

## SUPPLEMENTARY INFORMATION

# Engineering kinetics and interfacial energetics of Ni/Ni–Mo catalyzed amorphous silicon carbide photocathodes in alkaline media

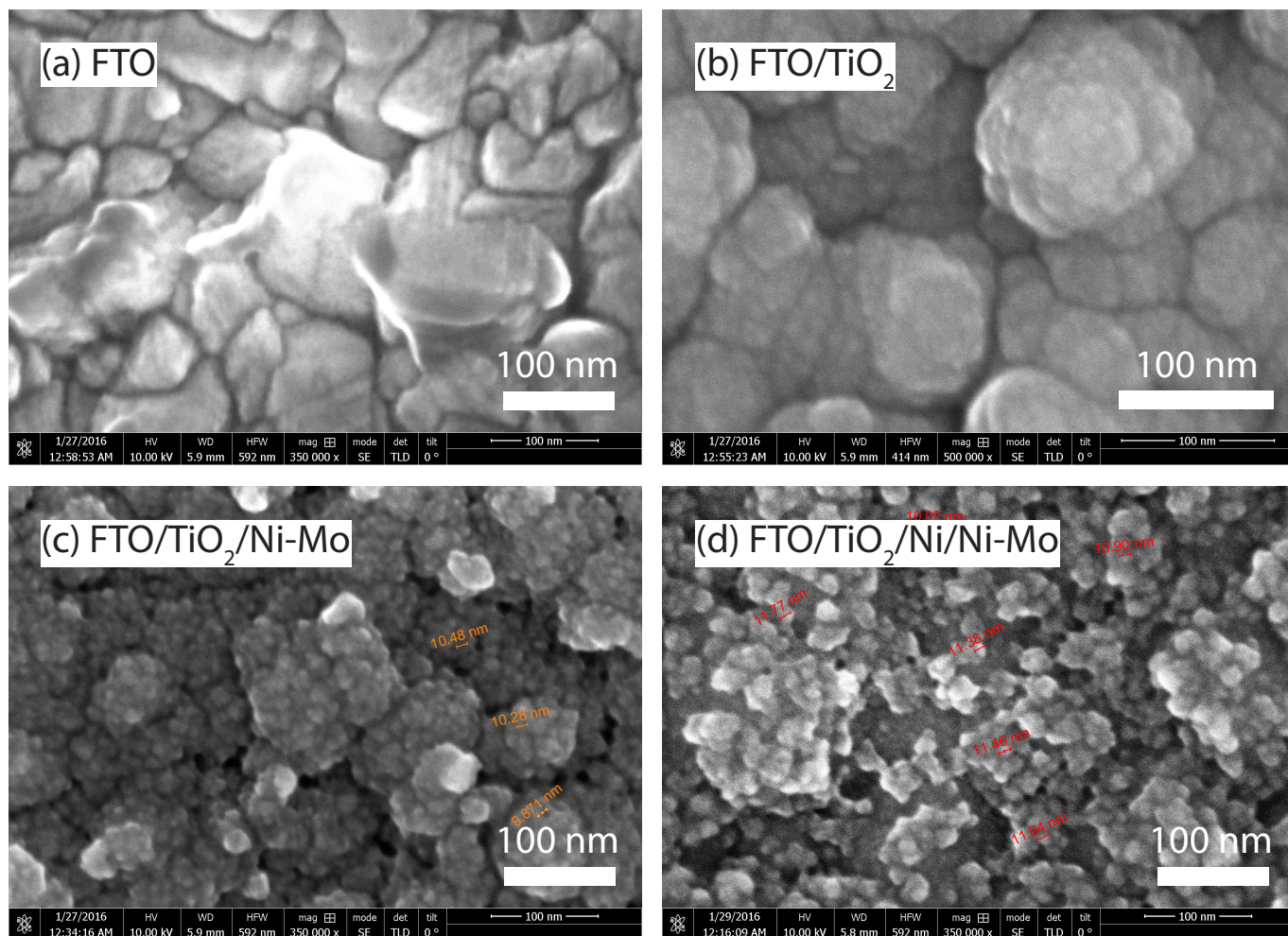
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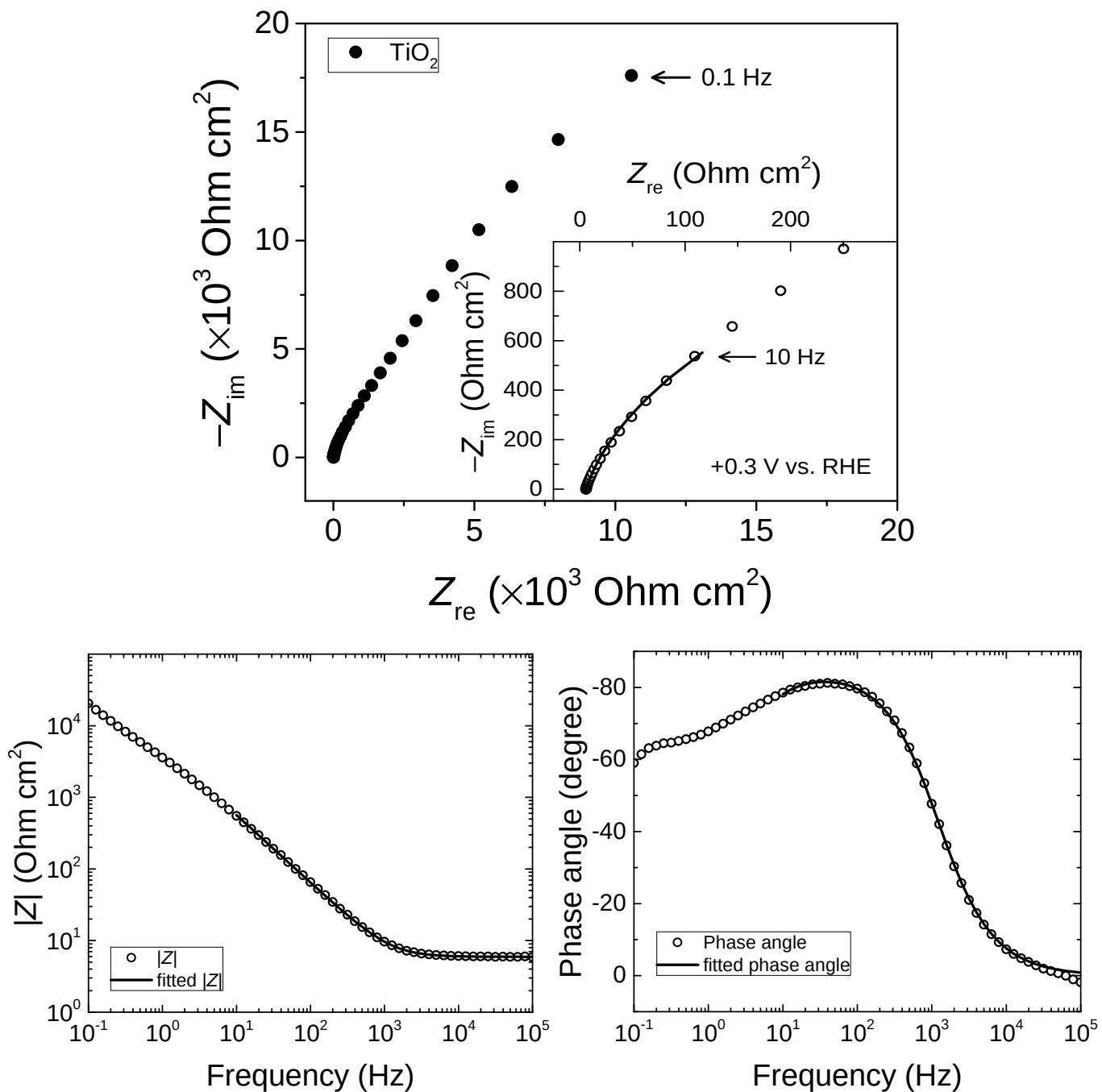
