Supporting information

Gold Nanoparticle based Supramolecular Assembly Design for Dye-sensitized H_2-Evolving Photocathodes

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Table S1. Dye and catalyst loadings for the NiO|**PCA**|**β- CD-AuNPs**|**Co**

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			Before PEC measurement	After PEC measurement
	PCA	AuNPs (S)	Catalyst (Co)	Catalyst (Co)
NiO|**PCA**	20 ± 2 nmol cm^{-2}	Not detected	-	-
NiO|**PCA**|**AuNPs**		detected	-	-
NiO|**PCA**|**AuNPs**|**Co**		detected	0.5 ± 0.3 nmol cm^{-2}	0.4 ± 0.3 nmol cm^{-2}

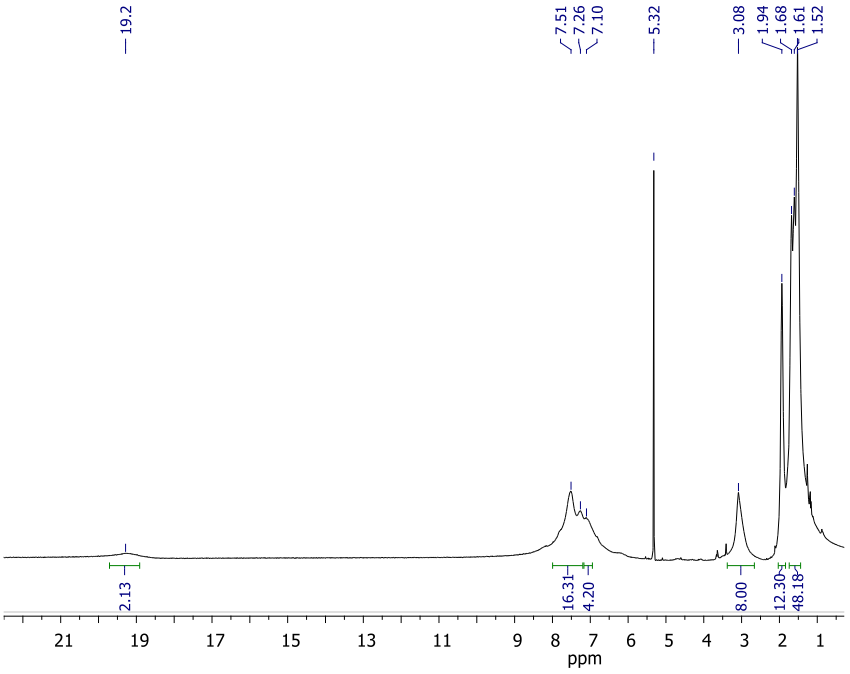

Figure S1. ^{1}H NMR spectrum of **Co** recorded in CD_2Cl_2.

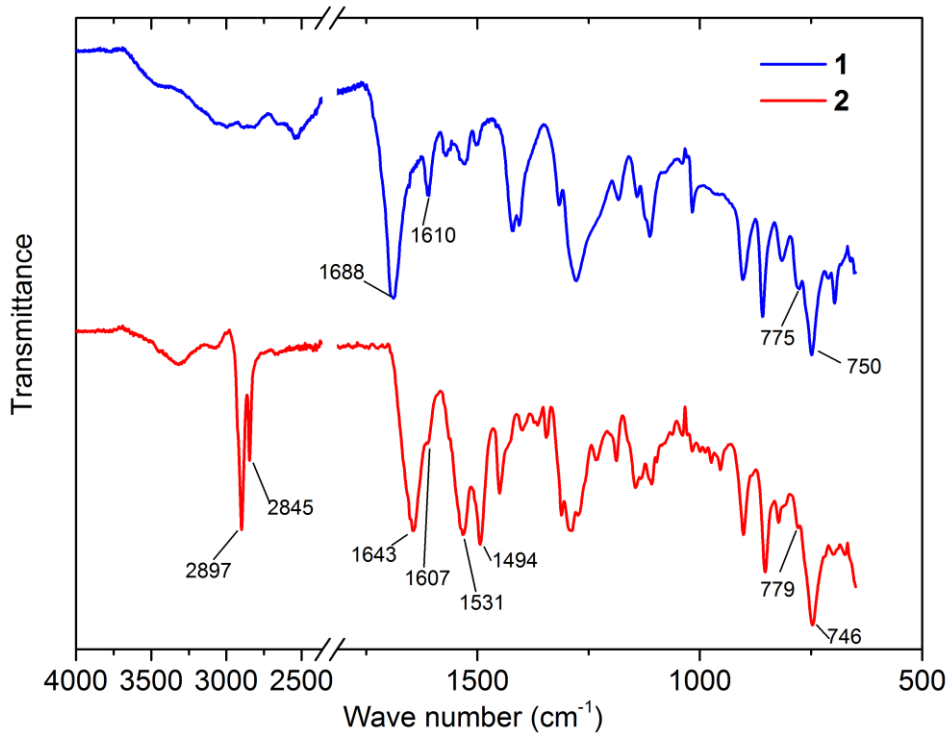

Figure S2. ATR-IR spectra of **1** (blue) and **Co** (red).

