

Supporting Information

A Diuranyl(VI) Complex and Its Application in Electrocatalytic and Photocatalytic Hydrogen Evolution from Neutral Aqueous Medium

Sabari Ghosh,[†] Ankit Kumar Srivastava,[†] Radha Govu,[‡] Ujjwal Pal,^{*,‡} Samudranil Pal^{*,†}

[†]School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

[‡]Department of Energy and Environmental Engineering, CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, India

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Corresponding Author

*E-mail: spal@uohyd.ac.in

Section S1

Electrocatalytic Hydrogen Evolution

Quantitative Hydrogen Evolution Experiment. The quantitative estimation of the evolved hydrogen was done using a locally constructed electrolysis setup¹ where the working electrode and the counter electrode are



placed in two separate chambers (image on the left). Bulk electrolysis at constant current of $-500\ \mu\text{A}$ was carried out for 5 h using the two electrode system and 0.1 M phosphate buffer of pH 7 as the electrolyte. Surface coated (with $[(\text{UO}_2)_2(\mu\text{-L})_2]$, carbon-black and Nafion) FTO electrode with surface area $0.5\ \text{cm}^2$ was used as the working electrode (cathode) and a spiral platinum wire was used as the counter electrode (anode). The loading of the catalyst on FTO was maintained at $1\ \text{mg}/\text{cm}^2$. During electrolysis hydrogen bubbles were formed at the surface modified FTO electrode which gradually accumulated in the graduated tube by displacing the electrolyte. The set up was constructed in such a way that the bubbles formed at the counter electrode could no way interfere with those formed on the working electrode.

Calculation of the Faradaic Efficiency.² From the above mentioned quantitative estimation of hydrogen using $[(\text{UO}_2)_2(\mu\text{-L})_2]$ /carbon-black/Nafion/FTO electrode, it was found that $0.18\ \text{mL h}^{-1}$ of hydrogen was evolved at ambient temperature and pressure. Therefore, the number of moles of hydrogen evolved in 1 h = $0.18/22400\ \text{mol} = 8.03 \times 10^{-6}\ \text{mol}$.

The controlled experiment was performed using carbon-black/Nafion/FTO electrode keeping all other experimental conditions identical. The total amount of hydrogen evolved in 5 h was $\sim 0.025\ \text{mL}$. Therefore, in terms of number of moles, the amount of hydrogen evolved in 1 h = $0.025/(5 \times 22400)\ \text{mol} = 0.22 \times 10^{-6}\ \text{mol}$.

Thus, the amount of hydrogen actually evolved = $(8.03 - 0.22) \times 10^{-6}\ \text{mol} = 7.81 \times 10^{-6}\ \text{mol}$

The ideal number of moles of hydrogen expected to be evolved $\text{H}_2(\text{ideal}) = Q/nF$, where Q is the total charged employed, n is the number of electrons involved for H_2 production and F is the Faraday constant. The value of n for HER is 2 as it is a two electron process and since we employed $-500\ \mu\text{A}$ current, $\text{H}_2(\text{ideal})$ in 1 h = $(0.5 \times 10^{-3} \times 3600)/(2 \times 96500) = 9.32 \times 10^{-6}\ \text{mol}$.

The expression used to calculate the Faradaic Efficiency is as follows:

$$\begin{aligned}\text{Faradaic Efficiency} &= \frac{\text{Moles of hydrogen evolved experimentally}}{\text{Moles of hydrogen evolved ideally}} \times 100 \\ &= \{(7.81 \times 10^{-6}) / (9.32 \times 10^{-6})\} \times 100 = 83.7\%\end{aligned}$$

Calculation of Turnover Frequency (TOF).³ The TOF (s^{-1}) can be calculated with the following equation: $TOF = I/2mF$, where, I is the current ($= 1.76 \times 10^{-5}$ A, the steady state value in the constant potential electrolysis (CPE) plot in Figure S6), F is the Faraday constant (in $C \text{ mol}^{-1}$), m is the number of active sites (in mol) and 2 is the number of electrons required to form one hydrogen molecule from two protons.