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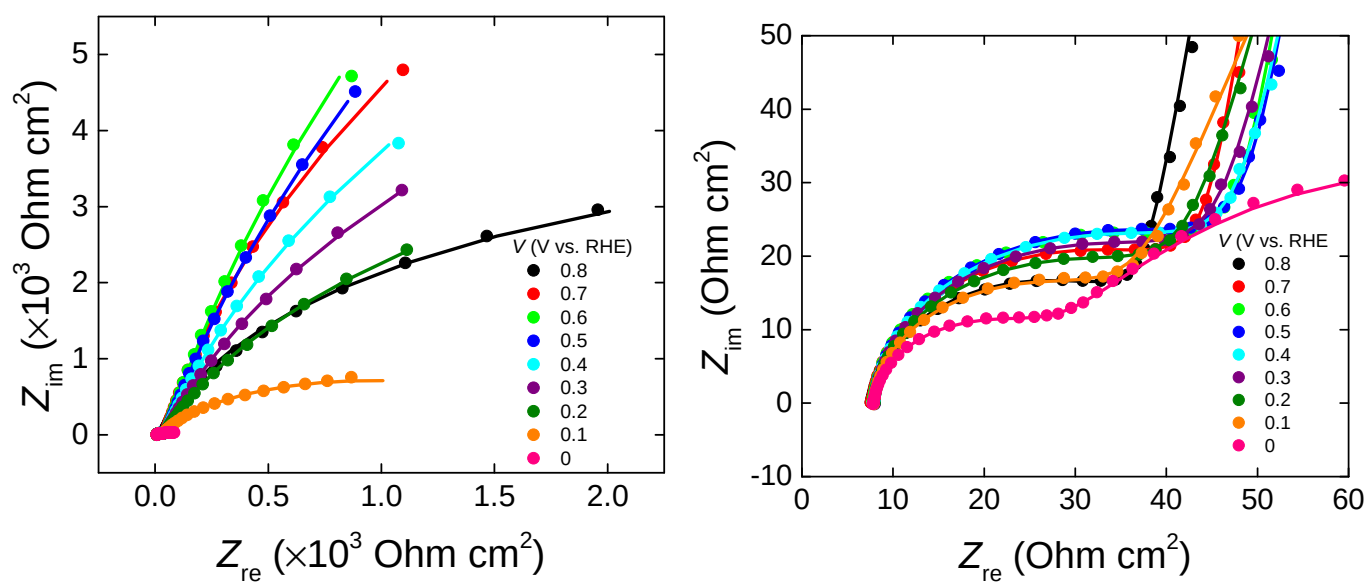
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**Fig. S1** Scanning electron microscopy (SEM) images of FTO, FTO/TiO<sub>2</sub>, FTO/TiO<sub>2</sub>/Ni-Mo, FTO/TiO<sub>2</sub>/Ni/Ni-Mo.