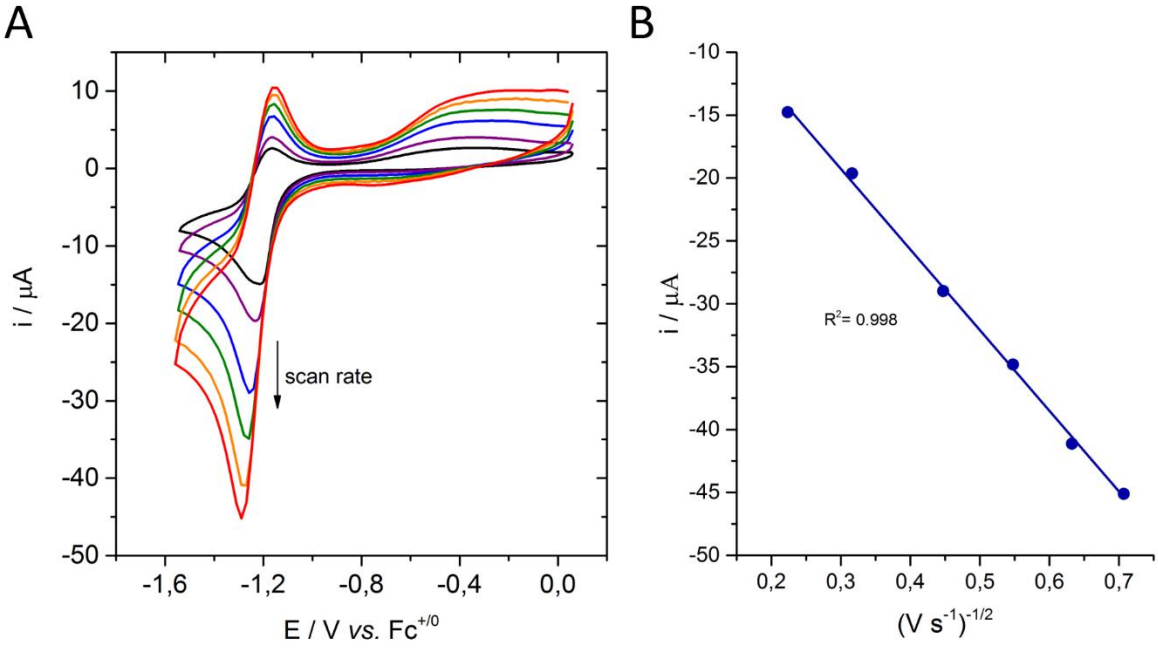

Figure S3. A) Cyclic voltammograms of **Co** (1 mM) recorded at different scan rates in DMF/0.1 M $TBAPF_6$ (second scan) and B) Variation of the cathodic peak currents with the square root of the scan rate. The addition of adamantane moiety did note modify the electrochemical response[1]

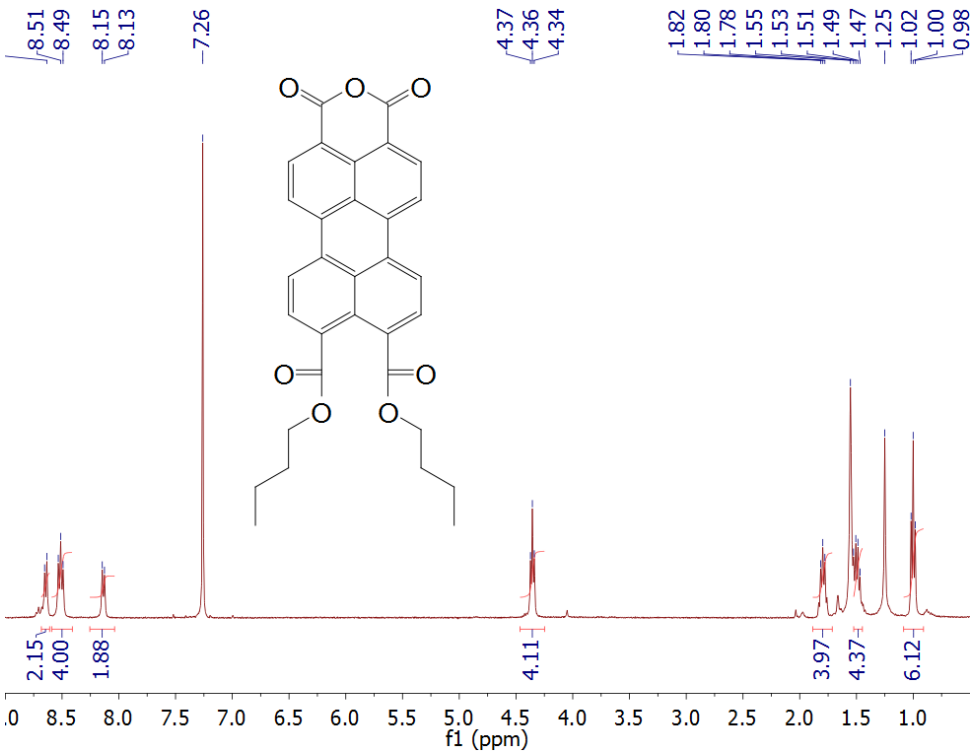

Figure S4. ^{1}H NMR spectrum of PCA recorded in $CDCl_3$.