The number of active sites m can be calculated using the equation, $m = Q/2F$, where, Q (1.65×10^{-4} C) is the charge calculated by integrating the current vs time plot (within the potential range -0.201 to -0.849 V) generated from the cyclic voltammogram trace (in Figure 3 and also in Figure S5) recorded using $[(UO_2)_2(\mu-L)_2]$ /carbon-black/Nafion/FTO as the working electrode under non-catalytic conditions (CH_3CN medium rather than phosphate buffer) and the factor $1/2$ is for the 2 electron reduction of the catalyst $[(UO_2)_2(\mu-L)_2]$.

Now, putting $Q/2F$ for m in the equation for TOF (in h^{-1}) we get:

$$TOF = (I/2mF) \times 3600 = (I/Q) \times 3600 = \{(1.76 \times 10^{-5})/(1.65 \times 10^{-4})\} \times 3600 = 384 \text{ h}^{-1}$$

Section S2

Photocatalytic Hydrogen Evolution.

Calculation of Turnover Number (TON) and Apparent Quantum Yield (AQY). The turnover number (TON) was calculated according to the following equation.⁴

$$\text{Turnover Number (TON)} = \frac{2 \times \text{No. of evolved hydrogen molecules } (\mu\text{mol g}_{\text{cat}}^{-1})}{\text{No. of dye molecules adsorbed } (\mu\text{mol g}_{\text{cat}}^{-1})}$$

The apparent quantum yields (AQY) have been measured under the same photoreaction conditions. An optical power/energy meter (Newport, Model: 842-PE) was used for determination of the number of incident photons (N_{photons}). The values of N_{photons} and AQY (%) was calculated using the following equations.^{4,5}

$$N_{\text{photons}} = \frac{P\lambda t}{hc}$$

Here, P represents power of the light ($0.16 \text{ J s}^{-1} \text{ cm}^{-2}$) in an area of 11.17 cm^2 , λ is the wavelength of the light (420 nm), t is the duration of irradiation (4 h), h is the Planck's constant ($6.626 \times 10^{-34} \text{ J s}$) and c is the velocity of light ($3 \times 10^8 \text{ m s}^{-1}$).

$$N_{\text{photons}} = \frac{0.16 \times 11.17 \times 420 \times 10^{-9} \times 4 \times 3600}{6.626 \times 10^{-34} \times 3 \times 10^8}$$

$$= 5.44 \times 10^{22}$$

$$AQY = \frac{2 \times \text{No. of evolved hydrogen molecules}}{\text{No. of incident photons}} \times 100$$

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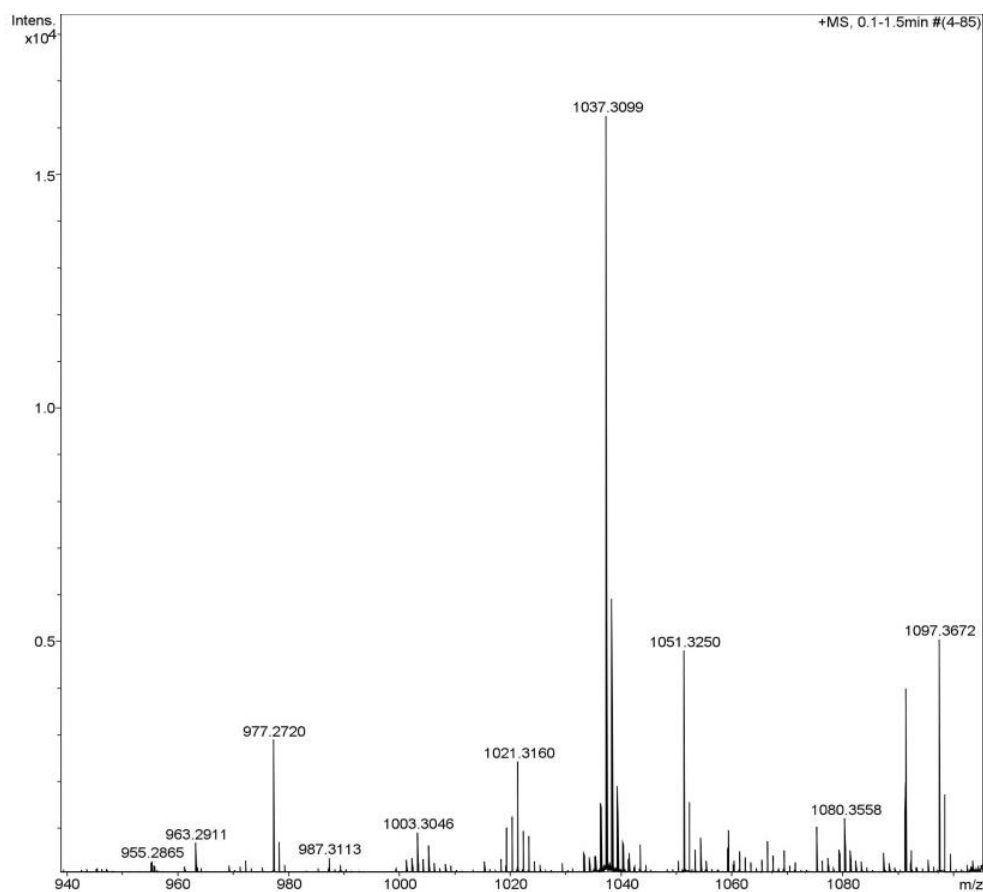


