Electronic Supplementary Information (ESI)

Hierarchical $Ti_{1-x}Zr_xO_{2-y}$ nanocrystals with exposed high energy facets showing co-catalyst free solar light driven water splitting and improved light to energy conversion efficiency

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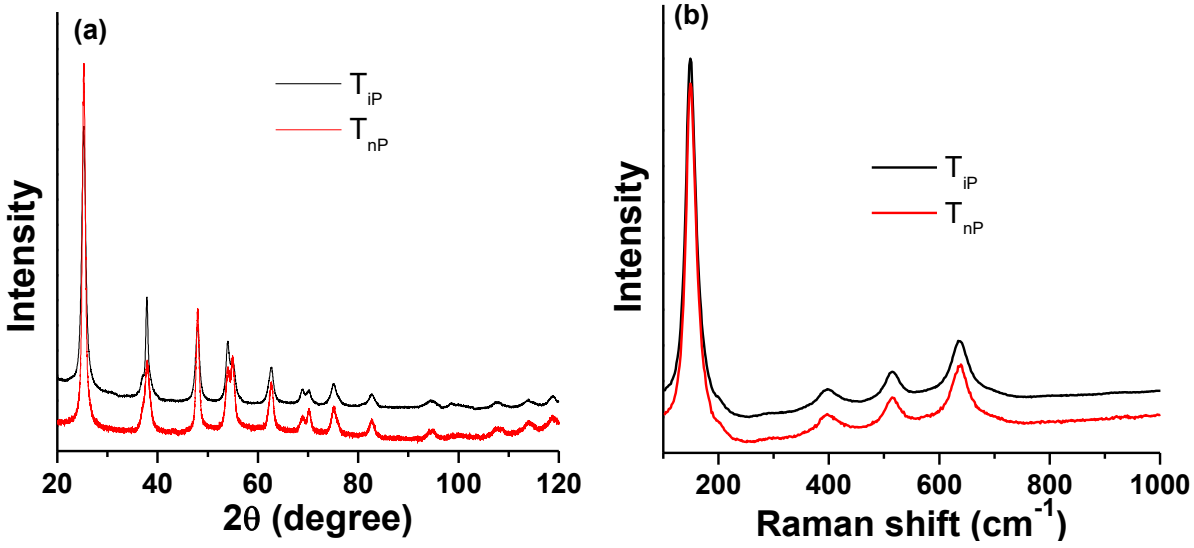

Fig. S1 (a) XRD and (b) Raman spectra of control TiO_2 samples T_{nP} and T_{iP}.

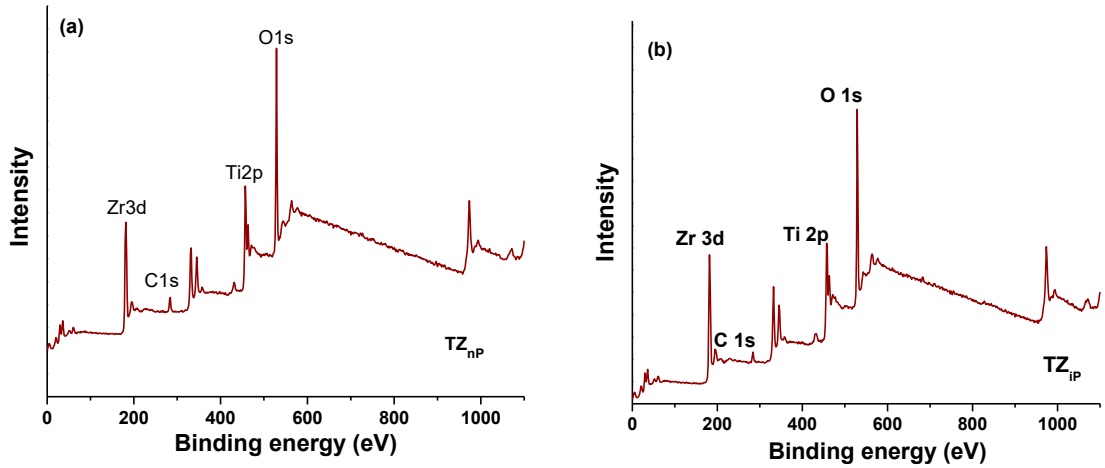

Fig. S2 XPS surface survey scan of (a) TZ_{nP} and (b) TZ_{iP}.

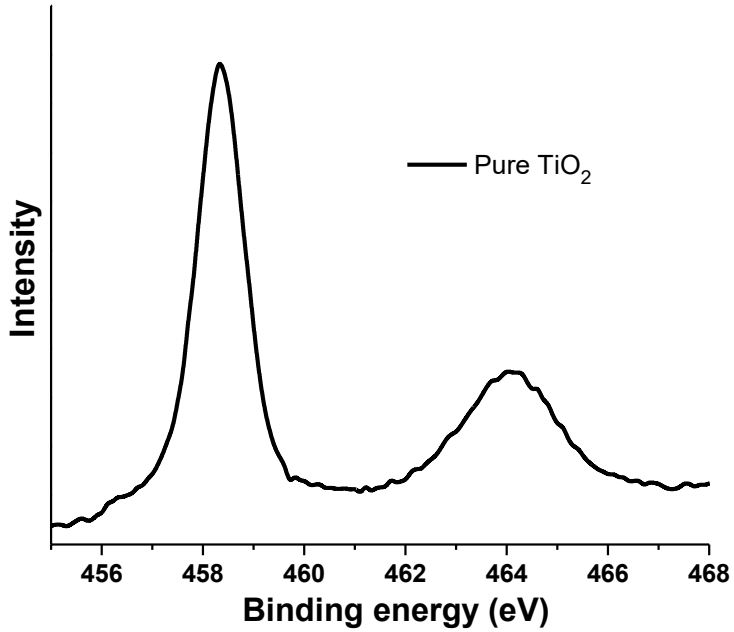

Fig. S3 XPS analysis of unmodified pure TiO_2 (T_{nP}/T_{iP}).