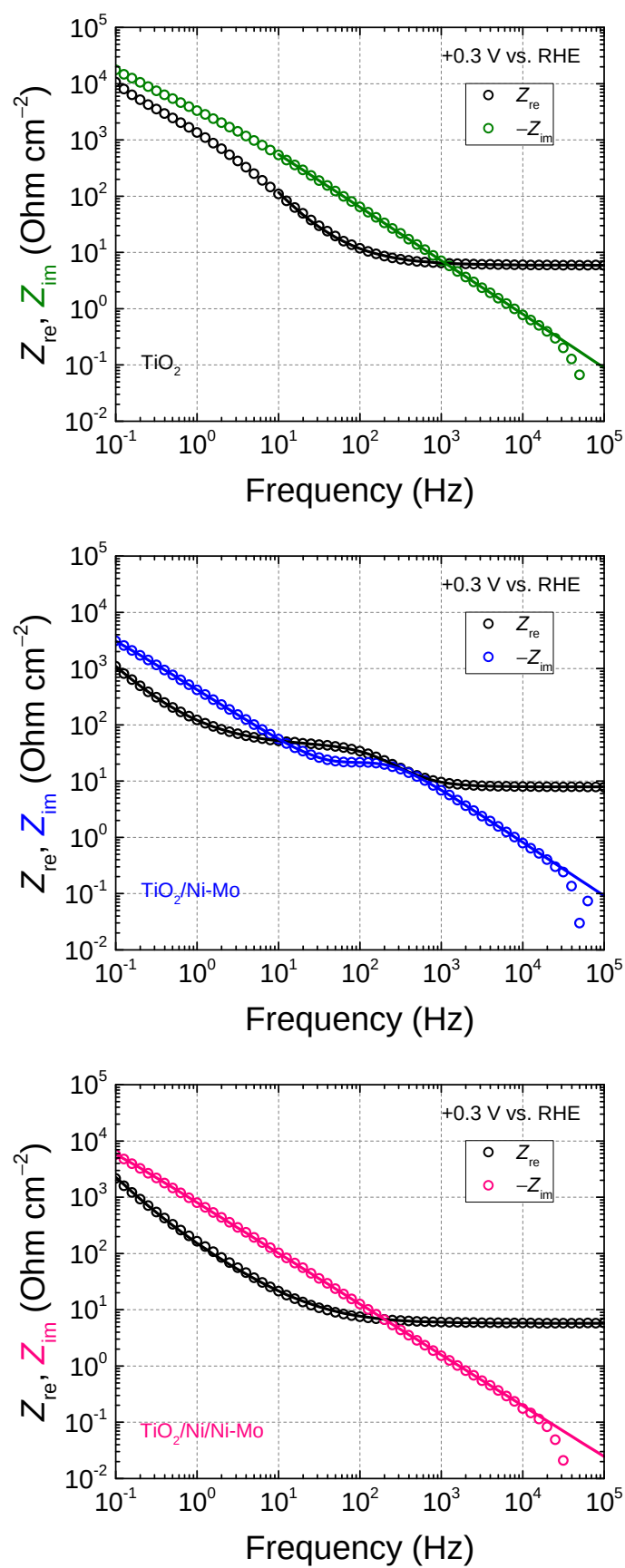


**Fig. S2** (top) Nyquist plot, (bottom left) bode plots of total impedance and (bottom right) phase angle of  $\text{TiO}_2$  at an applied potential of  $+0.3 \text{ V vs. RHE}$ .

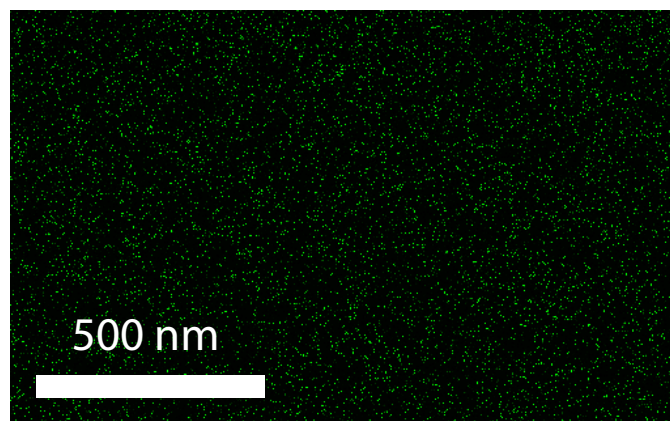
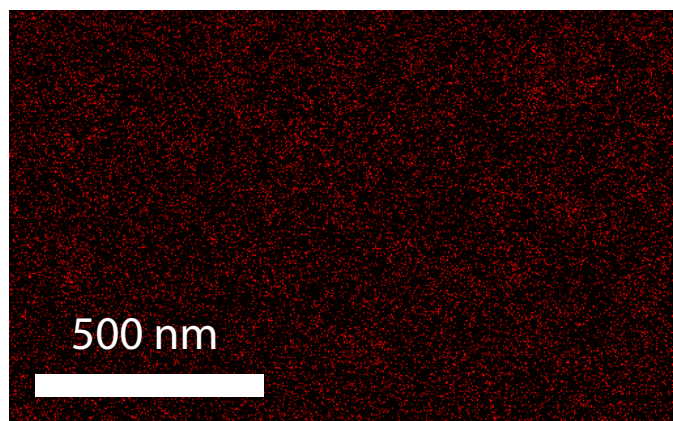
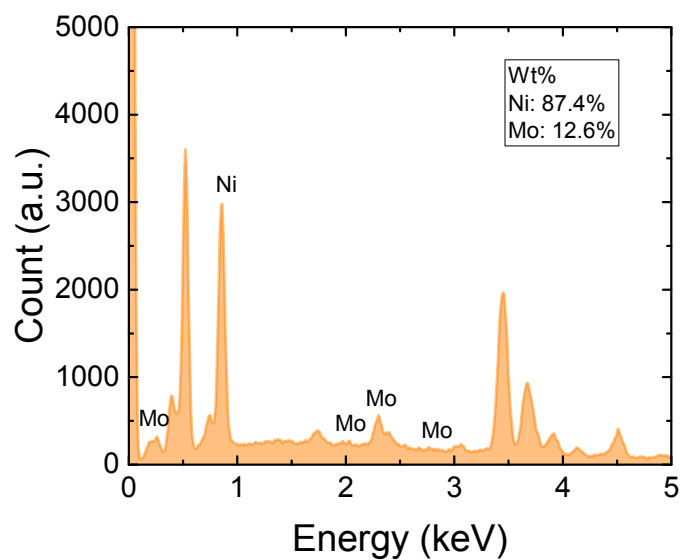
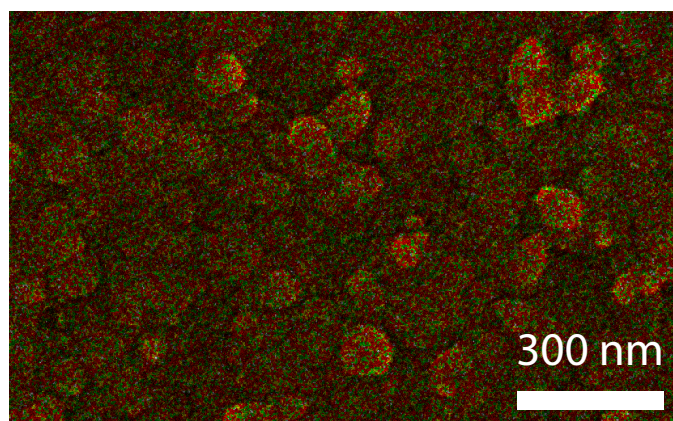


**Fig. S3** (left) Nyquist plots of  $\text{TiO}_2/\text{Ni-Mo}$  at various applied potentials. The solid lines represents the fitted impedance data using the equivalent circuit in Fig. 4c. (right) The magnification of figure in the left, showing the fitted high-frequency impedance (*i.e.*, the low semicircles)

