

Supplementary Data

# Nanoporous TiN/TiO<sub>2</sub>/Alumina Membrane for Photoelectrochemical Hydrogen Production from Sewage Water

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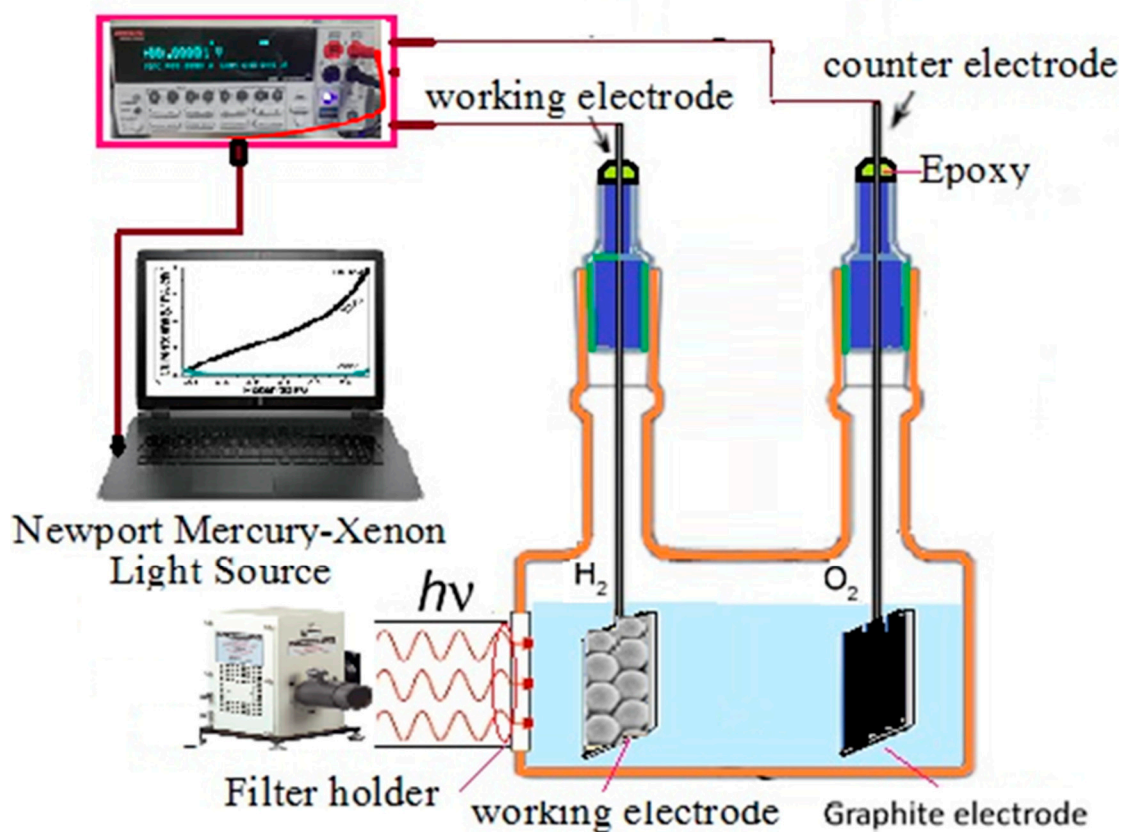


Figure S1. Testing the prepared materials as a photocathode.