Figure S1. ESI mass spectrum of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ in dimethylformamide.

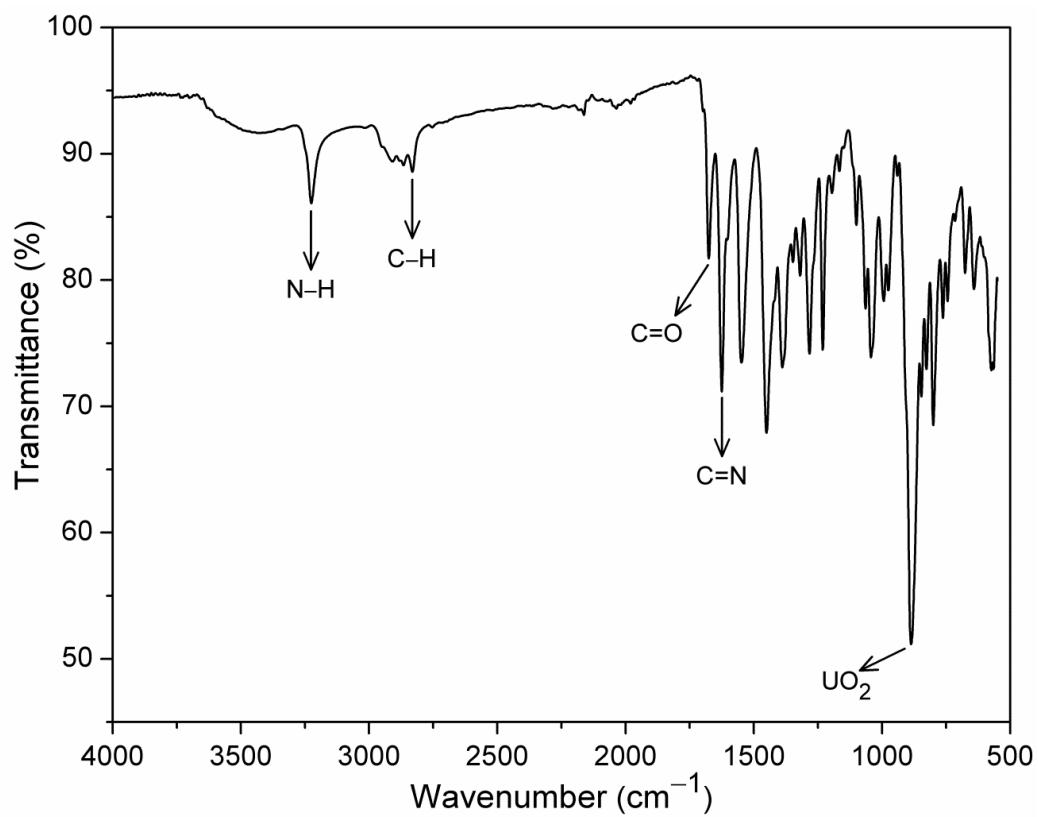


Figure S2. Infrared spectrum of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ in powder phase.

