Supporting information

Protoporphyrin IX Sensitized Titanium Oxide Gel

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S.1 Sol-Gel Synthesis Recipes

S.1.1 General remarks

All the synthesis involving PPIX were performed in the dark and the resulting modified ITO electrodes were also kept in dark, in order to prevent from PPIX photodegradation.

S.1.2 Preparation of the Ti(O) sol

The titanium oxide sol without functionalization, denoted as **Ti(O)**, was prepared as follows. To a 10 mL vial containing 200 µL of $Ti(OBu)_4$ (5.7×10^{-4} mol), 24 µL of AA (2.3×10^{-4} mol) was added dropwise under stirring. The vial was then closed and the mixture was further stirred for 30 minutes. 2 mL of PrOH (dried and stored on Na_2SO_4) was added to the mixture and the stirring was continued for 1 minute. Then 100 µL of deionized water (5.5×10^{-3} mol) was added dropwise. The vial was closed again to stir another 10 minutes to get a yellow sol solution finally.

S.1.3 Preparation of the Ti(O)/FCA and Ti(O)/PPIX sols

The titanium oxide sols functionalized by FCA and by PPIX, denoted as **Ti(O)/FCA** and **Ti(O)/PPIX**, respectively, were prepared as follows. In a 10 mL vial containing 3.24 mg of PPIX (5.7×10^{-6} mol) or 13.5 mg of FCA (5.7×10^{-5} mol), 200 µL of $Ti(OBu)_4$ (5.7×10^{-4} mol) was added under stirring. The vial was then closed and the mixture was stirred for 30 minutes for PPIX or 1 hour for FCA to get clear solutions. Then 24 µL of AA (2.3×10^{-4} mol) was added drop wise. The vial was closed again to stir another 30 minutes. 2 mL of PrOH and subsequently 100 µL of deionized water (5.5×10^{-3} mol) were added dropwise under stirring. After further stirring for 10 minutes, an orange (FCA) or red (PPIX) sol solution was obtained.

S.1.4 Preparation of the Ti(O)/PPIX-FCA sol

The titanium oxide based sol functionalized by both FCA and PPIX, denoted as **Ti(O)/PPIX-FCA**, was prepared as follows. First, the complexation of PPIX and FCA with $Ti(OBu)_4$ were run at the same time in two different reactors to prevent from complexation competition:

Reactor (a): In a 1 mL vial containing 13.5 mg of FCA (5.7×10^{-5} mol), 100 µL of $Ti(OBu)_4$ (2.9×10^{-4} mol) was added under stirring. The vial was closed and stirred for 1 hour, then 100 µL of PrOH and 12 µL of AA (1.1×10^{-4} mol) were added. The vial was closed again to stir for 30 minutes.

Reactor (b): In a 10 ml vial containing 3.24 mg of PPIX (5.7×10^{-6} mol), 100 µL of $Ti(OBu)_4$ (2.9×10^{-4} mol) was added under stirring. The vial was closed and stirred for 30 minutes. Then 100 µL of PrOH and 12 µL of AA (1.1×10^{-4} mol) were added, followed by stirring for another 30 minutes.

After the complexation step, 1.8 mL of PrOH added to reactor (a) by several times. After each addition, the solution in the reactor (a) was transferred to reactor (b). After mixing two solutions, the obtained mixture was stirred for 1 minute and 100 µL of water (5.5×10^{-3} mol) was added dropwise under stirring. The vial was further stirred for 10 minutes and finally a red sol solution was obtained.

S.2 XPS Spectra

The XPS analyses were carried out on ITO/Ti(O)/PPIX-FCA electrodes freshly prepared.