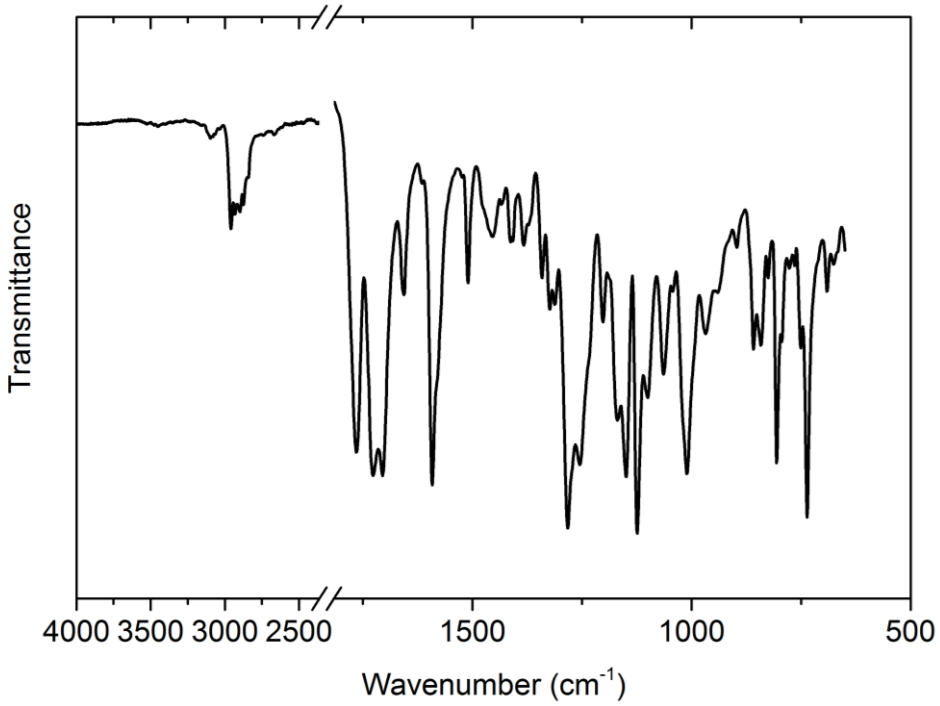

Figure S5. ATR-IR spectra of PCA. Consistent with what it reported in literature.[2]

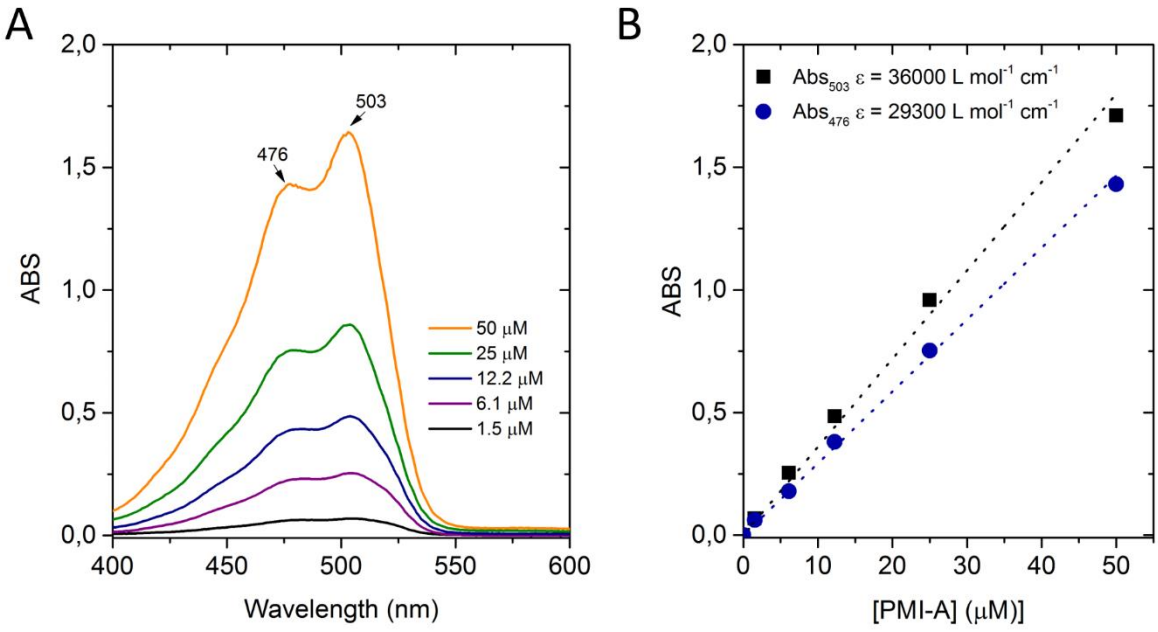

Figure S6. A) UV-vis spectra of PCA in CH_2Cl_2 at various concentration and B) Calibration plot at 503 and 476 nm.