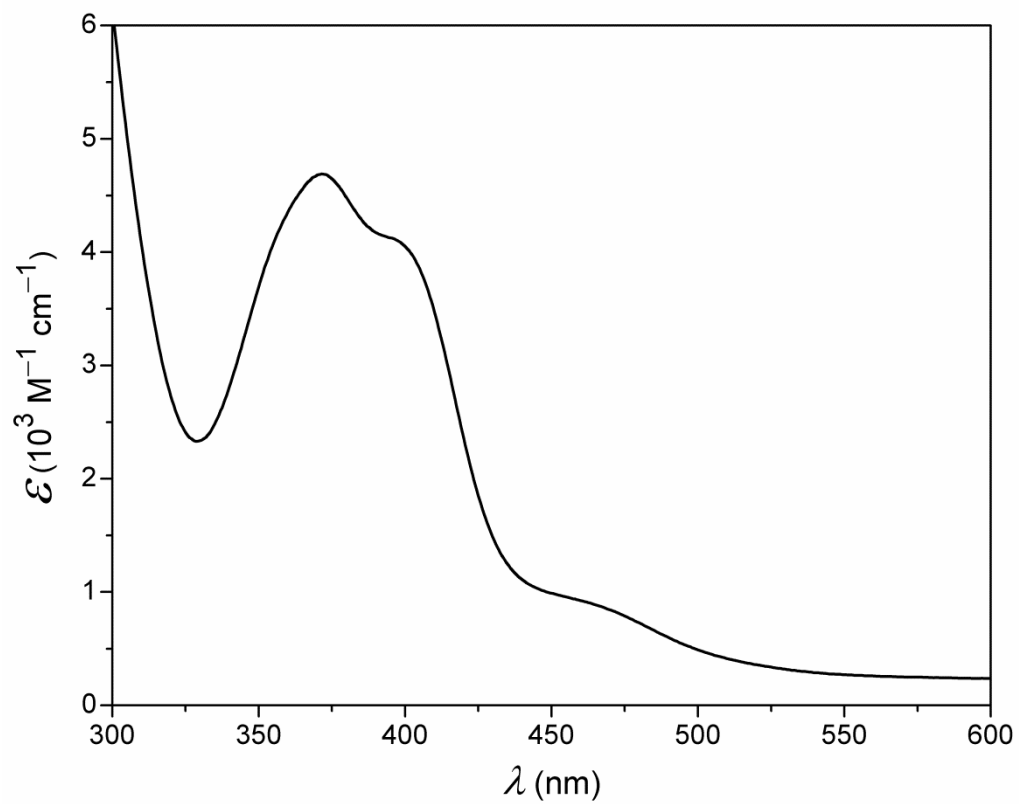


Figure S3. Electronic spectrum of $[(\text{UO}_2)_2(\mu\text{-L})_2]$ in dimethylformamide.