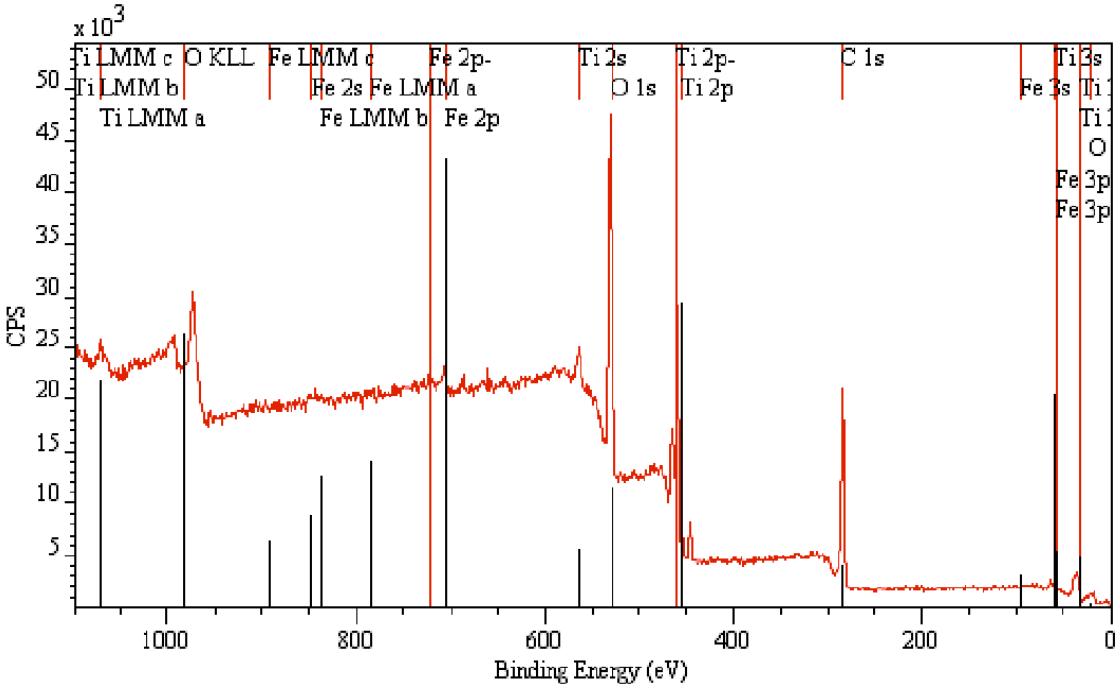

Figure S1. XPS spectrum of an ITO/Ti(O)/PPIX-FCA electrode freshly prepared.

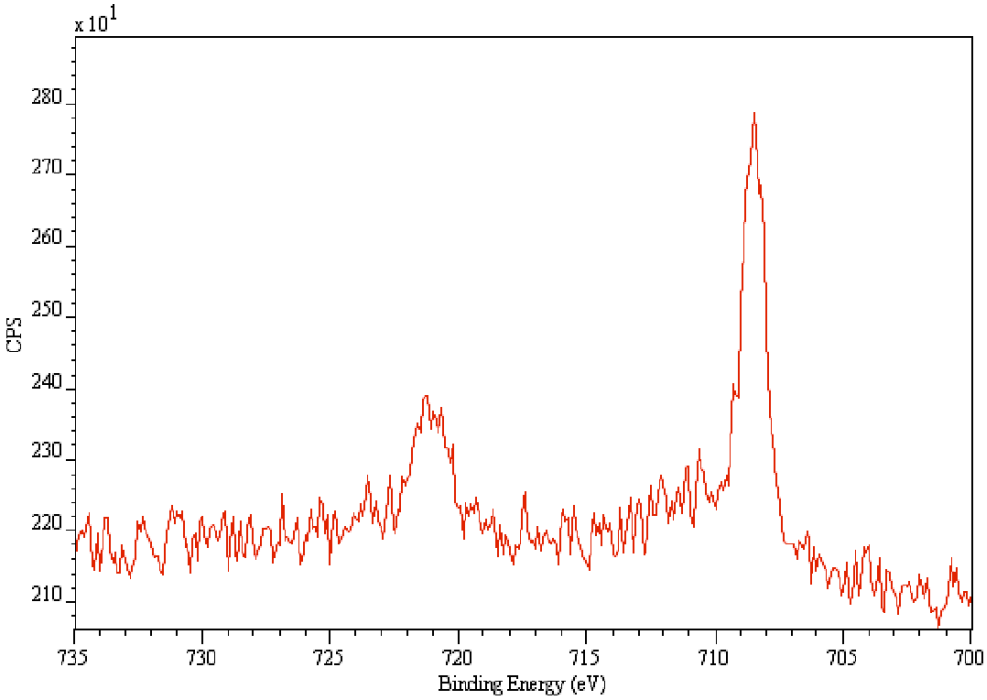

Figure S2. Fe 2p signal in the ITO/Ti(O)/PPIX-FCA electrode.