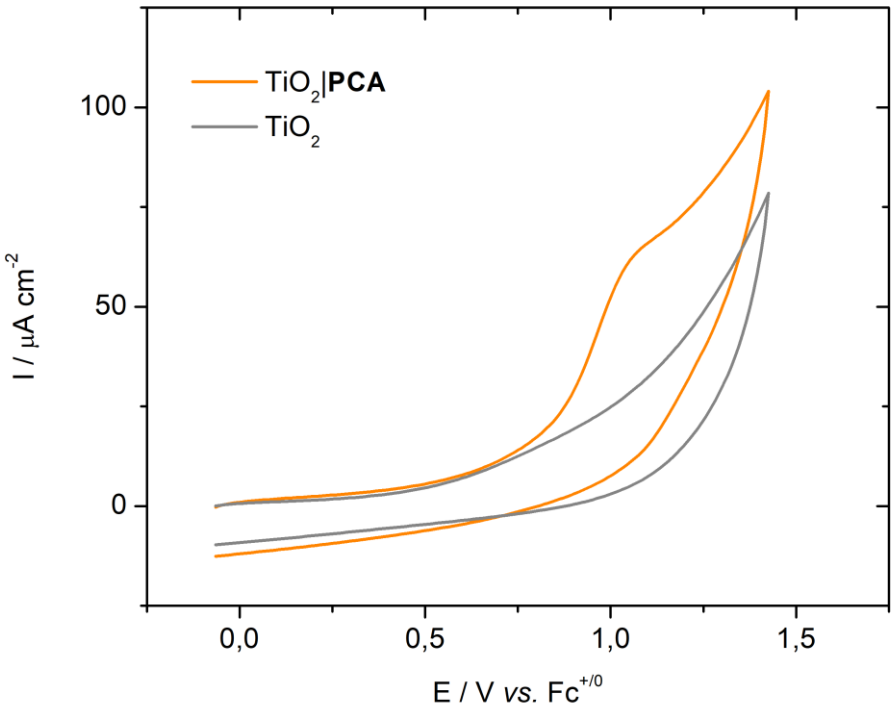

Figure S7. Cyclic voltammograms of bare TiO_2 and TiO_2|**PCA** electrodes in MeCN (0.1 M $TBAPF_6$). Measurements were carried out at 100 $mV \cdot s^{-1}$

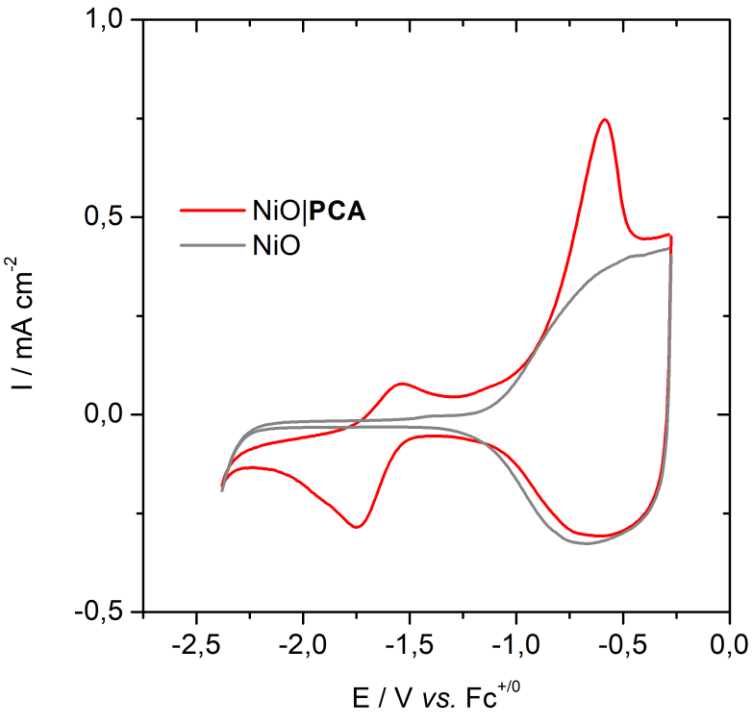

Figure S8. Cyclic voltammograms of bare NiO and NiO|**PCA** electrodes in MeCN (0.1 M $TBAPF_6$). Measurements were carried out at 100 $mV \cdot s^{-1}$

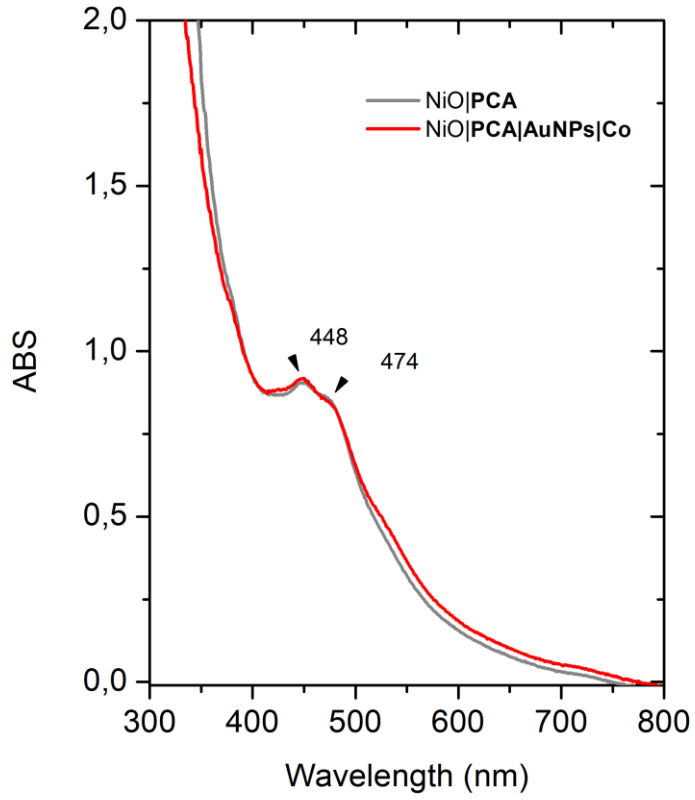

Figure S9. Transmission UV-Vis spectrum of NiO|**PCA** (grey) and NiO|**PCA|β-CD-AuNPs |Co** (red). NiO electrodes were used to set the background.