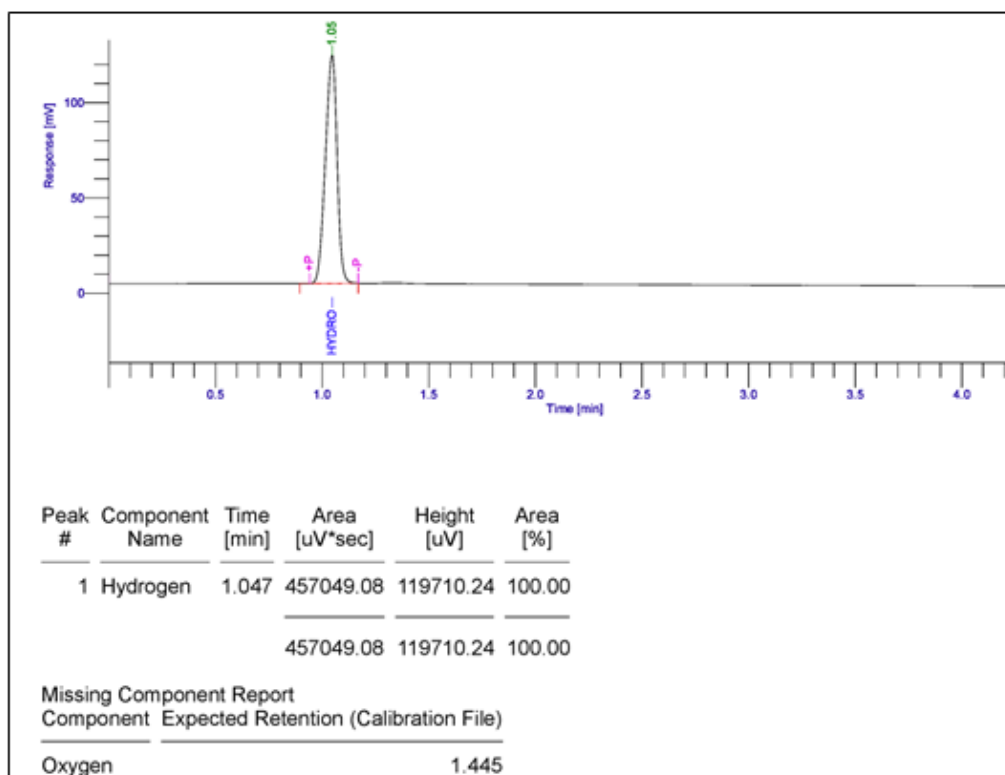
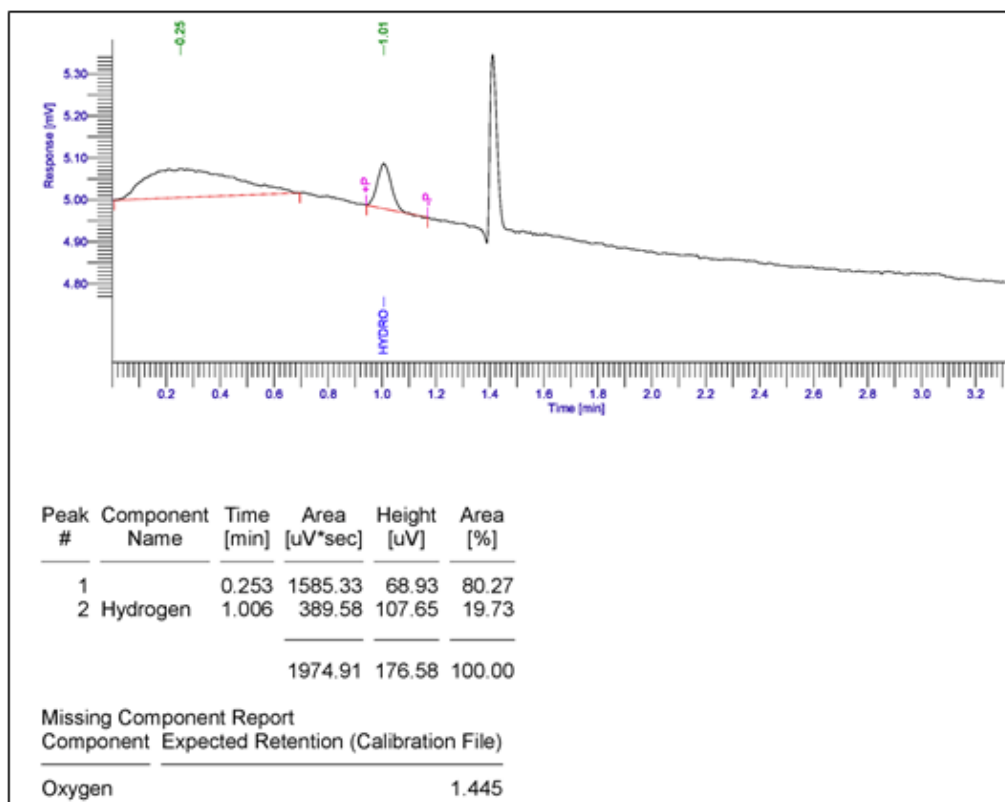


Figure S4. Chromatograms of the gas evolved in electrolysis (top) and hydrogen (bottom). In the first chromatogram, the oxygen peak is due to slight contamination by air during sample collection from the headspace.