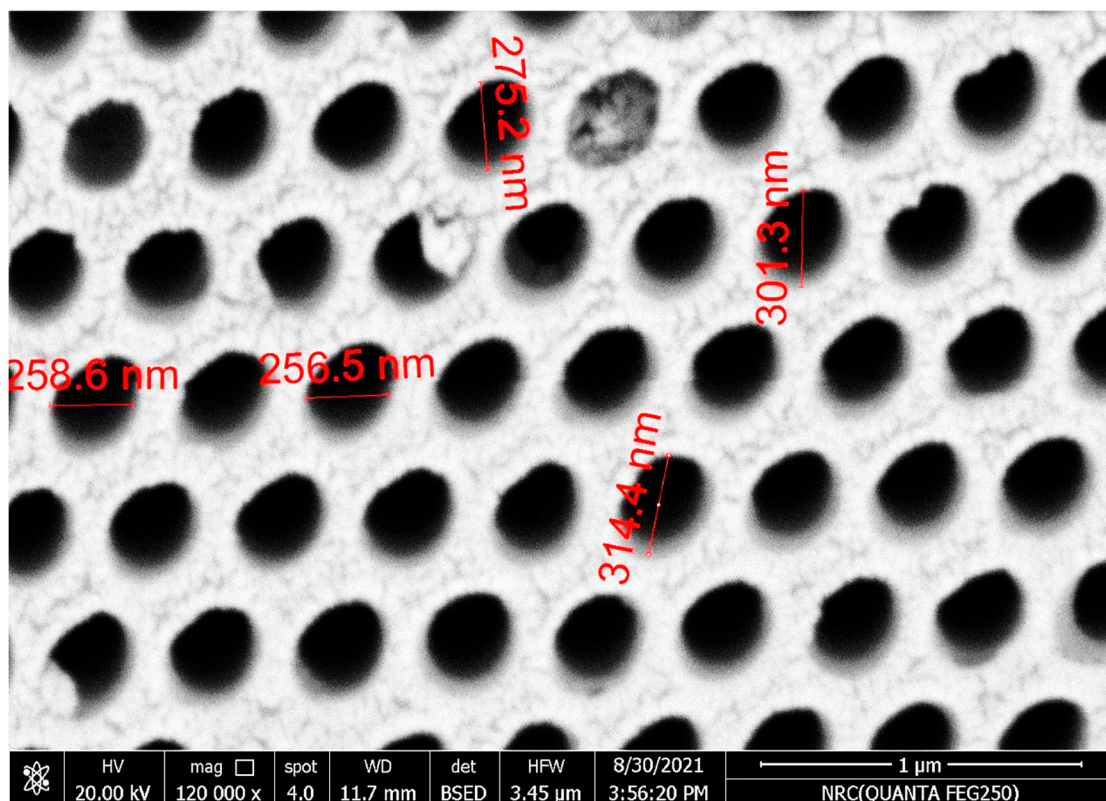


Figure S2. SEM image of Au/TiN/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.