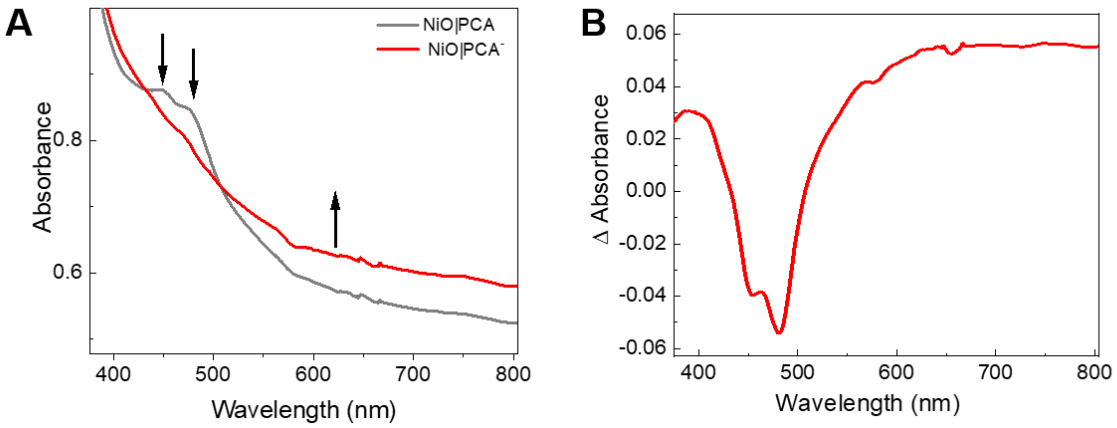

Figure S10. A) Spectroelectrochemistry measurements of PCA on a thin NiO film (1 layer, 0.3 µm) under applied bias of - 1.8 V *vs*. $Fc^{+/0}$ in N_2 degassed acetonitrile/0.1 M TBAP. Upon applying the potential, the absorption spectrum changes from the grey line to the red line. B) difference spectrum, highlighting the PCA bleach at 448 and 474 nm and a broad absorption tailing into the red.

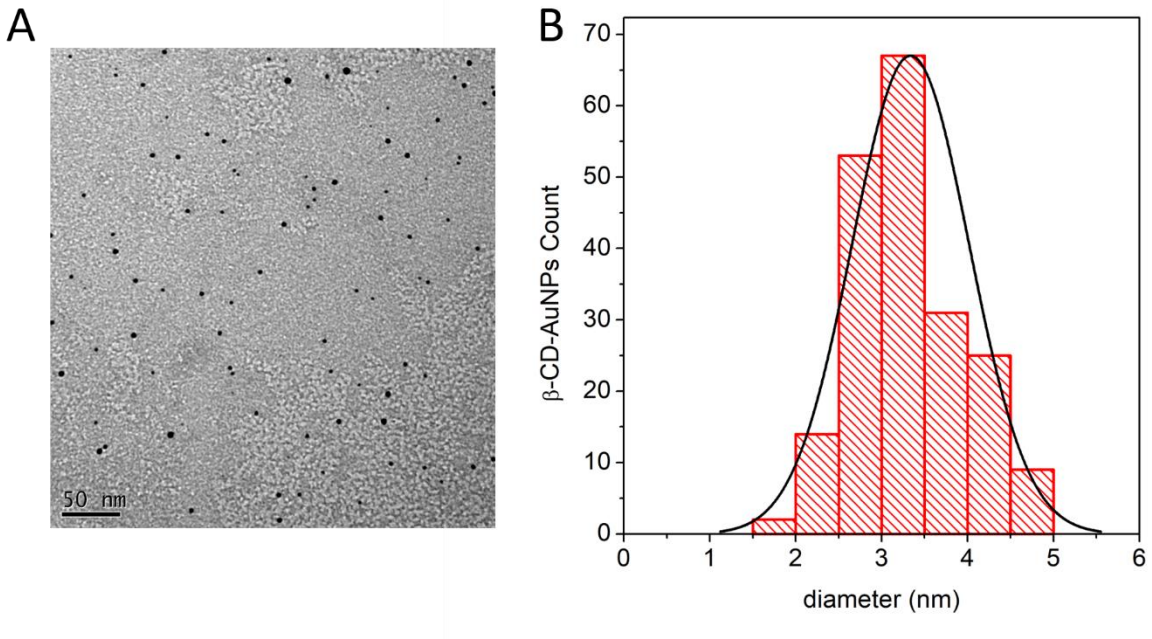

Figure S11. A) TEM image of the obtained AuNPs and B) their size distribution histogram.