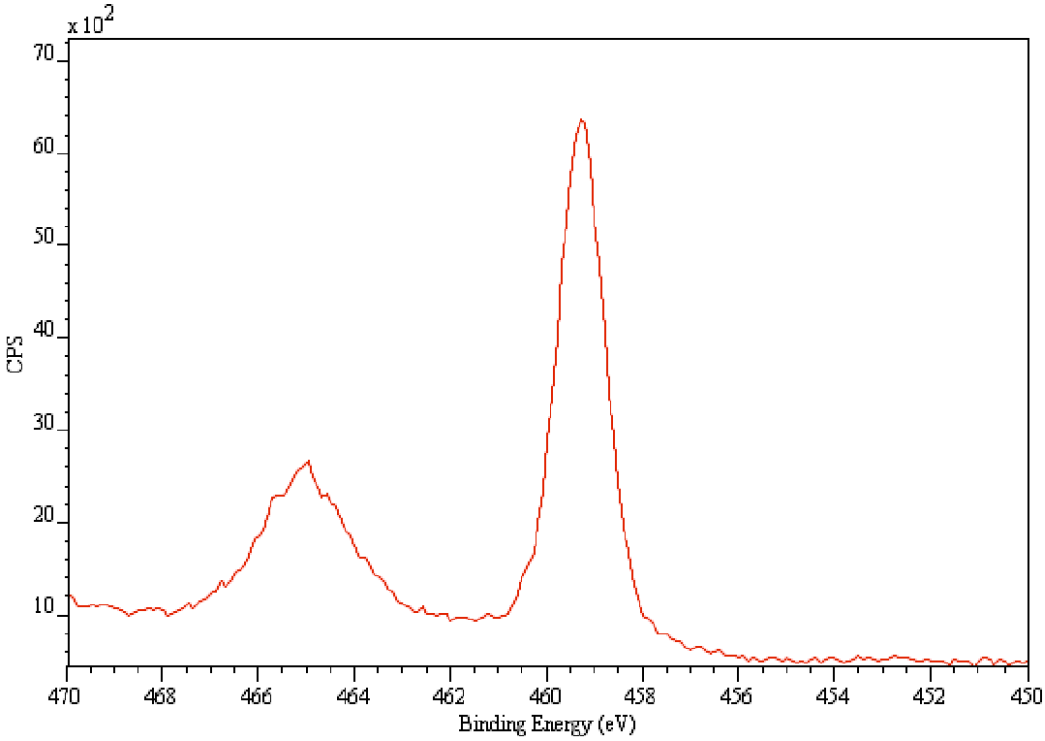

Figure S3. Ti 2p signal in the ITO/Ti(O)/PPIX-FCA electrode.

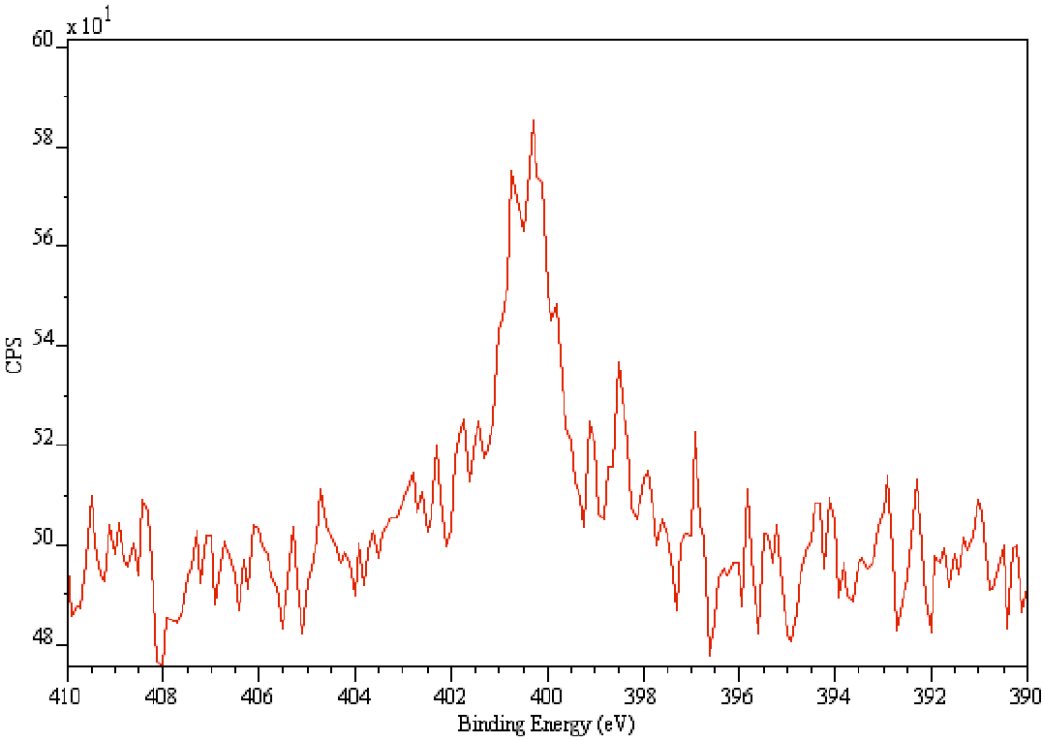

Figure S4. N 1s signal in the ITO/Ti(O)/PPIX-FCA electrode.

