

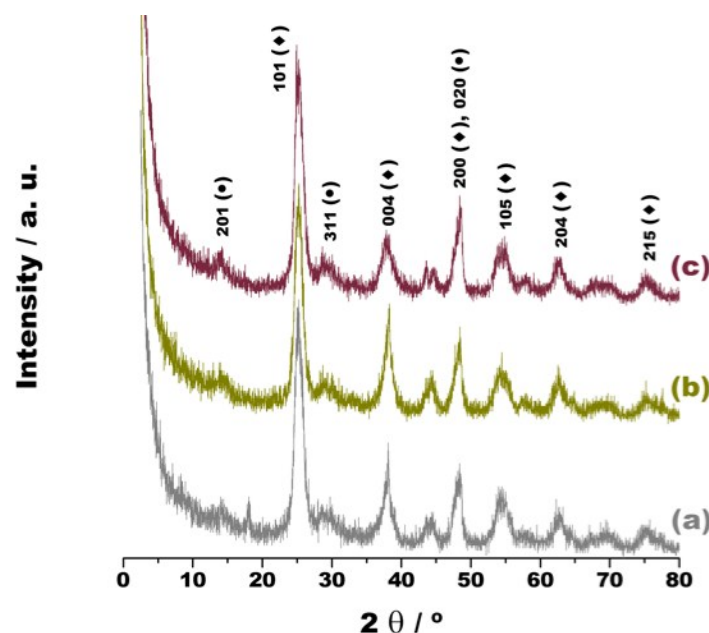
## TiO<sub>2</sub> pillaring and NiO<sub>x</sub> loading as alternatives for the photoactivity enhancement of K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> towards water splitting<sup>†</sup>