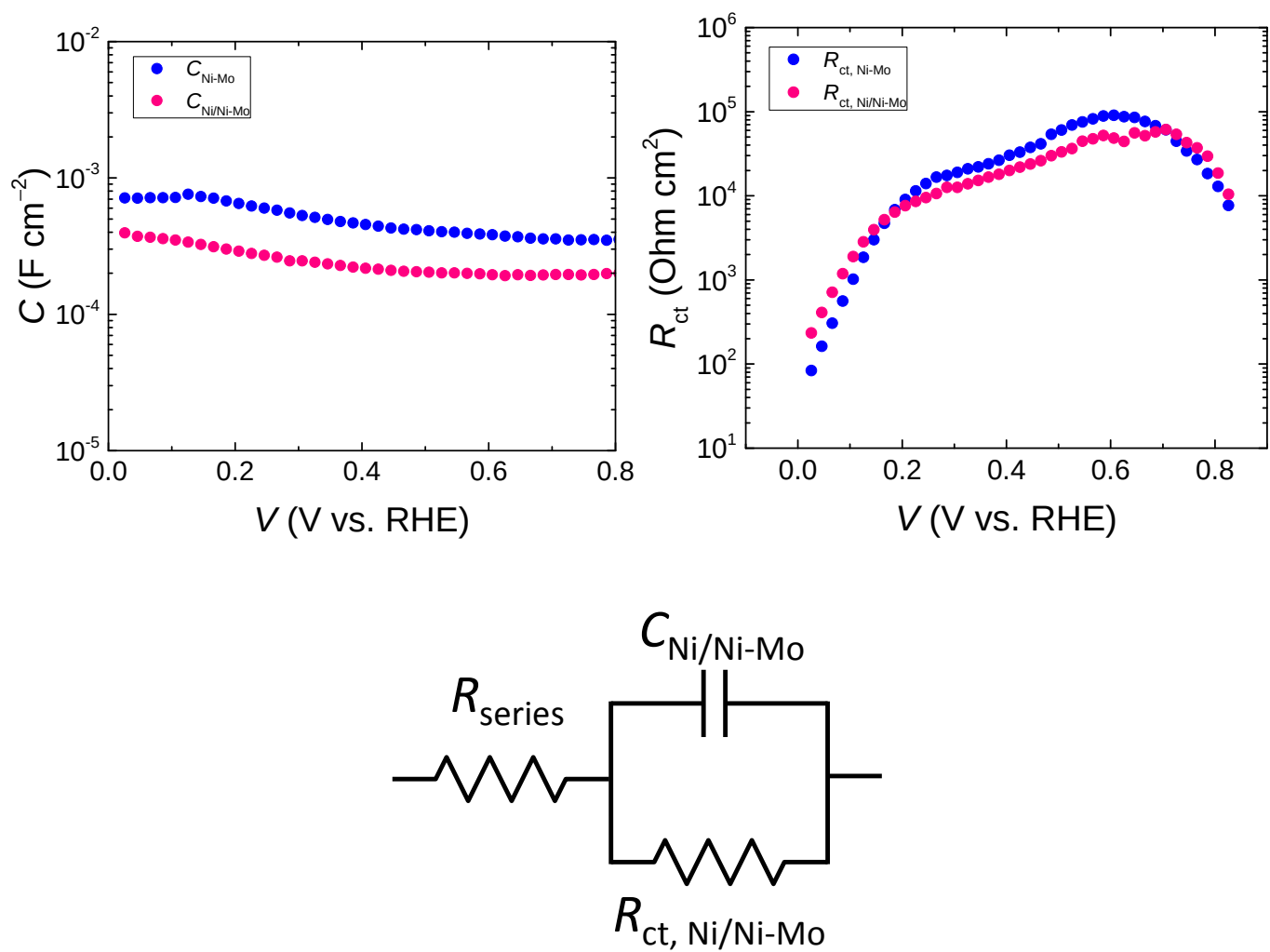




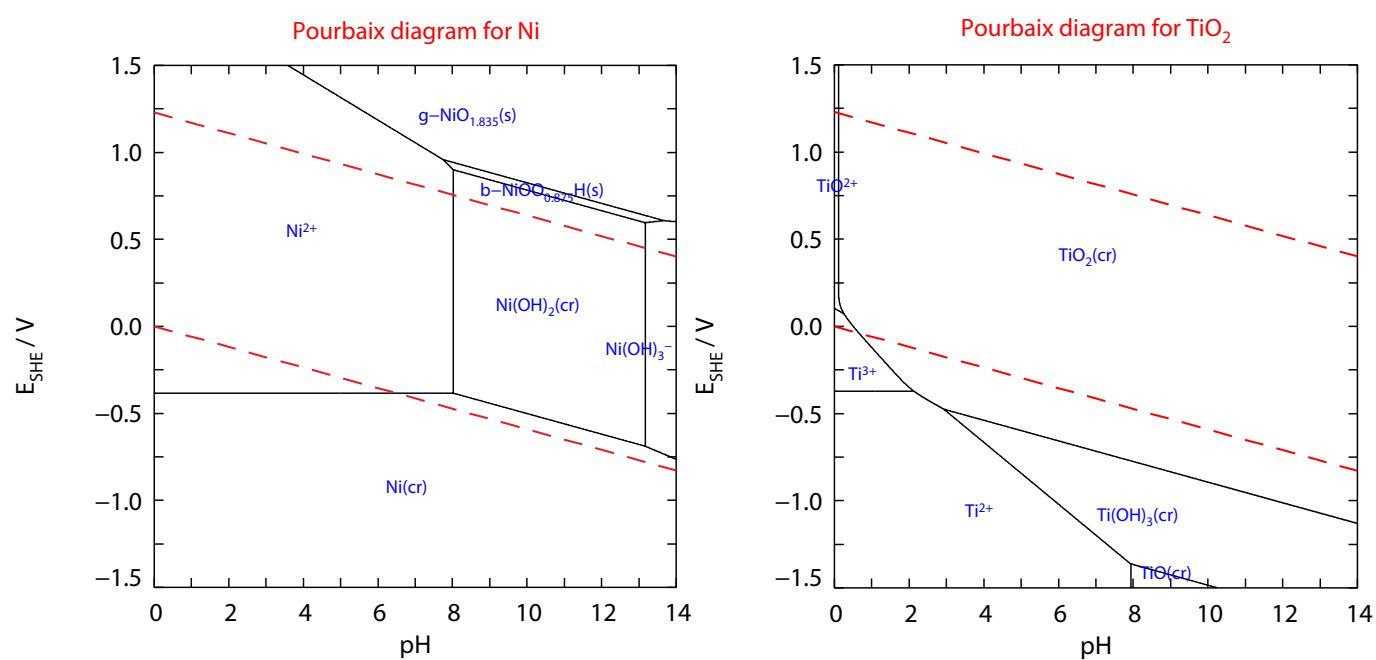
**Fig. S4** The real part ( $Z_{re}$ ) and the imaginary part ( $Z_{im}$ ) of impedance spectra of TiO<sub>2</sub> with and without the catalysts at an applied potential of +0.3 V vs. RHE. The solid lines represent the fitted data using the equivalent electronic circuits