S.3 SEM Micrographs

Prior to SEM observations, the titanium oxide film coated ITO electrodes were dried under low pressure (10^{-6} – 10^{-7} millibars) and a layer of amorphous carbon (about 20 nm) was deposited, to prevent from the surface charging that causes erratic electron beam deflexion and unstable signal collection.

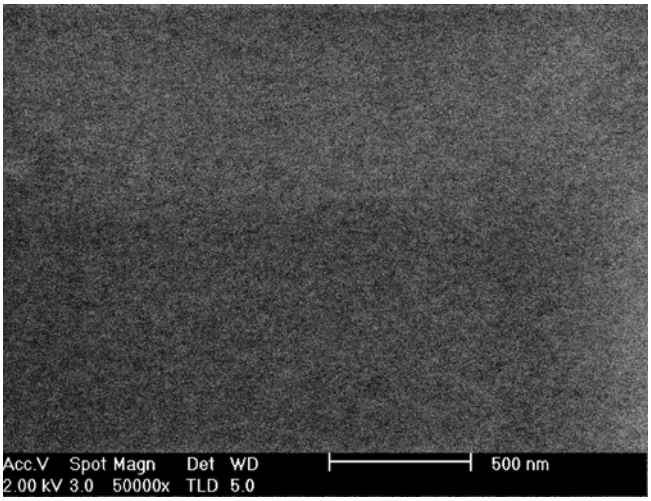

Figure S5. SEM top view of an ITO/Ti(O)/PPIX-FCA electrode freshly prepared.

S.4 Electrochemical Response of FCA in the Films

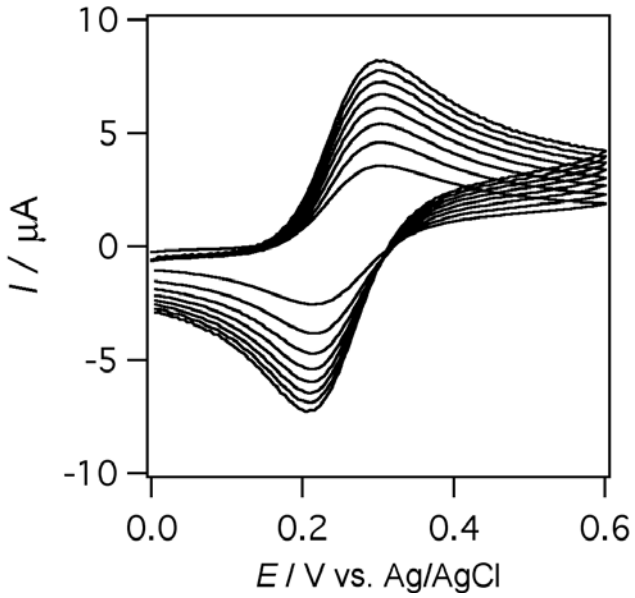

Figure S6. CVs of an ITO/Ti(O)/PPIX-FCA electrode in 0.1 M LiCl at various scan rates: 0.025, 0.050, 0.075, 0.100, 0.125, 0.150, 0.175 and 0.200 V s^{-1} from inner to outer (Staircase CV, potential step 5 mV).