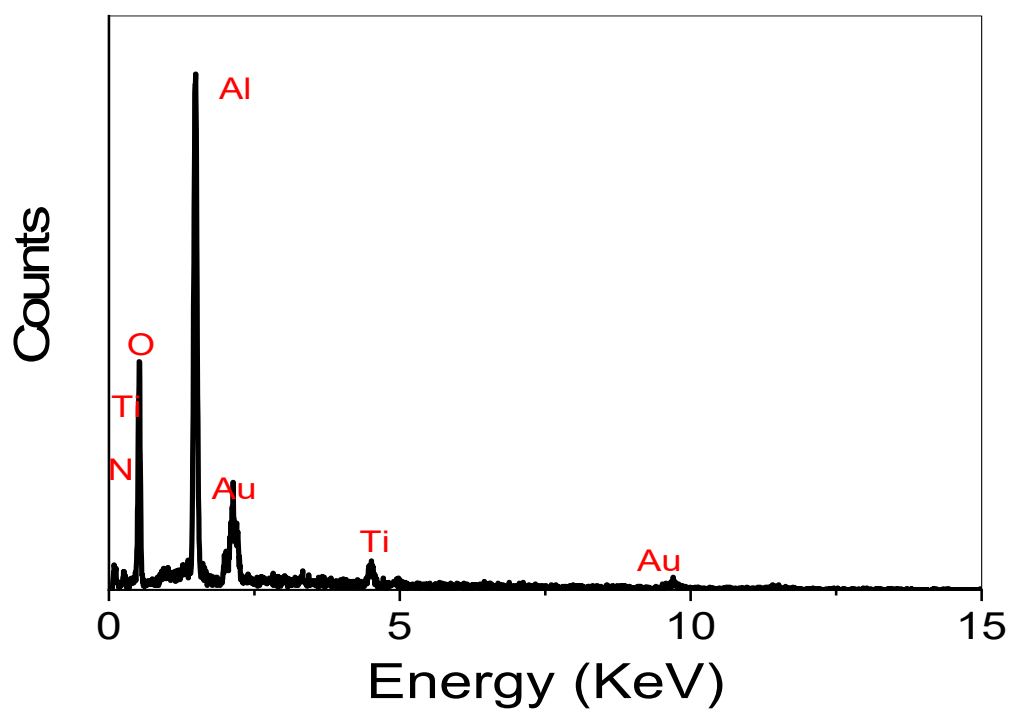


Figure S3. EDX of Au/TiN/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.

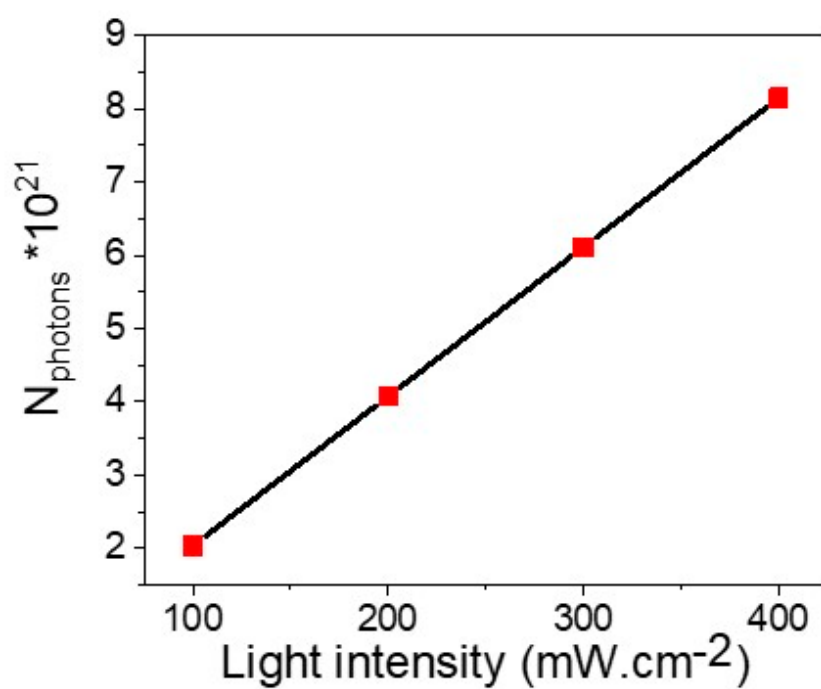


Figure S4. The relation between the number of photons per second and the incident light intensity.