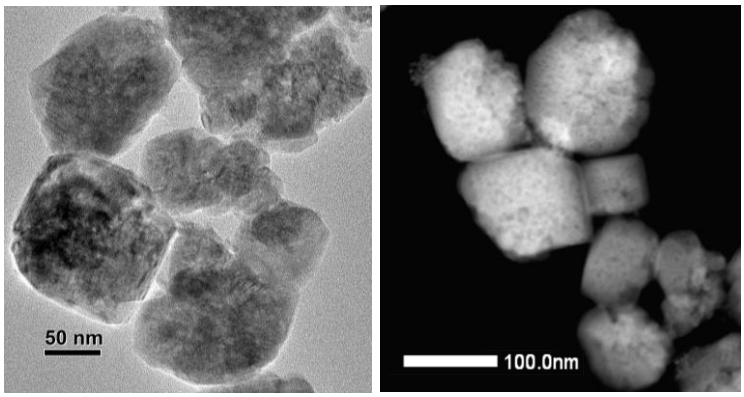

Fig. S4 (a) Bright field and (b) dark field TEM images of TZ_{nP} showing the mesoporosity present in the cubic morphology.

Table S1 Crystallographic data obtained from the PXRD data collected using Cu Kα (λ = 1.5406 Å) rotating anode within 2θ range of 10-120° and scan rate of 0.12°/minute

Sample	Chemical Formula	Lattice parameters	Reliability Factors	Atomic coordinates and thermal parameters	
				Ti/Zr	O
TZ_{nP}	$Ti_{0.665}Zr_{0.335}O_{1.955}$	Crystal family: Tetragonal (space group: $I4_1/amd$) a=3.8502(2) Å c=9.8951(7) Å	R_p=3.04 wR_p=4.68 GoF=4.24	x=0.5 y=0.5 z=0 U_{iso}=0.0065(5) Atom site occupancy: 1[0.665(14)/0.335(14)]	x=0.5 y=0 z=0.0411(2) U_{iso}=0.0021(16) Atom site occupancy: 0.9775
TZ_{iP}	$Ti_{0.912}Zr_{0.088}O_{1.963}$	Crystal family: Tetragonal (space group: $I4_1/amd$) a=3.8290(2) Å c=9.7560(7) Å	R_p=1.58 wR_p=2.17 GoF=1.99	x=0.5 y=0.5 z=0 U_{iso}=0.0029(7) Atom site occupancy: 1[0.912(14)/0.088(14)]	x=0.5 y=0 z=0.0383(3) U_{iso}=0.014(2) Atom site occupancy: 0.9815

Table S2 Bond distances and angles between atoms in comparison to Horn et. al. (ref 39)

Sample	Ti/Zr–O (Å)	Ti/Zr–O ∥[001] (Å)	O–O (Å)	O–O shared edge (Å)	Nearest Ti/Zr–Ti/Zr (Å)	O–Ti/Zr–O (°)
TZ_{nP} ($Ti_{0.665}Zr_{0.335}O_{1.955}$)	1.9675(5)	2.067(2)	2.543(2)	2.8413(10)	3.1346(3)	101.92(7)
TZ_{iP} ($Ti_{0.912}Zr_{0.088}O_{1.963}$)	1.9506(6)	2.065(3)	2.555(3)	2.8088(11)	3.1007(3)	101.04(8)
Anatase TiO_2 (Horn et. al.)	1.9338(5)	1.9797(23)	2.4658(29)	2.7924(13)	3.0394(2)	101.90(7)

S1. Calculation of light to power conversion efficiency (ɳ):

The overall solar light to power conversion efficiency (η) for a solar cell is defined in terms of the photocurrent density i.e. short-circuit current (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor of the cell (*ff*) and intensity of the incident light (P_{in}). The following equation was used to calculate the efficiency value.

$$\eta = \frac{output\ power}{Input\ power} \text{ x } 100\ (\%)$$

$$= \frac{P_{max}\ (mW\ cm^{-2})}{P_{in}\ (mW\ cm^{-2})} \text{ x } 100\ (\%)$$

$$= \frac{J_{sc}\ (mA\ cm^{-2}) \times V_{oc}\ (V) \times ff}{incident\ light\ intensity\ (mW\ cm^{-2})} \text{ x}100\ (\%);\ [P_{in} = 100\ \text{mW cm}^{-2}\ \text{for 1 Sun condition}]$$

$$= J_{sc}\ (mA\ cm^{-2}) \times\ V_{oc}(V) \times ff\ (\%)$$