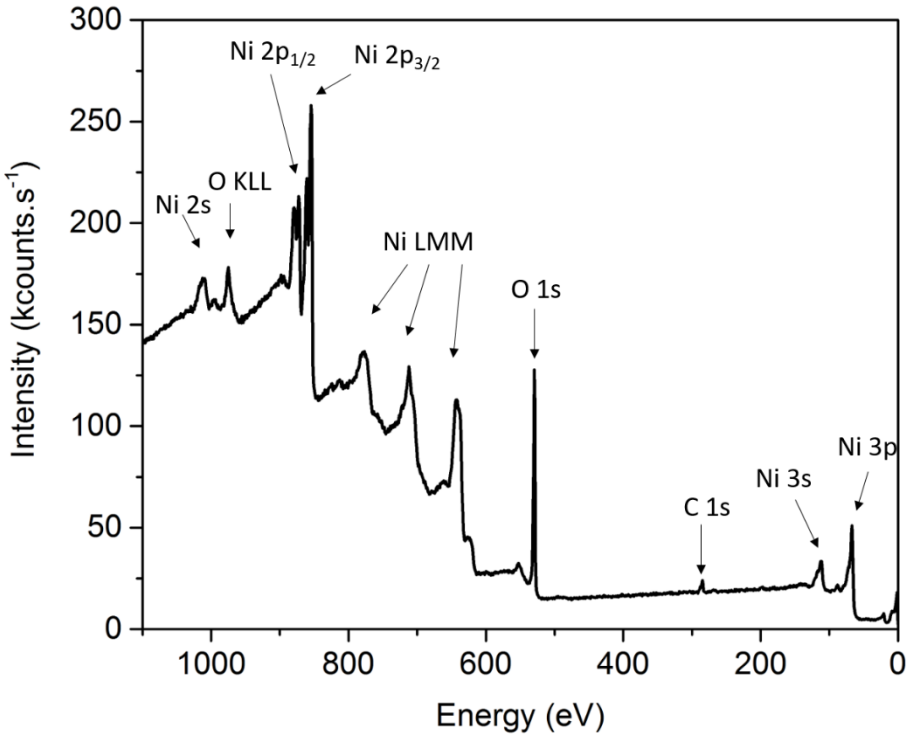

Figure S12. XPS analysis of screen printed NiO electrode sintered at 450°C in the survey mode. The C 1s peak was used as a reference for energy calibration. The presence of carbon is probably residual from the preparation of NiO.

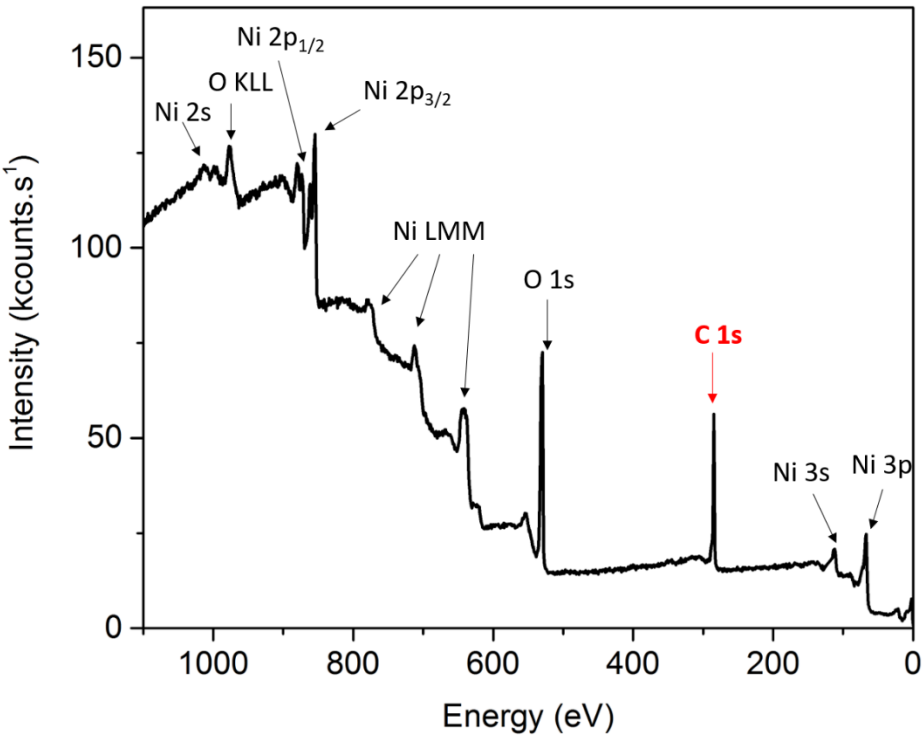

Figure S13. XPS analysis of a NiO|PCA electrode in the survey mode. The same features are observed as for the NiO electrode except the intensity of the C 1s peak is largely increased due to the presence of the dye on the electrode surface.

