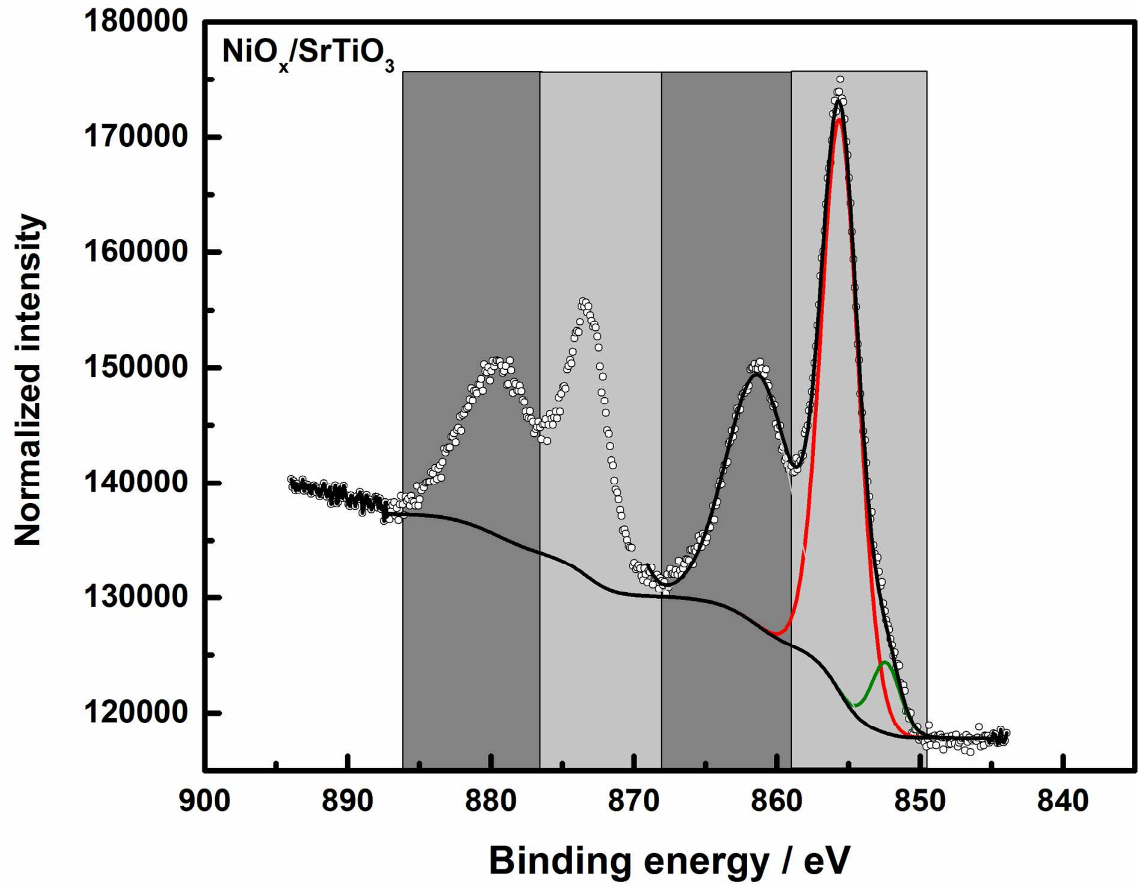

Fig. S6 XPS spectra of the full Ni2p region of the BSTO1000-NiO$_x$ sample after regeneration for 48 h and additional testing in photocatalytic overall water splitting.

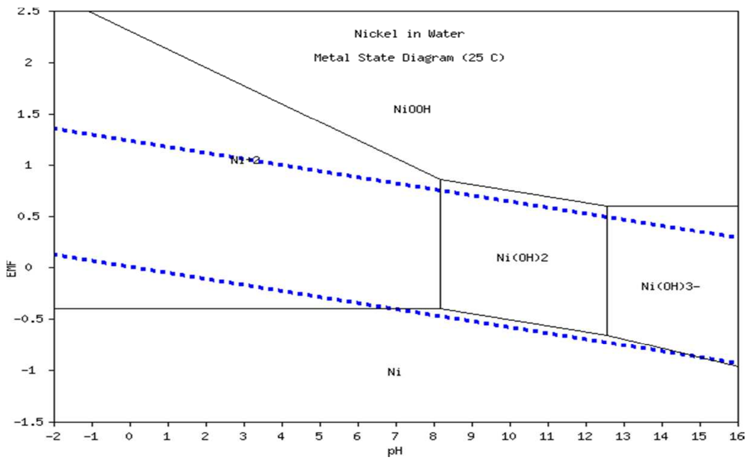

Fig. S7Pourbaix diagram of Ni.[5] The pH of the slurry applied in this study was close to 9.