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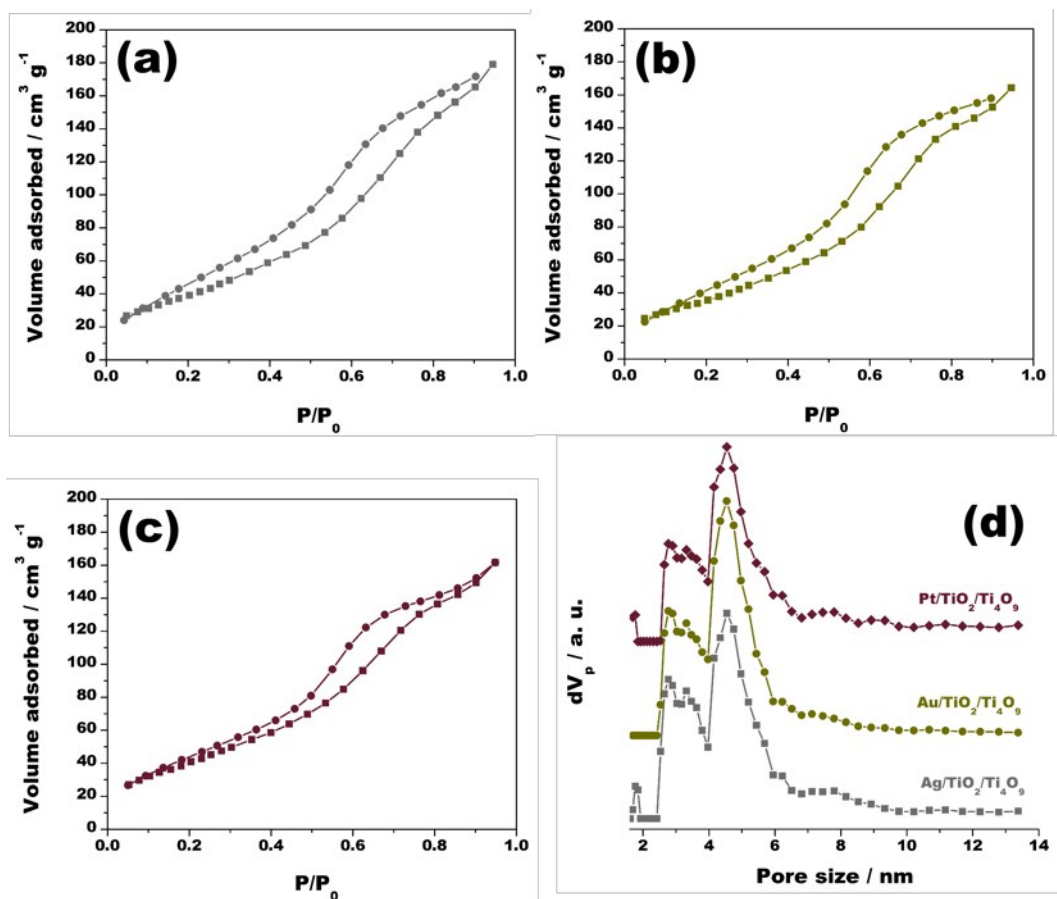
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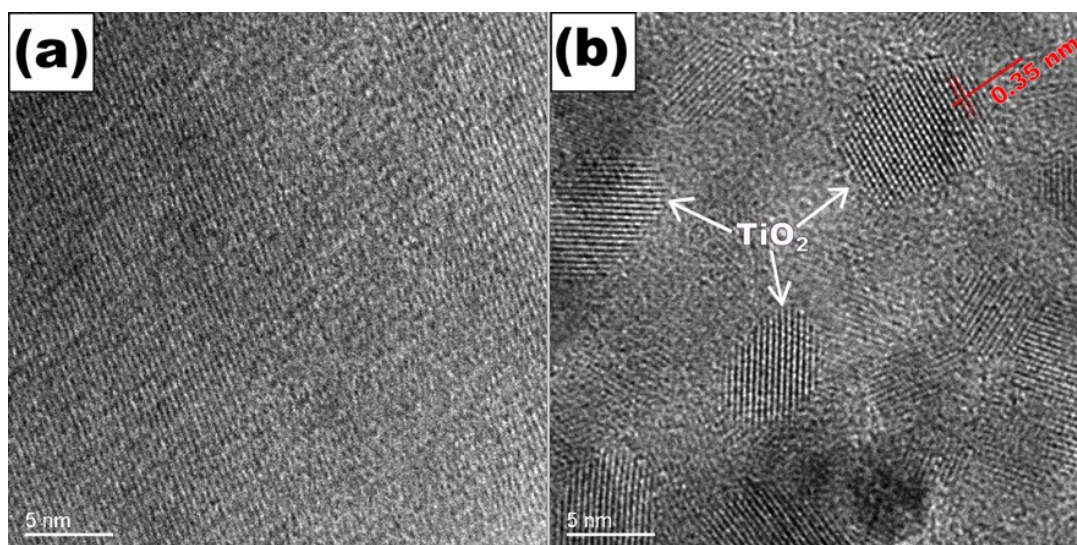
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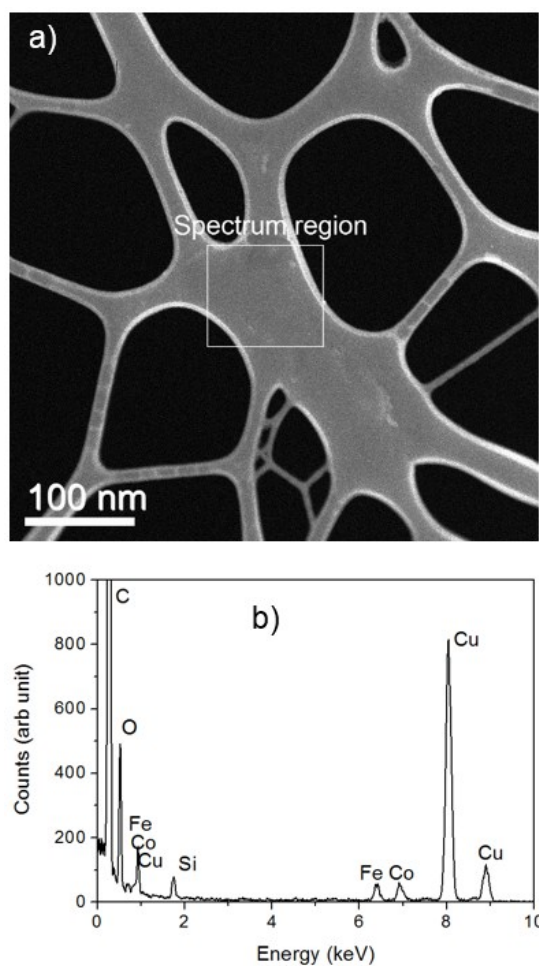
**Fig. S1** X-ray diffraction patterns of the materials (a) Ag/TiO<sub>2</sub>/Ti<sub>4</sub>O<sub>9</sub>, (b) Au/TiO<sub>2</sub>/Ti<sub>4</sub>O<sub>9</sub>, and (c) Pt/TiO<sub>2</sub>/Ti<sub>4</sub>O<sub>9</sub>.