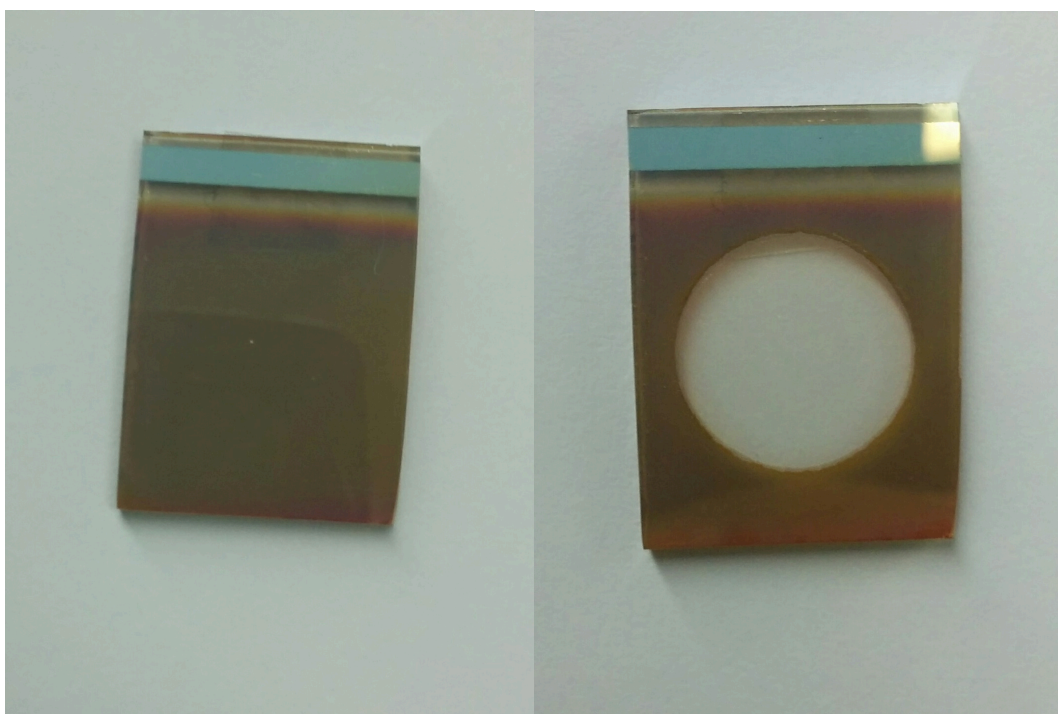
**Fig. S5** Energy dispersive X-ray spectroscopy (EDS) elemental mapping of TiO<sub>2</sub> with 2 nm of Ni and Ni-Mo particles.



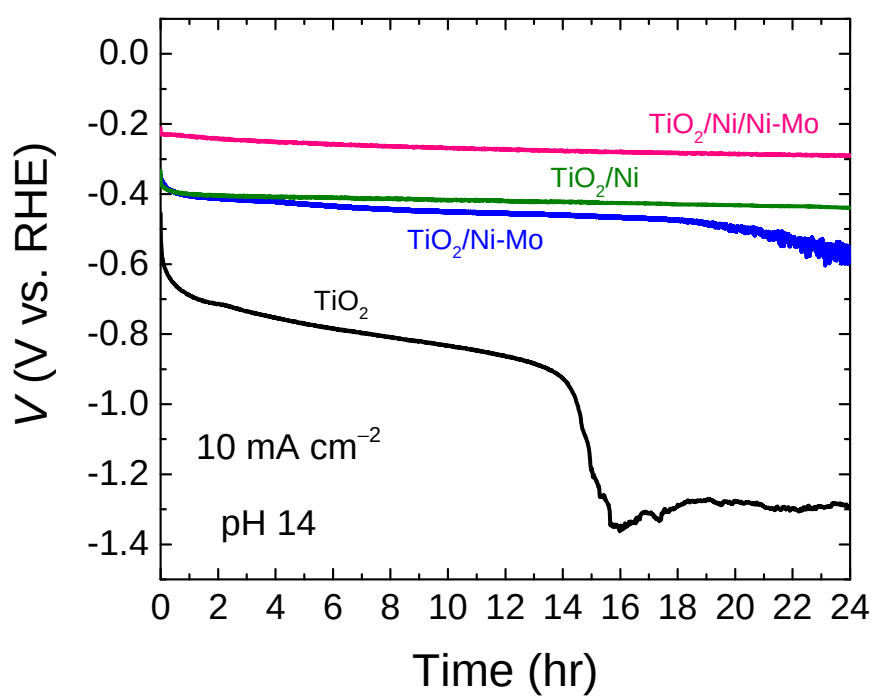
**Fig. S6** (top left) Capacitance and (top right) charge transfer resistance of the Ni–Mo and Ni/Ni–Mo. The values are obtained from the fitted impedance data. (bottom) Equivalent circuit to fit the impedance data of TiO<sub>2</sub>/Ni/Ni–Mo.