Table S1. Ni loading of the BSTO1000-NiO_x sample before illumination NiO_x/STO (as prep.),and after illumination NiO_x/STO (meas.).

	Ni loading [wt%]
Ni@NiO_x/STO (as prep.)	2.4
Ni@NiO_x/STO (meas.)	2.3

Table S2. Comparison of Ni leaching during photocatalytic water splitting observed in this study compared to previous work by Crozier et al.[6]

	sample	Ni loading [μmol]	Ni in solution after testing [μmol]
Crozier et al.[6]	0.2 g TiO_2 with 1 wt% NiO_x	26.8	4
Our work	30 mg $SrTiO_3$ with 3wt% NiO_x	12.1	0.3

According to ICP analysis, significantly less leaching of Ni occurs from $SrTiO_3$ (this study) as compared to TiO_2 (Crozier et al. [6]). This might be related to the relatively high pH of our suspension (close to 9) as compared to the natural pH of TiO_2 suspensions, although the applied pH was unfortunately not mentioned by Crozier and coworkers.[6]

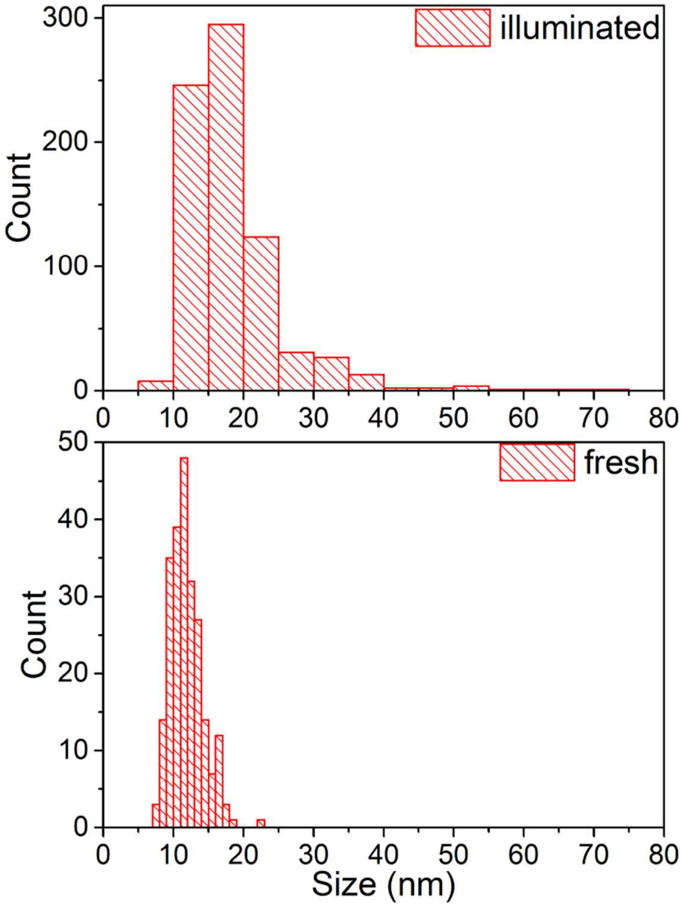

Fig. S8 NiO_x particle size distribution of the as-prepared and the illuminated Ni@NiO_x $SrTiO_3$ composite material.

Table S3.d-spacings obtained from FFT analysis of the as-prepared, the illuminated, and the regeneratedNi@NiO$_x$ SrTiO$_3$ composite materials.

Sample	d-spacing (Å)	Assignment
NiOx/STO (as prep.)	2.06	Ni
	2.41	NiO
NiOx/STO (meas.)	6.7 2.96 2.36	NiOOH
	2.41	NiO
	2.06	Ni
NiOx/STO (reg.)	4.6 2.6 2.1	Ni(OH)$_2$
	2.46	NiO
	2.06	Ni

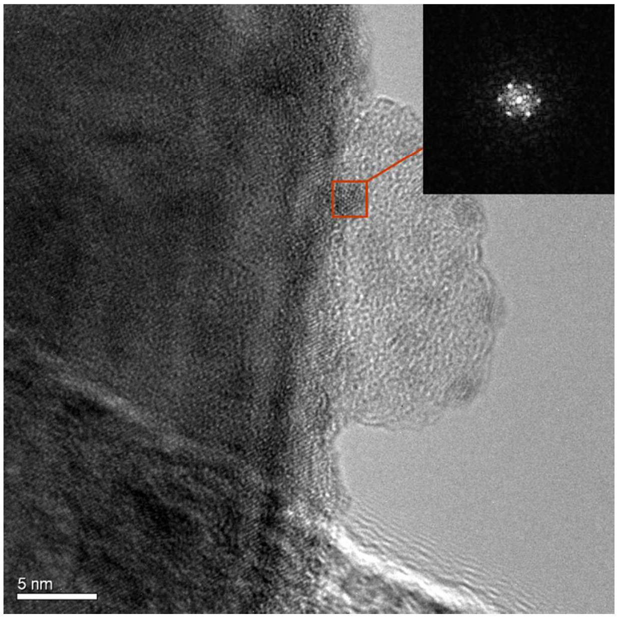

Fig. S9 The FFT analysis (inset)confirms the particle with the larger contrast consists of metallic Ni.

