

Experimental details for in-situ UV-vis spectroelectrochemical measurements

In-situ UV-vis spectroelectrochemical measurements were carried out using an UV-Vis spectrophotometer (Lambda 35, Perkin-Elmer) equipped with a diffuse reflectance accessory dedicated for registration of reflectance ability for non-transparent materials. In the Fig. S1 the whole experimental setup was shown and the path of light beam inside the spectrophotometer was indicated. As an electrochemical cell, a typical quartz cuvette with an additional glass cap was used (Fig. S2). This glass cup allows to introduce all electrodes and thin teflon tubes serving as an inlet and outlet of argon gas. The electrochemical cell was filled with 0.1M K_2SO_4 solution. The electrolyte was purged with argon for 20 min. before measurements in order to remove oxygen from the solution. The titanium plate covered with nanotube arrays was used as a working electrode (WE) that was faced towards the light beam. The pseudoelectrode: silver wire covered with silver chloride (Ag/AgCl) was used here as reference electrode (REF), because of limited space in the cuvette adapted for electrochemical cell. The relationship between the pseudoelectrode and Ag/AgCl/0.1M KCl used in 0.1M K_2SO_4 is expressed as: $E \text{ vs. Ag/AgCl/0.1MKCl} = E \text{ vs. Ag/AgCl} + 0.158 \text{ V}$. The platinum mesh placed behind WE, was used as a counter electrode (CE). All electrodes have been placed carefully inside the electrochemical cell so as not to come into contact with each other.

Using the spectrophotometer software, the changes in reflectance was registered in time whereas linear voltammetry was used as an electrochemical technique for control of WE potential. Thus, during the in-situ measurement, the changes in reflectance were registered together with simultaneous potential changes of the working electrode. The potential of WE was decreased from +0.2 V towards -0.9 V vs. Ag/AgCl. The scan rate was established at 1 mV s^{-1} and the changes in reflectance were registered at 550 nm that stayed as a wavelength at which maximum in absorbance is observed in the visible range and it is attributed to electron trapped as Ti^{III} centers. Similarly to results reported by Świątek et al.²⁸, the decrease in the scan rate below 1 mVs^{-1} did not result in further changes of the onset potential. Additionally, the changes in reflectance were recalculated to Kubelka-Munk function: $KM = (1-R)^2/2R$, R – the intensity of radiation reflected from the sample.

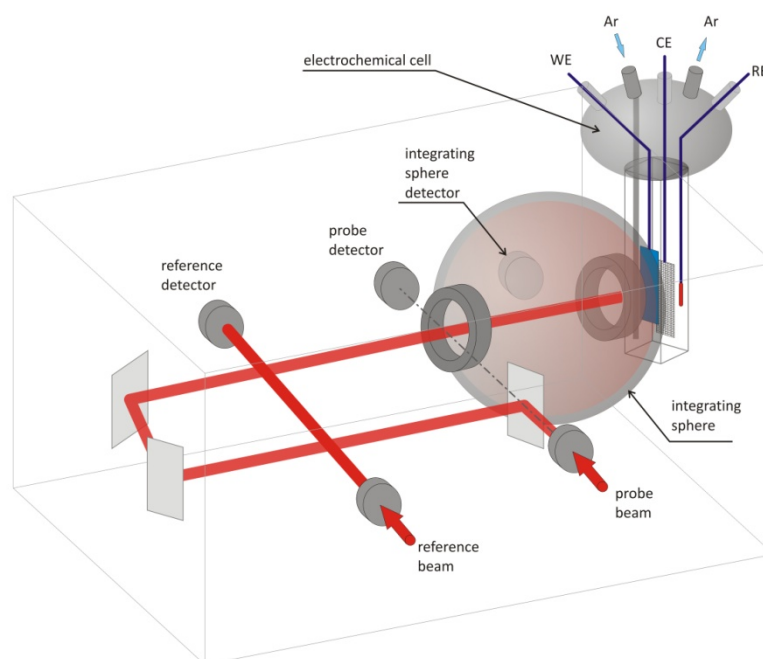


Fig. S1 Experimental setup for in-situ UV-vis spectroelectrochemical measurements.

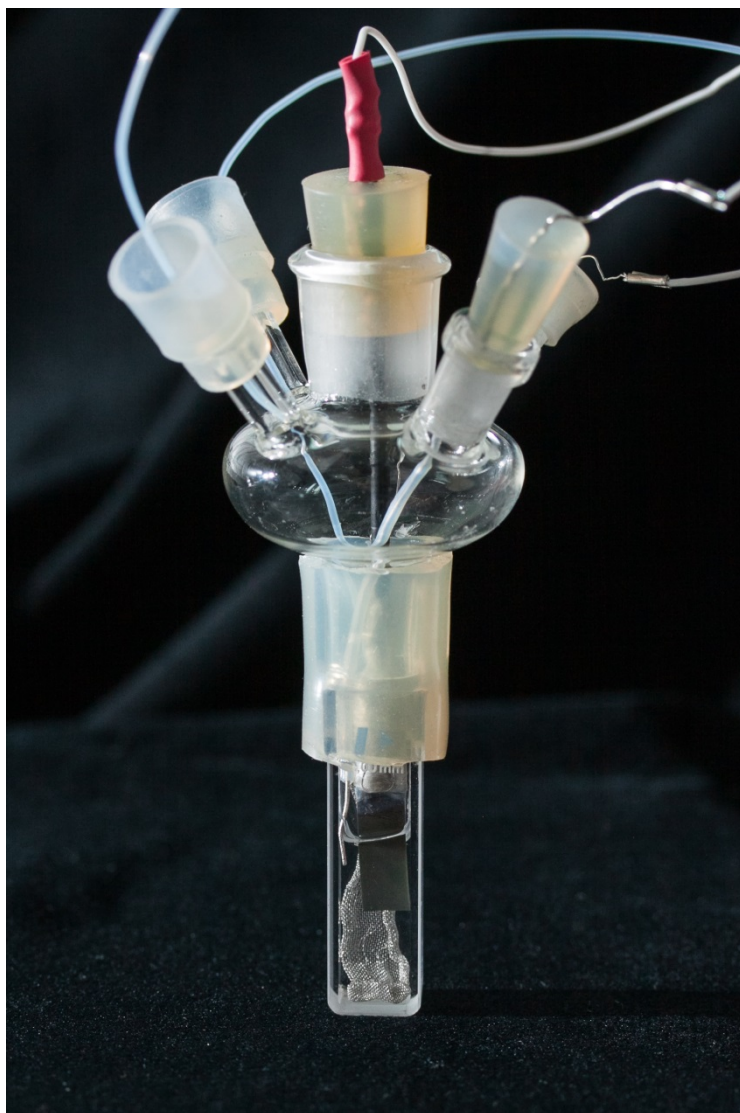


Fig. S2 The real photo of electrochemical cell dedicated for in-situ UV-vis spectroelectrochemical measurements.