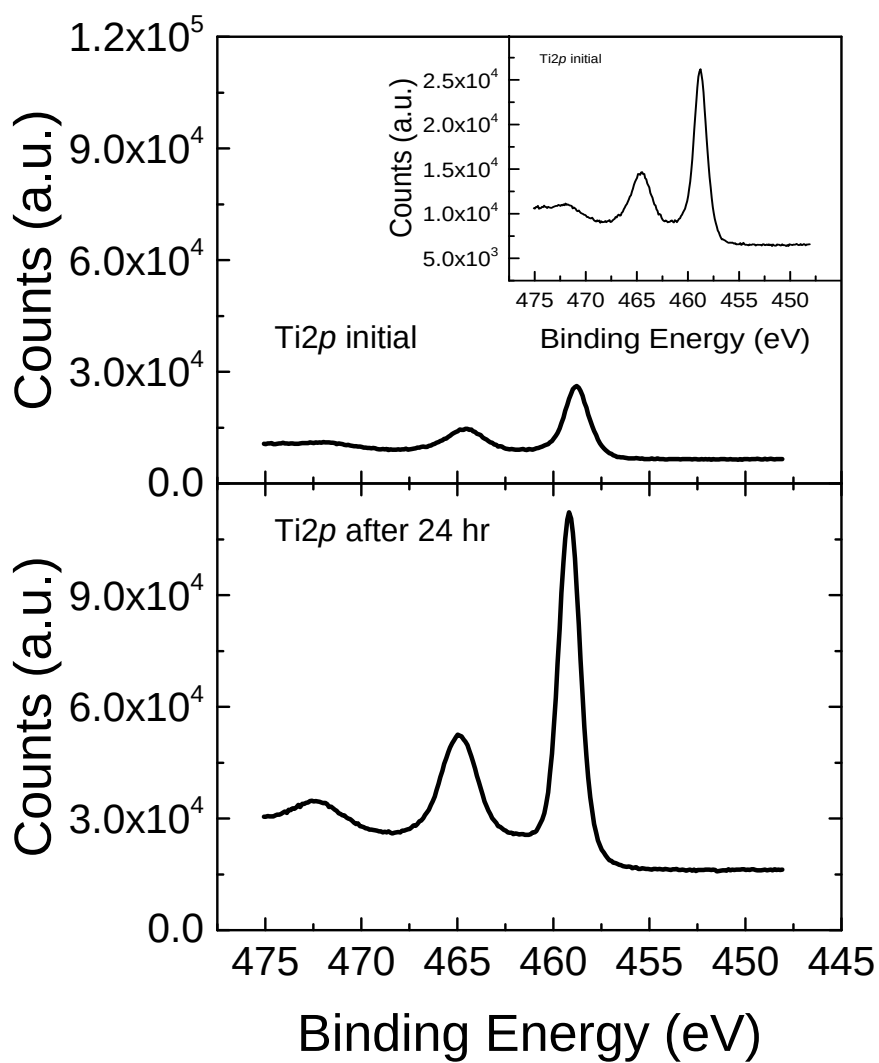
**Fig. S7** Pourbaix diagram for Ni (left) and  $\text{TiO}_2$  (right) at  $T = 25\text{ }^\circ\text{C}$ , for  $[\text{Ni}^{2+}] = 10\text{ }\mu\text{M}$ , generated using Medusa (<http://www.kth.se/che/medusa/>).



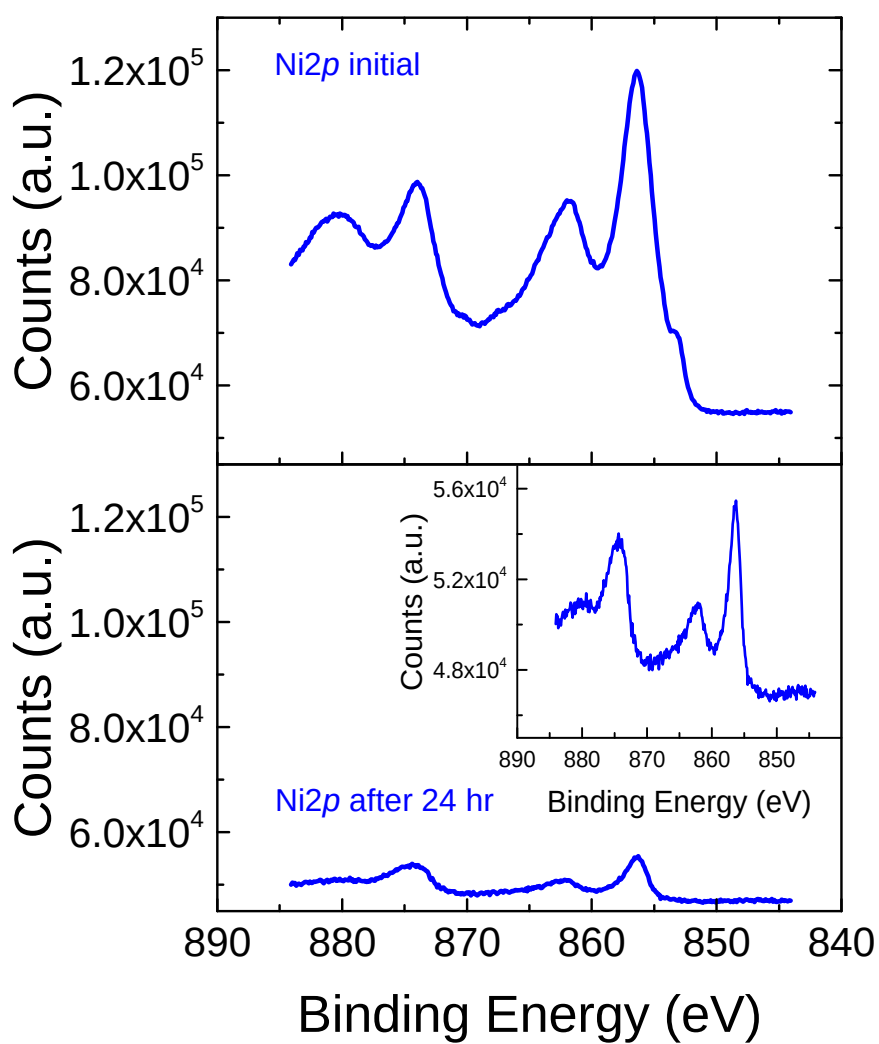
**Fig. S8** (left) Photograph of a-SiC without  $\text{TiO}_2$  layer and (right) a-SiC after being soaked in 1 M KOH in the dark (no applied bias) for 1 hour. The transparent circular area is the active area that was exposed area to the electrolyte, indicating that a-SiC was completely dissolved after 1 hour.



