Supporting Information

Unbiased Spontaneous Solar Hydrogen Production Using Stable TiO$_2$-CuO Composite Nanofiber Photocatalysts

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Figure S1 FESEM images illustrates the change in the diameter of TiO$_2$-CuO composite nanofiber, a) before annealing, b) after annealing
Figure S2 EPR spectra of TiO$_2$ nanofibers annealed in oxygen

Figure S3 XPS survey spectra for the samples A1 and A4
Figure S4 FESEM images illustrates the structural stability of the fabricated nanofibers after irradiation with a 300 W xenon arc lamp in 1M KOH solution. a) Ti NFs, b) Ti-Cu NFs composite annealed in oxygen atmosphere, c) Ti NFs, and d) Ti-Cu NFs composite annealed in air atmosphere.

To understand the role of individual participating moieties in the catalyst, the photoelectrochemical activity of the fabricated nanofibers to split water was evaluated using a three-electrode cell, where glassy carbon electrode loaded with the nanofiber was used as the working electrode, while platinum foil was used as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode in 1 M KOH. As shown in Figure S5. TiO$_2$-CuO composite nanofibers annealed in air showed superior photocurrent density than that of TiO$_2$ nanofibers, indicating the positive effect of CuO when combined
with TiO₂ to form a more efficient photocatalyst to split water. The enhanced behavior of TiO₂-CuO composite nanofibers can be related to the nature of the defects formed due to CuO incorporation. To this end, a defect sensitivity factor (S) is defined as:

\[ S = \frac{C_{\text{dark}}}{C_{\text{light}}} \]

(1)

where \( c \) is the current density shift term that can be defined as \( c = \frac{J_{\text{gas}}}{J_{\text{air}}} \) and was calculated for samples A1 and A4. The sensitivity factor was found to be 0.325, indicating the formation of shallow impurity levels that facilitate the transfer of more electrons to the conduction band of TiO₂, which explains the increase in the photocurrent density for TiO₂-CuO composite nanofibers compared to that of TiO₂ nanofibers.

![Photoelectrochemical measurements of the samples A1 and A4 in dark and under illumination.](image)

**Figure S5** Photoelectrochemical measurements of the samples A1 and A4 in dark and under illumination.

**References**