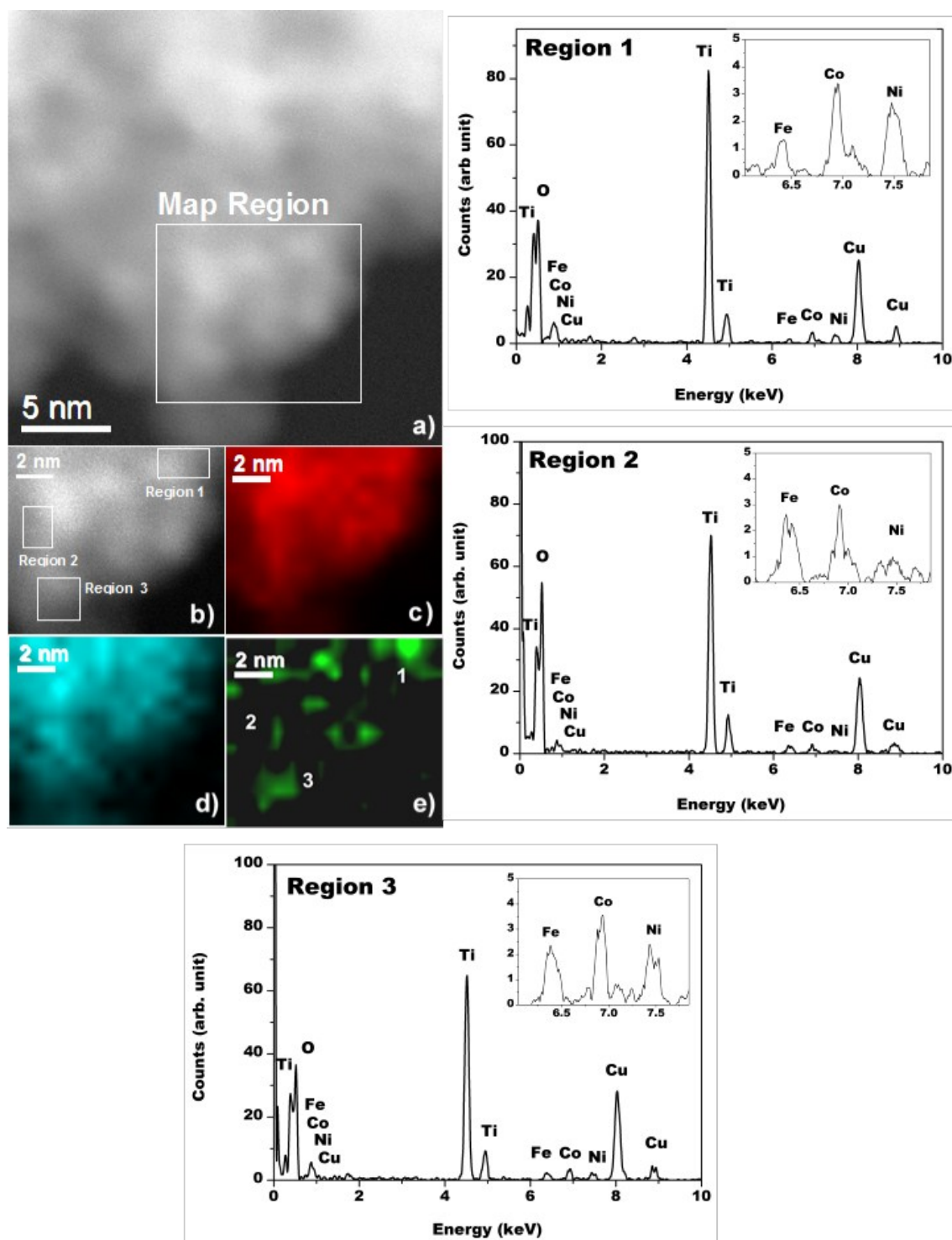
**Fig. S2** N<sub>2</sub> adsorption-desorption isotherms of the mesoporous solids (a) Ag/TiO<sub>2</sub>/Ti<sub>4</sub>O<sub>9</sub>, (b) Au/TiO<sub>2</sub>/Ti<sub>4</sub>O<sub>9</sub>, and (c) Pt/TiO<sub>2</sub>/Ti<sub>4</sub>O<sub>9</sub>; and (d) respective pore size distribution curves.