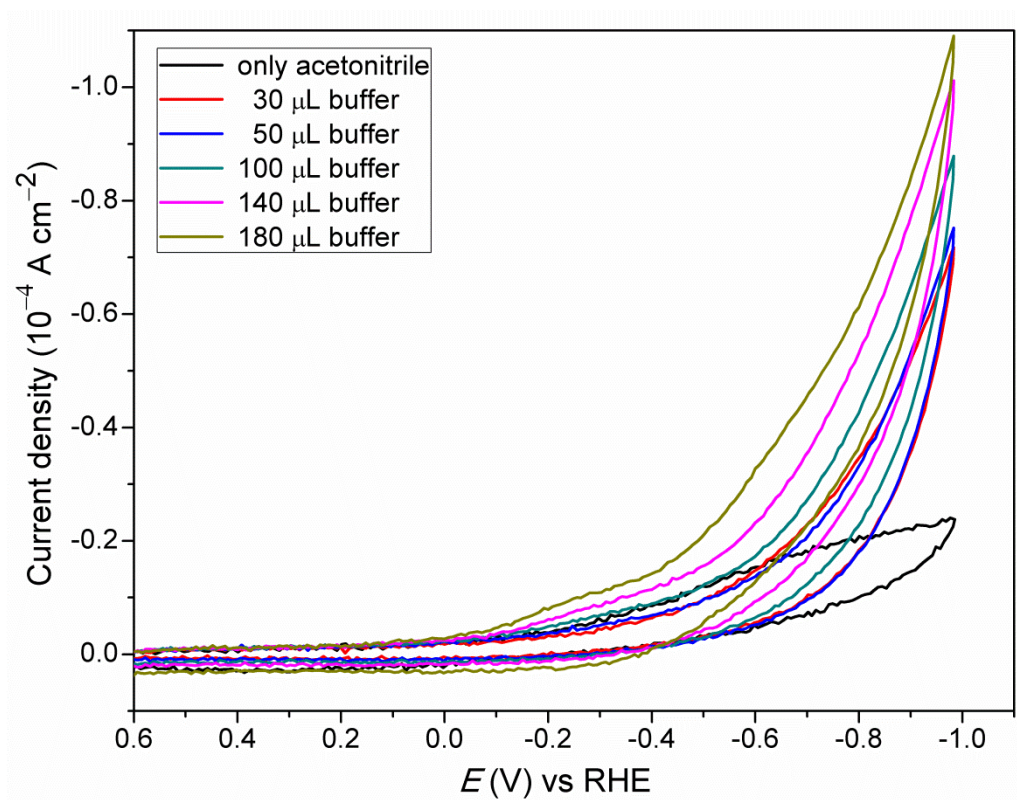


Figure S5. Electrocatalytic hydrogen evolution using the surface coated FTO electrode in acetonitrile with subsequent addition of phosphate buffer of pH 7.