**Fig. S9** Chronopotentiometry test of  $\text{TiO}_2$  with catalysts at a fixed applied current of  $-10 \text{ mA cm}^{-2}$ , measured in  $1 \text{ M KOH}$  at  $\text{pH } 14$ .

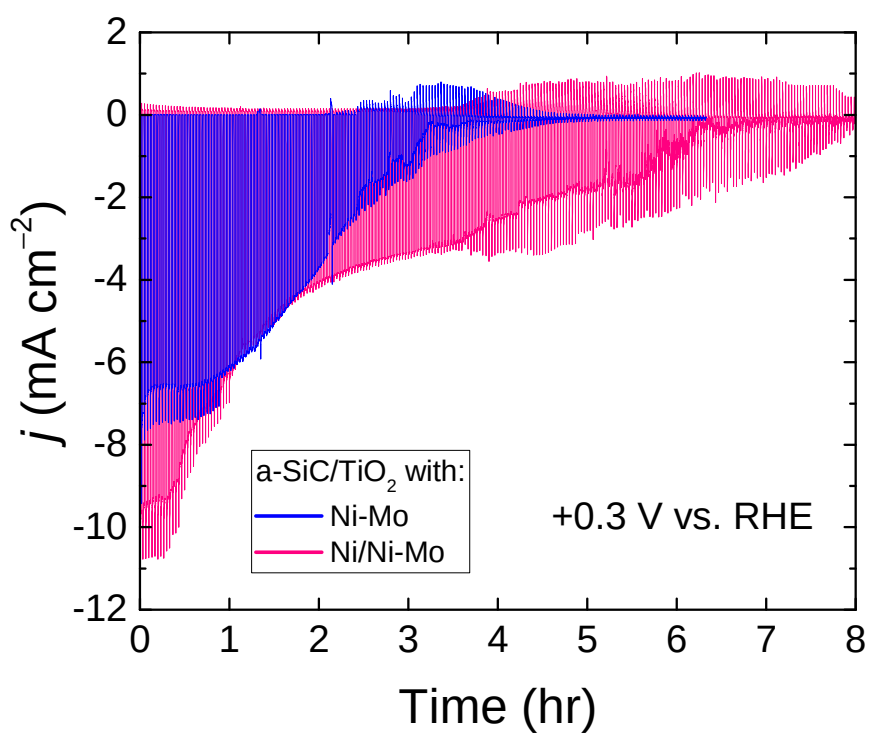


**Fig. S10** Ti 2p signal from XPS spectra of TiO<sub>2</sub> coated with Ni before (top graph) and after chronopotentiometry test (bottom graph) at a fixed current of  $-10 \text{ mA cm}^{-2}$  for 24 hours. The XPS spectra shows a weaker Ti 2p signal before the chronopotentiometry measurement because the TiO<sub>2</sub> is still covered by Ni.

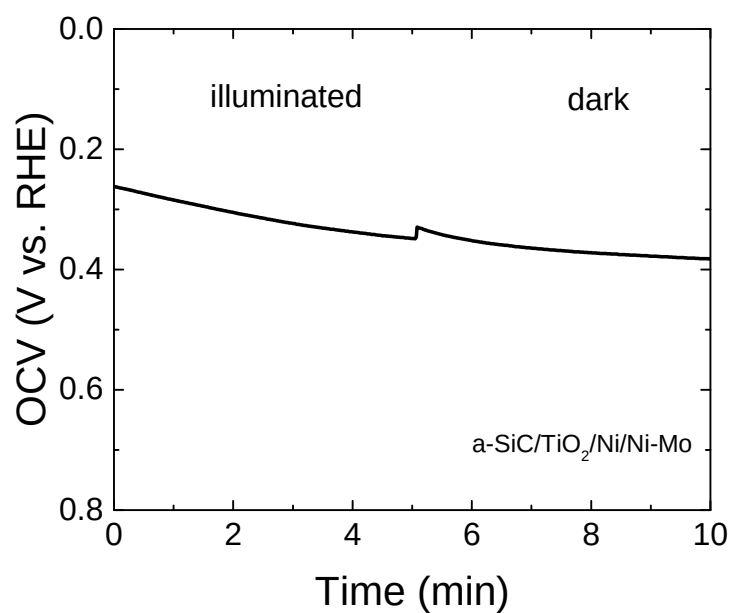


**Fig. S11** Ni 2p signal from XPS spectra of TiO<sub>2</sub> coated with Ni before (top graph) and after chronopotentiometry test (bottom graph) at a fixed current of  $-10 \text{ mA cm}^{-2}$  for 24 hours. The Ni 2p signal is weaker after the 24-hour measurement because the Ni was detached from TiO<sub>2</sub> during the test.