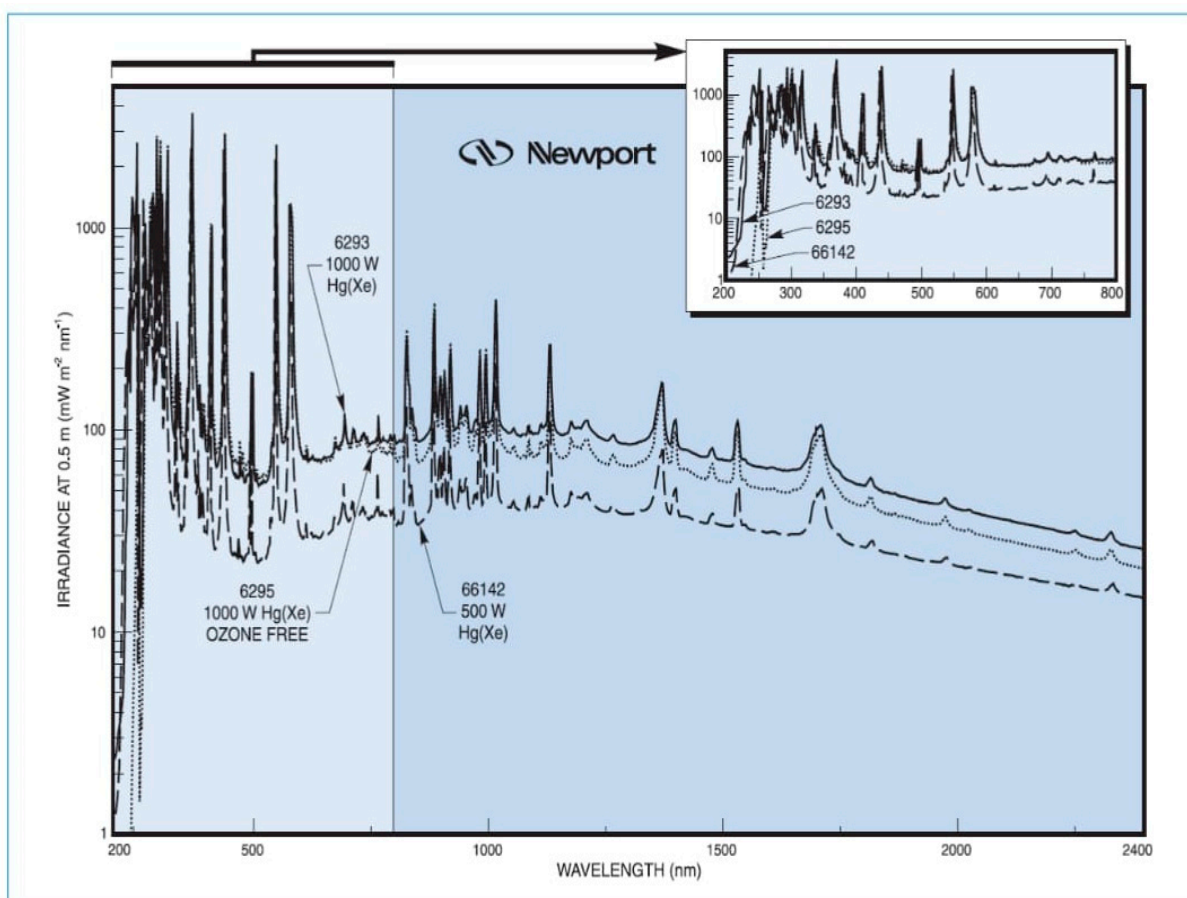
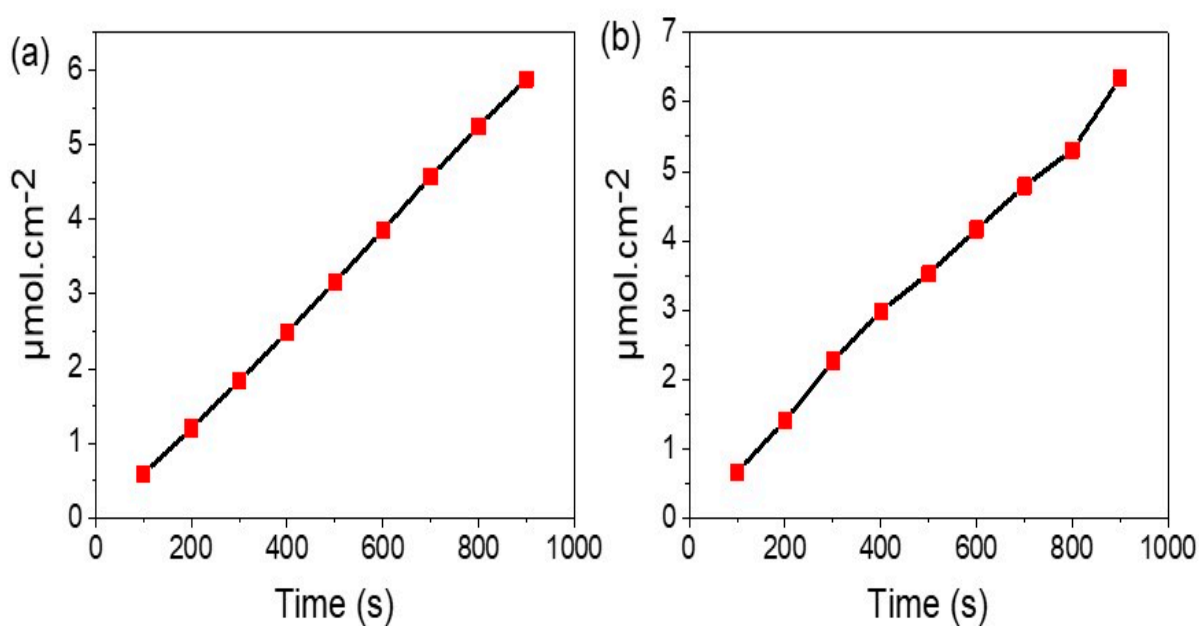