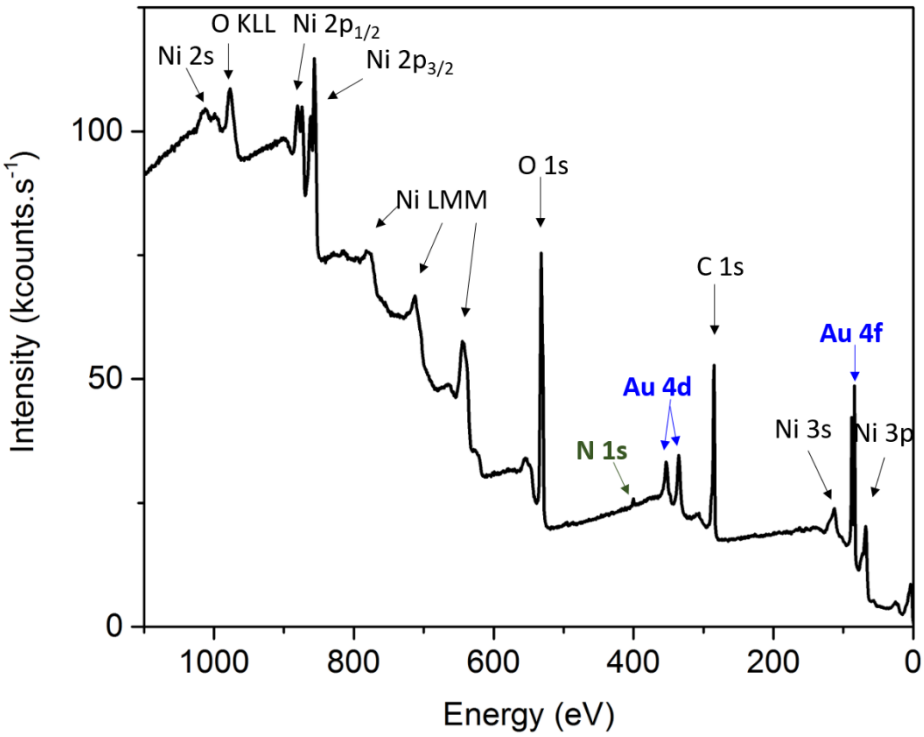

Figure S14. XPS analysis of a NiO|**PCA|AuNPs|Co** electrode in the survey mode.

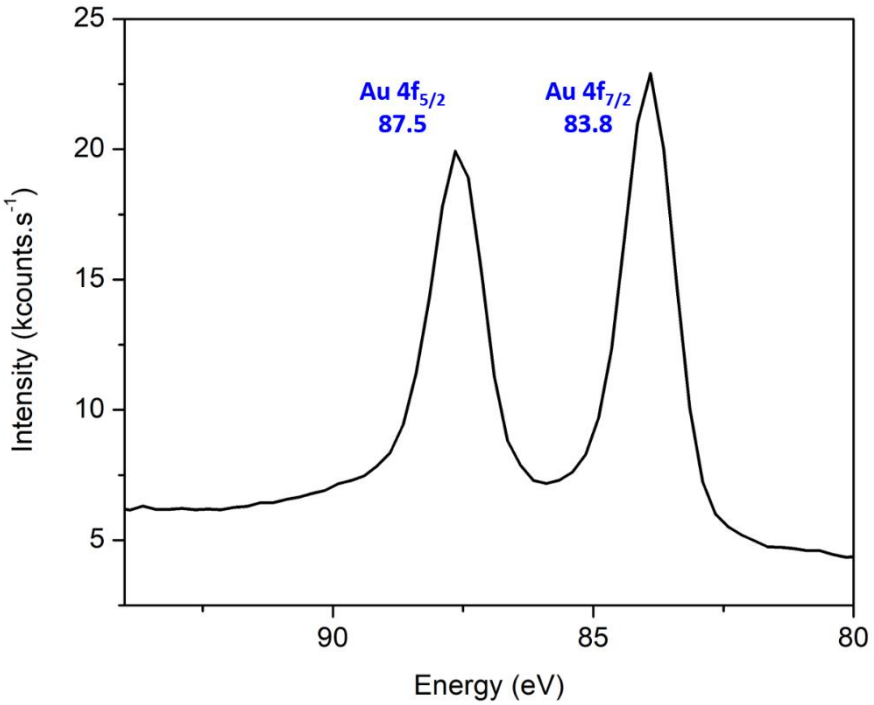

Figure S15. XPS spectrum of the Au 4f region for the NiO**|PCA|AuNPs** electrode showing the Au $4f_{7/2}$ and $4f_{5/2}$ doublet with binding energies of 83.8 and 87.5 eV respectively. These are typical values for Au^0.

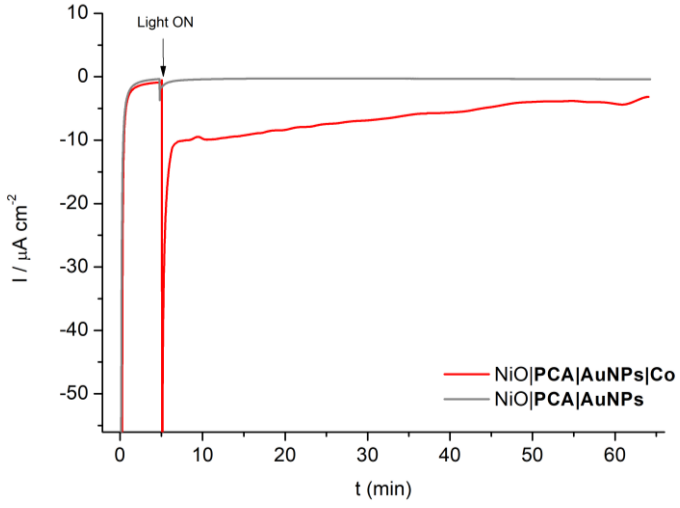

Figure S16. Chronoamperograms of NiO**|PCA|β-CD-AuNPs** and NiO**|PCA|β-CD-AuNPs|Co** photocathodes at an applied bias of -0.1 V *vs.* Ag/AgCl.