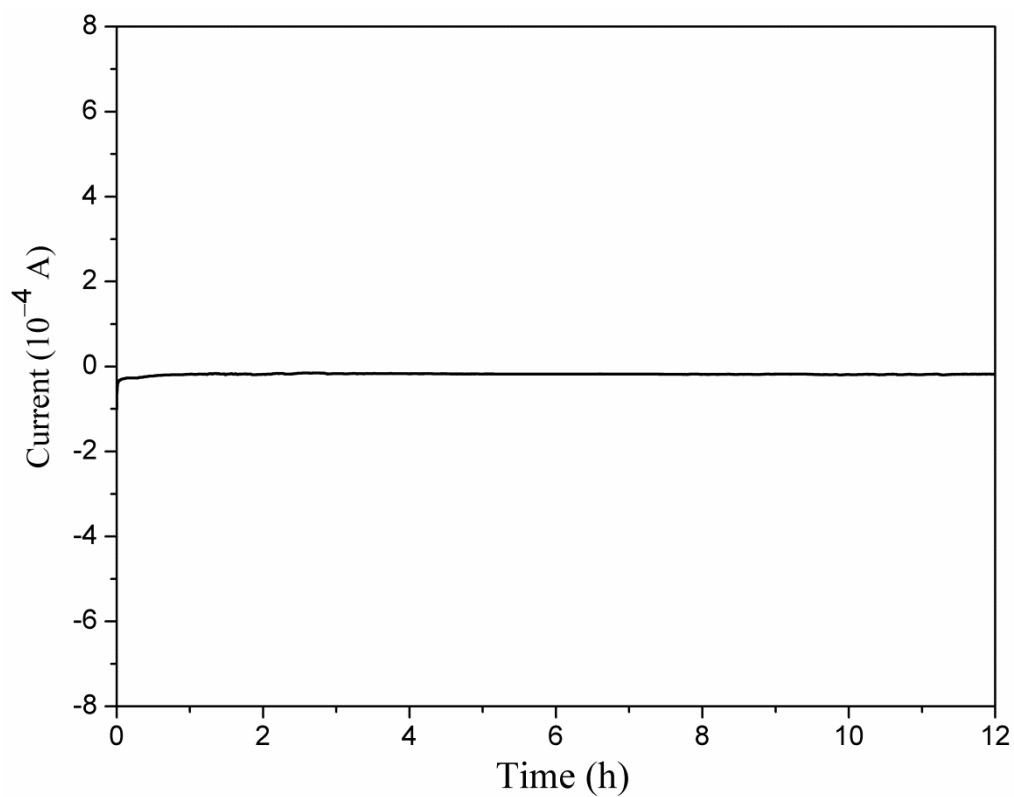


Figure S6. Constant potential electrolysis (CPE) using the surface coated FTO electrode in 0.1 M phosphate buffer of pH 7 for 12 h at a constant potential of -1.1 V (vs Ag/AgCl).