Figure S5. Irradiance spectrum of 66142 500 W Hg(Xe) lamp.



**Figure S6.** The number of moles evolved (a)  $\text{H}_2$  and (b)  $\text{O}_2$  gas.

**Table S1.** The chemical composition of the sewerage water used for the  $\text{H}_2$  generation.

Material or element	Concentration (mg/L)
Phenols	0.015
$\text{F}^-$	1.0
$\text{Al}^{3+}$	3.0
$\text{NH}_3$	5.0
$\text{Hg}^{2+}$	0.005
$\text{Pb}^{2+}$	0.5
$\text{Cd}^{3+}$	0.05
$\text{As}^{3+}$	0.05
$\text{Cr}^{3+}$	1.0
$\text{Cu}^{2+}$	1.5
$\text{Ni}^{3+}$	0.1
$\text{Fe}^{3+}$	1.5
$\text{Mn}^{2+}$	1.0
$\text{Zn}^{2+}$	5.0
$\text{Ag}^+$	0.1
$\text{Ba}^{3+}$	2.0
$\text{Co}^{2+}$	2.0
Other cations	0.1
Pesticides	0.2
$\text{CN}^-$	0.1
Industrial washing	0.5
Coli groups	4000/100 $\text{cm}^3$

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### Determination of $\Delta H^*$ and $\Delta S^*$ values

In the same manner, the enthalpy ( $\Delta H^*$ ) and entropy ( $\Delta S^*$ ) can be estimated from the Eyring equation, Equations S1 and S2, using the Boltzmann constant ( $k_B$ ) and Planck constant ( $h$ ).

$$k = T \cdot \frac{k_B}{h} \cdot e^{\Delta S/R} \cdot e^{-\Delta H/RT} \quad (S1)$$

$$\ln\left(\frac{k}{T}\right) = \ln\frac{k_B}{h} + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (S2)$$

For calculation  $\Delta H^*$ , we have to plot the relation between  $\ln(k/T)$  and  $1/T$ , from the slope value, we can determine the  $\Delta H^*$  value. From the same relation,  $\Delta S^*$  value can be determined from the intercept, in which the intercept value equal  $\ln\frac{k_B}{h} + \frac{\Delta S}{R}$ .

For calculating the  $\Delta H^*$  and  $\Delta S^*$  values, the slope, and intercept from Figure 8 (e, f) are used. The values of  $\Delta H^*$  for TiN/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Au/TiN/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> electrodes are 24.26 and 15.77 J.mol<sup>-1</sup>, respectively, while  $\Delta S^*$  values are 238.1 and 211.5 J.K<sup>-1</sup>.mol<sup>-1</sup>.