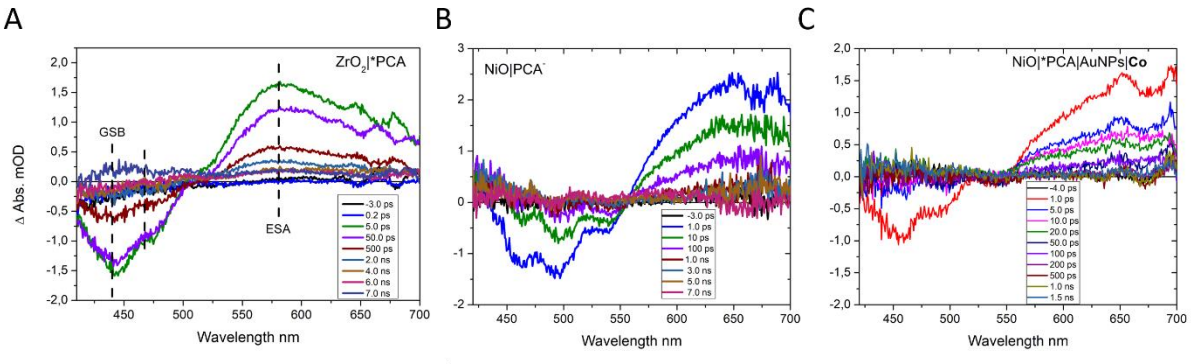

Figure S17. fs TA spectra of A) ZrO_2|PCA, B) NiO|PCA^-, and C) NiO|PCA|AuNPs|**Co**.

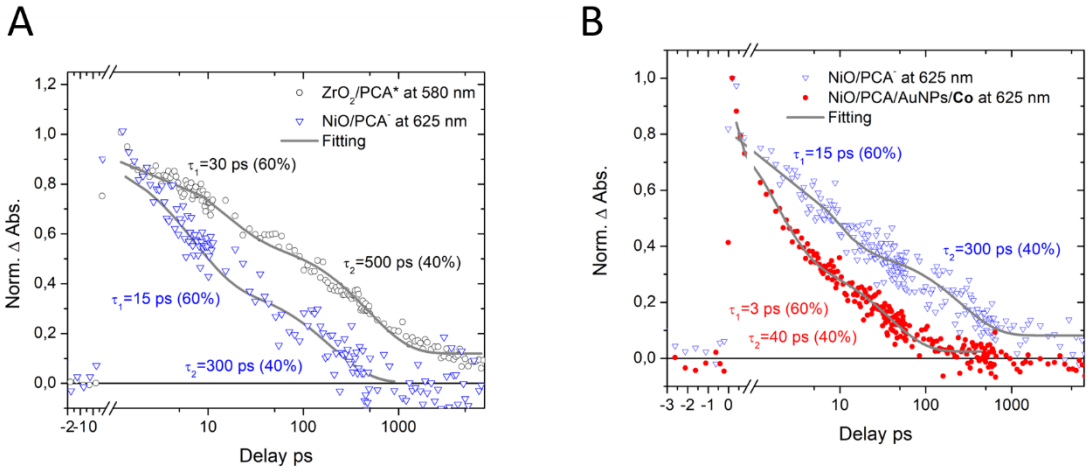

Figure S18. Transient absorption traces of A) ZrO_2|PCA at 580 nm (black circles) showing the decay of the excited dye and NiO|**PCA** at 625 nm (blue triangles) showing the decay of the reduced dye ; B) time traces of NiO|$\mathbf{PCA}^-$ (blue triangles) and NiO|**PCA|AuNPs|Co** catalyst (red dots) at 625 nm (reduced dye).

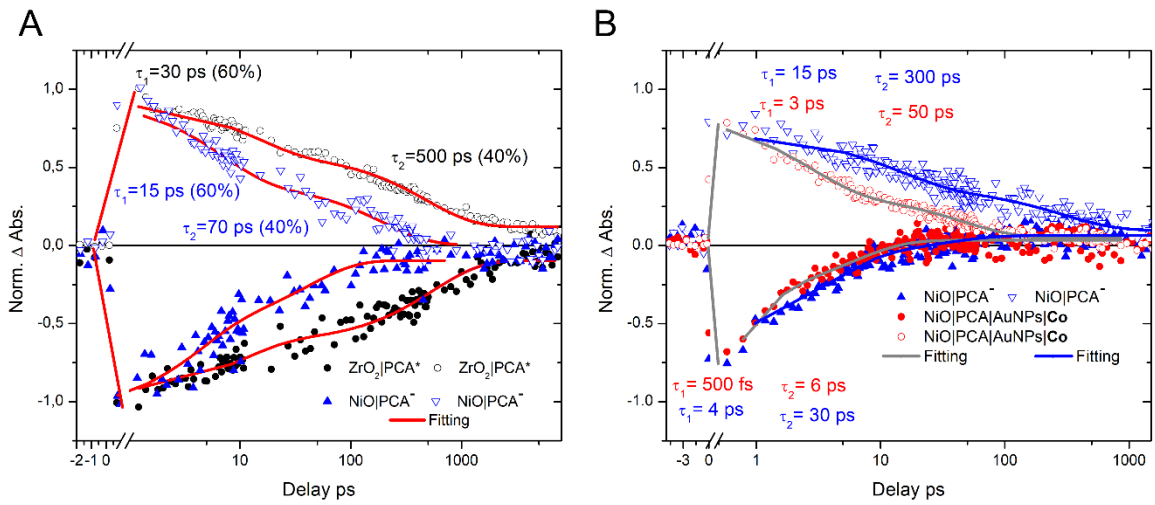

Figure S19. Time traces of A) PCA attached to ZrO_2 and NiO at the GSB (filled) and ESA (empty), B) time traces of NiO|PCA and NiO|PCA|AuNPs|**Co** catalyst at both GSB (filled) and ESA (empty).

1. Roy, S.; Huang, Z., et al., *J. Am. Chem. Soc.* **2019,** *141* (40), 15942.
2. Webb, J. E. A.; Chen, K., et al., *Physical Chemistry Chemical Physics* **2016,** *18* (3)1712.