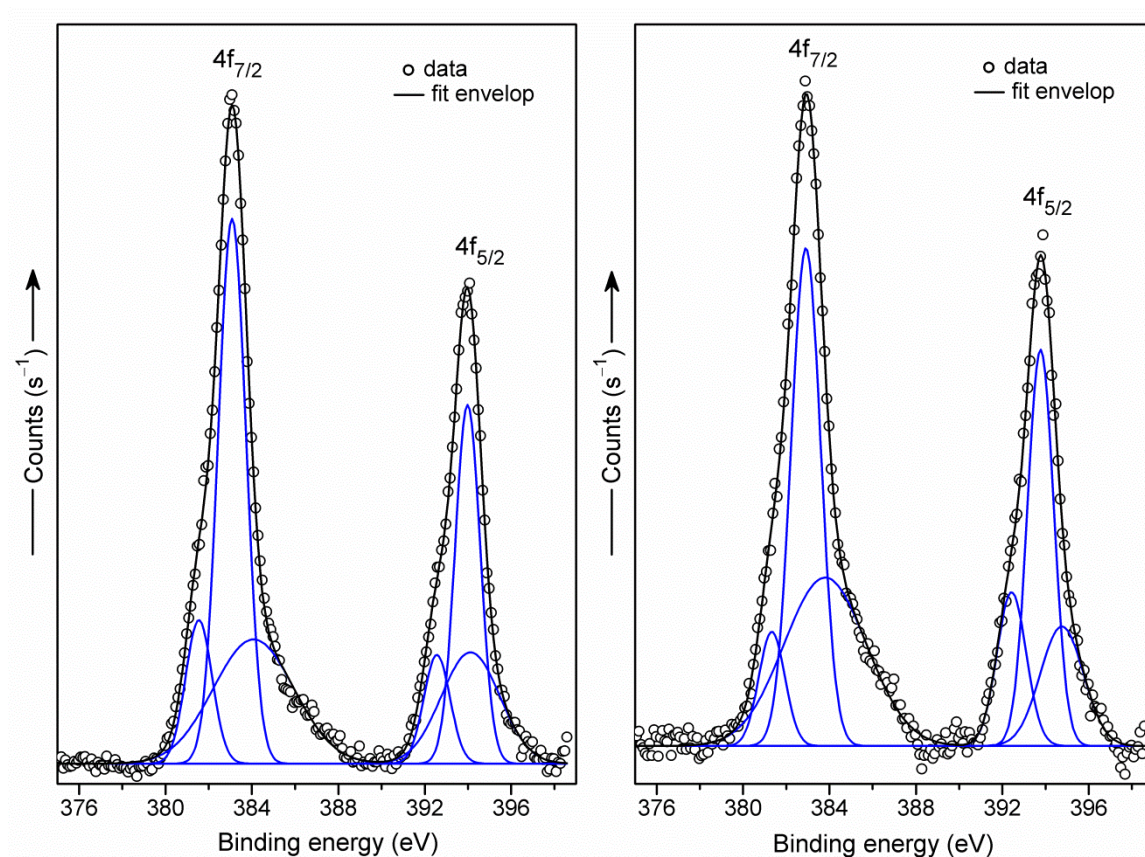


Figure S7. XPS spectra of surface coated FTO electrode before (left) and after (right) 500 cyclic voltammetry cycles.

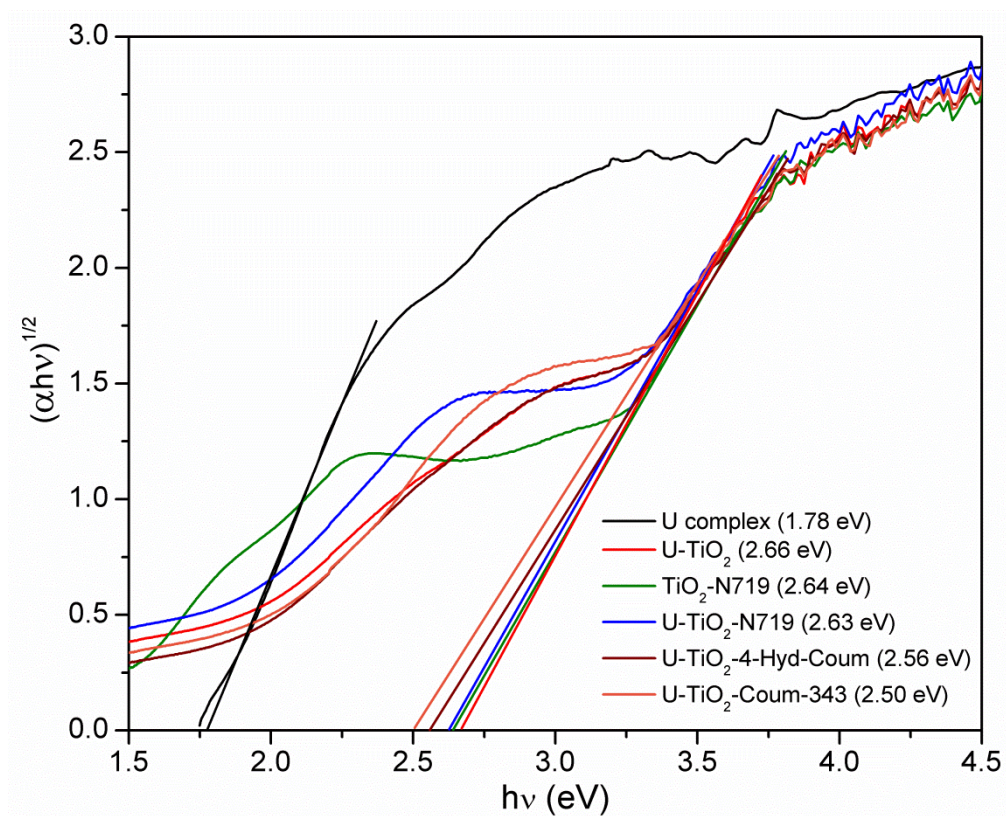


Figure S8. Tauc plots for different catalyst composites.