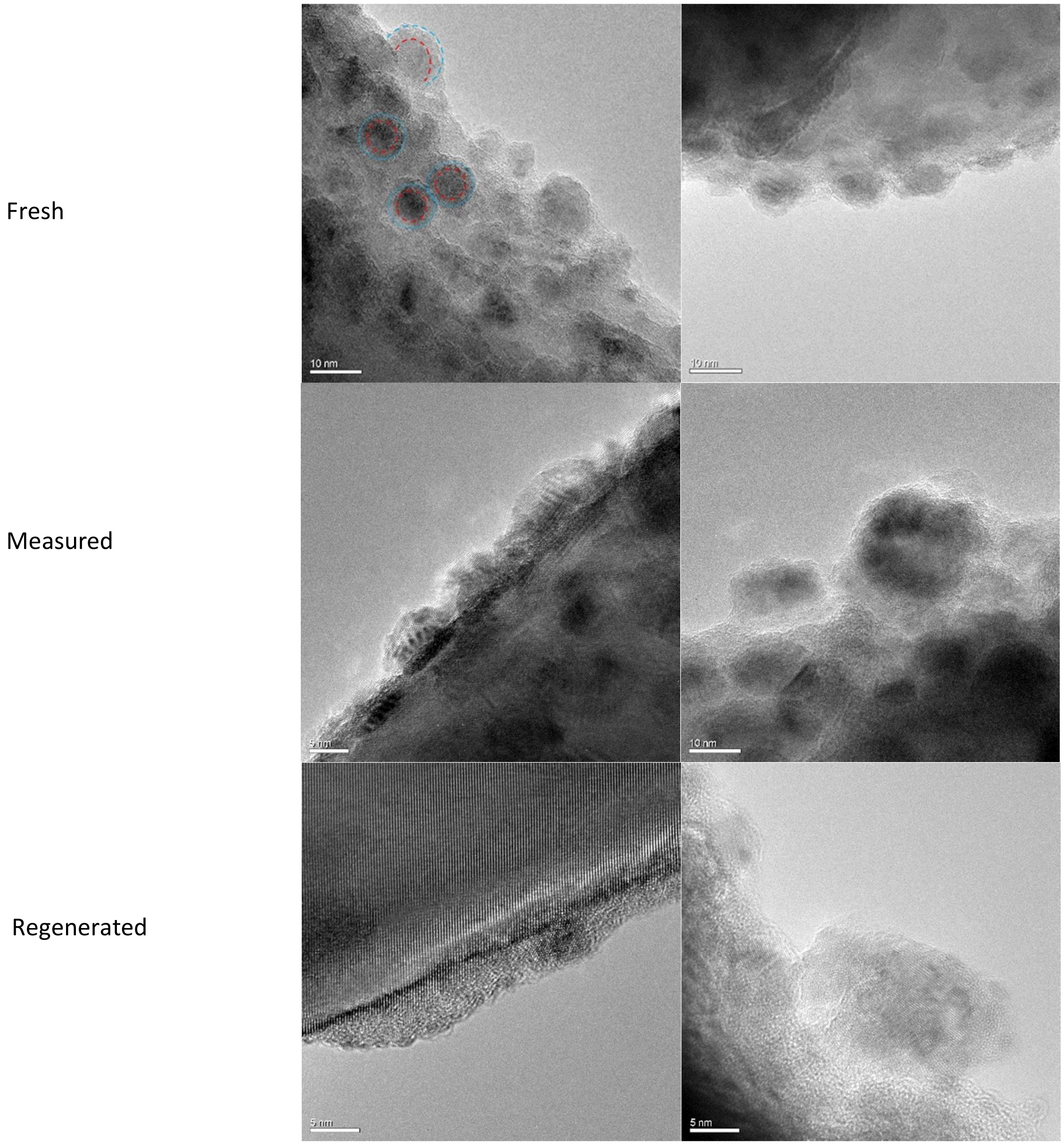

Fig. S10 HRTEM images of fresh (first row), illuminated (second row), and regenerated (third row) BSTO1000-NiO_x sample.

References

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