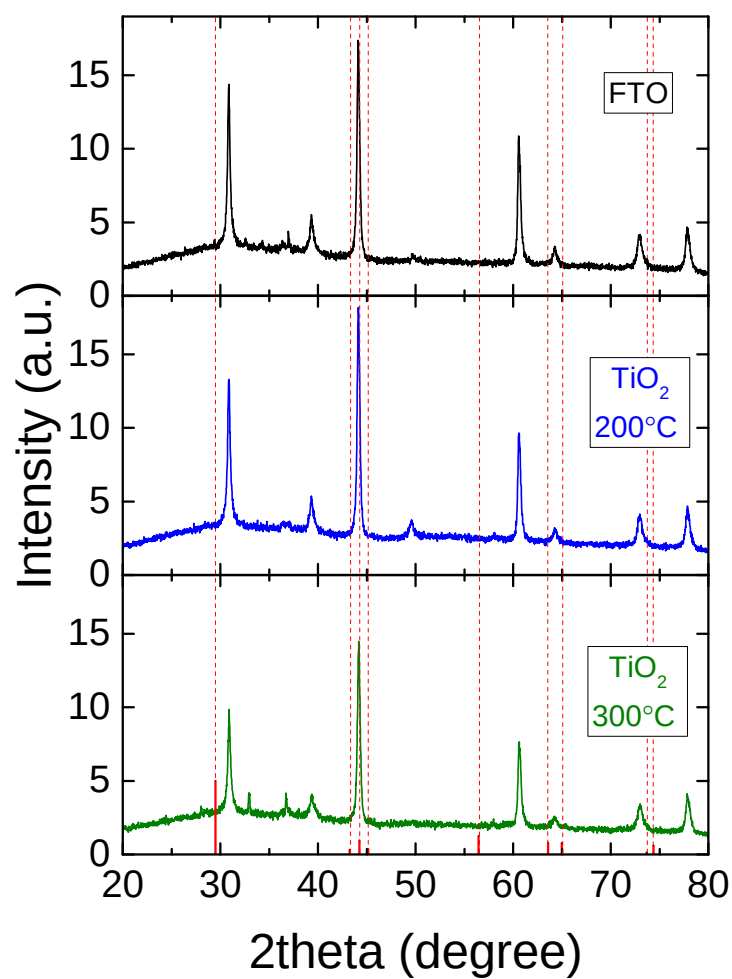




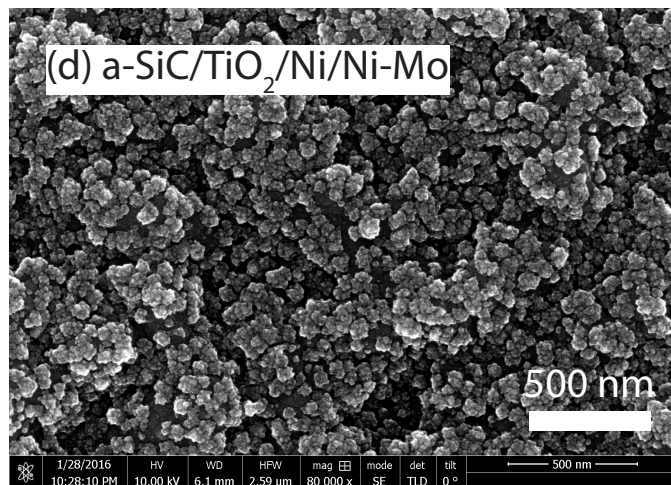
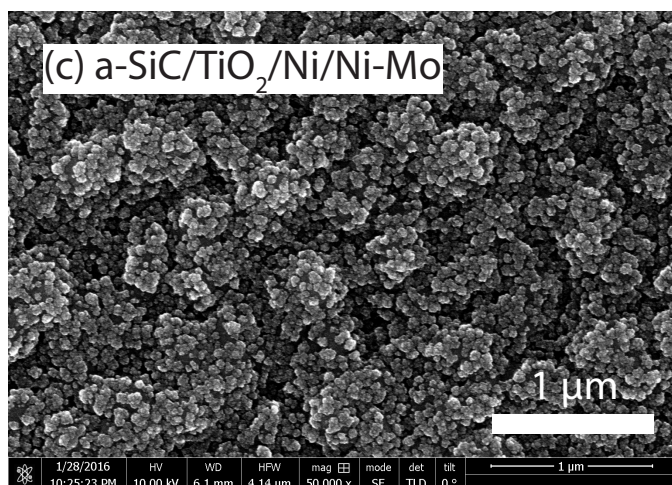
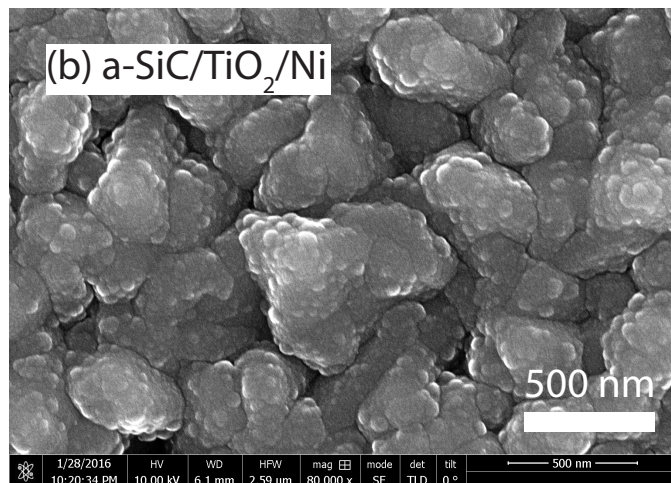
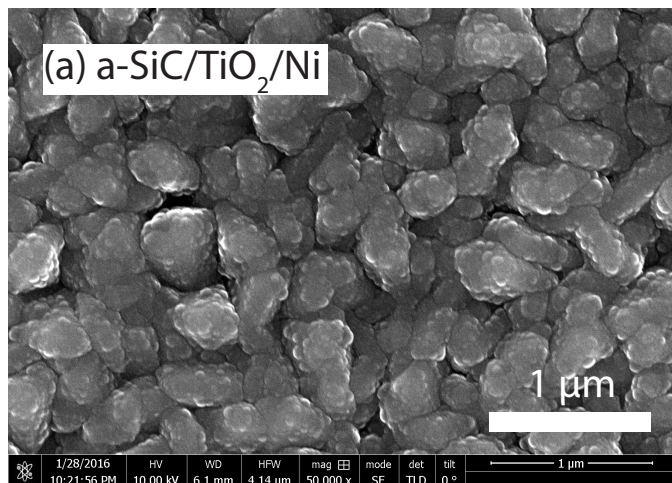
**Fig. S12** Chronoamperometry test of a-SiC/TiO<sub>2</sub> with Ni-Mo and Ni/Ni-Mo catalysts at an applied potential of +0.3 V vs. RHE, measured under chopped illumination in 1 M KOH electrolyte at pH 14.



**Fig. S13** Open circuit voltage of a-SiC/TiO<sub>2</sub> annealed at 400 °C in vacuum, measured in the dark and under illumination, showing no photovoltage.



**Fig. S14** X-ray diffractogram (XRD) of ALD TiO<sub>2</sub> deposited on FTO substrate at 200 °C and 300 °C. For comparison, the XRD of the FTO is shown. The red dash lines indicate the peak locations of crystalline anatase TiO<sub>2</sub>.



**Fig. S15** SEM images of (a) a-SiC/TiO<sub>2</sub>/Ni and (b) its magnification, (c) a-SiC/TiO<sub>2</sub>/Ni/Ni-Mo and (d) its magnification.