**Fig. S3** High-resolution transmission electron microscopy (HR-TEM) images of (a)  $K_2Ti_4O_9$  and (b)  $TiO_2/Ti_4O_9$ .



**Fig. S4** TEM image and EDS spectrum of the grid used for the surface mappings of  $NiO_x/TiO_2/Ti_4O_9$ .



**Fig. S5** EDS mapping of (a) and (b) a selected region of  $\text{NiO}_x/\text{TiO}_2/\text{Ti}_4\text{O}_9$  surface, detecting the elements (c) titanium, (d) oxygen and (d) nickel; and three different EDS spectra correlated to the regions 1, 2 and 3 indicated in (b). The spectra show that Region 1 is rich in nickel, Region 2 has no nickel and region 3 possess nickel in lower amount compared to Region 1. The absence of the peak at 7.5 keV in the spectrum of Region 2 proves that the detected nickel belongs to the sample and not to the grid holder.

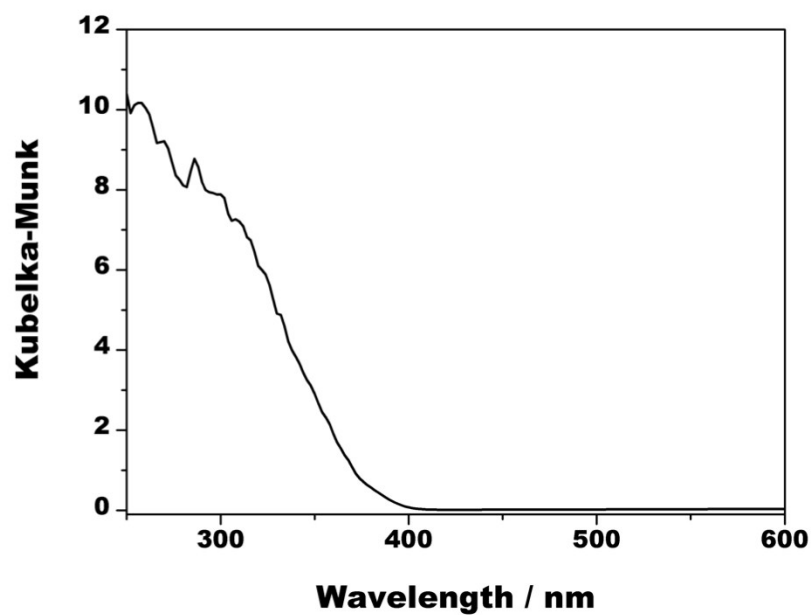


Figure S6. UV-Vis diffuse reflectance spectrum of the synthesized TiO<sub>2</sub> anatase nanoparticles.