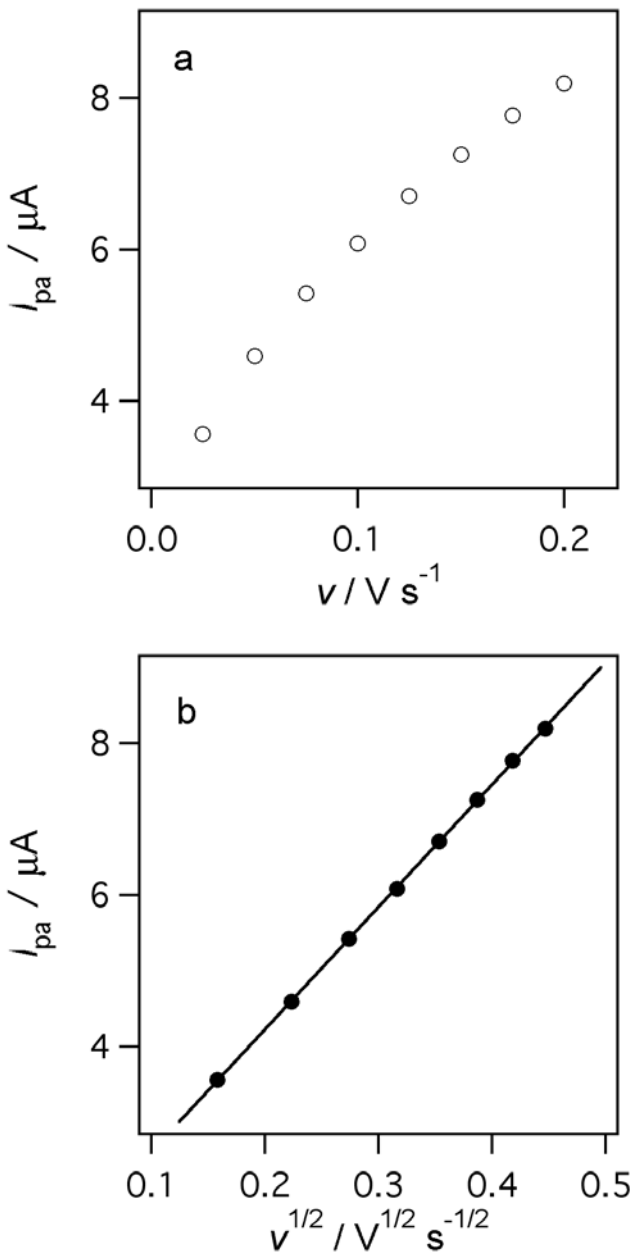

Figure S7. Dependence of the anodic peak current on the scan rate (a) and the square root of scan rate (b).

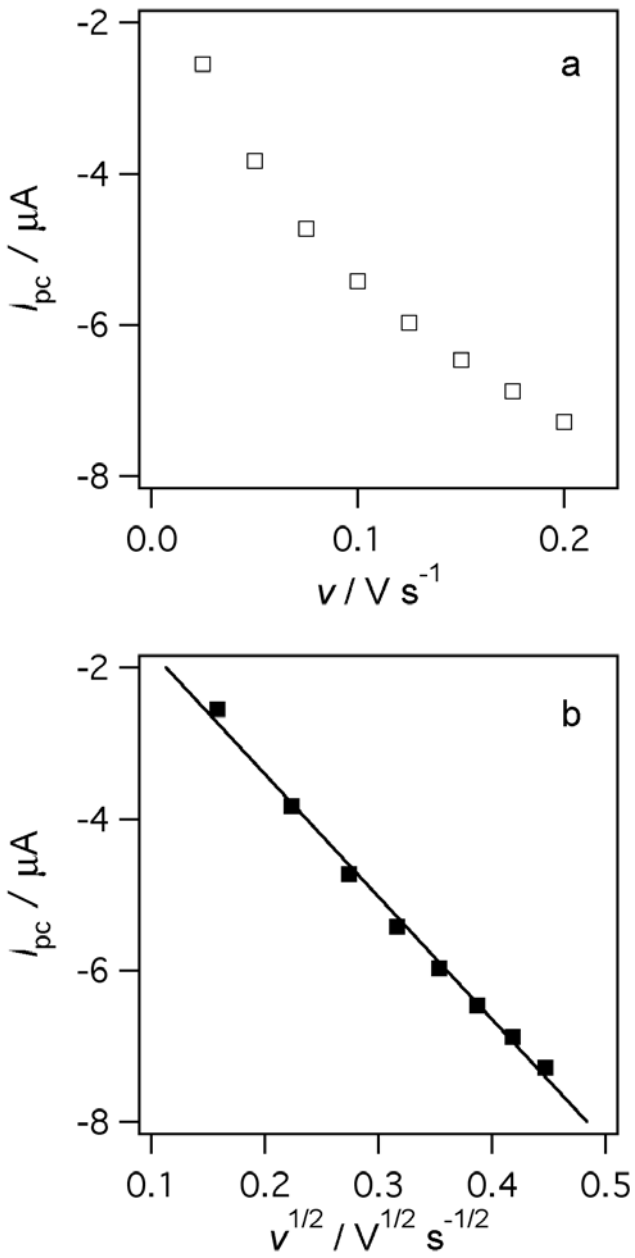

Figure S8. Dependence of the cathodic peak current on the scan rate (a) and the square root of scan rate (b).