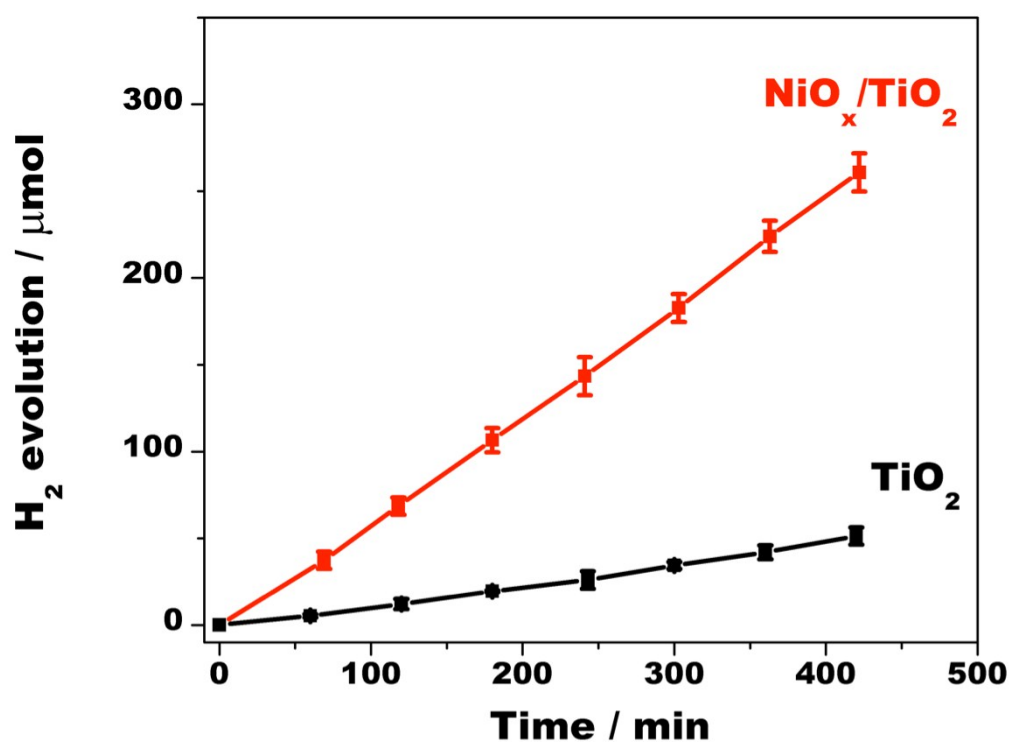
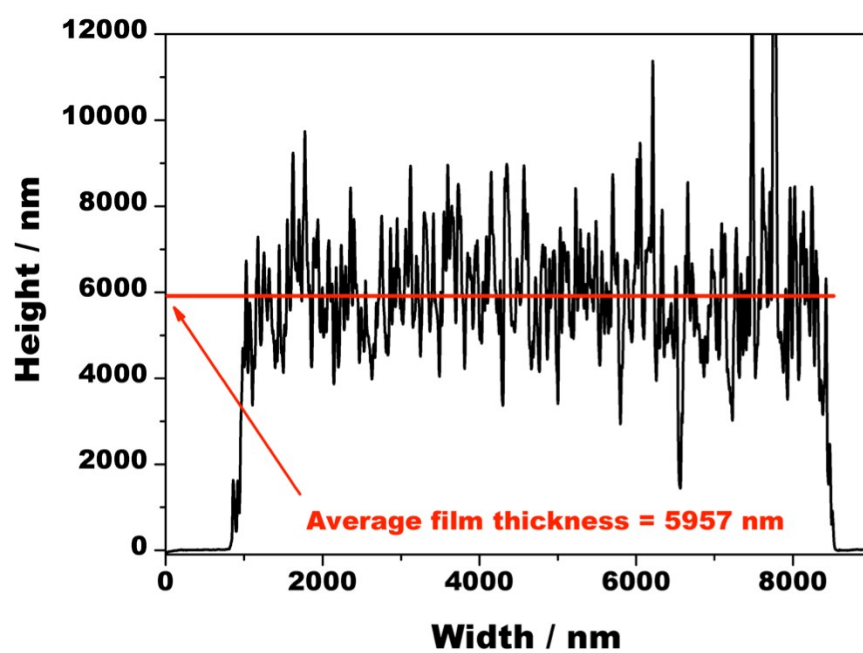


Figure S7. H<sub>2</sub> evolution over 50 mg of TiO<sub>2</sub> P25 and NiO<sub>x</sub>/TiO<sub>2</sub> suspended in 50 mL of a 20 % (v/v) aqueous methanol solution. The system was irradiated with a 300 W Xe arc lamp with light power of 224 mW cm<sup>-2</sup>.



**Figure S8.** Profilometer scan of one of the  $\text{TiO}_2/\text{Ti}_4\text{O}_9$  films prepared for the SPS measurements.