Impact of Polymorphism vs Shape of Titania Nanocrystals towards Hydrogen Evolution Reaction

Ankur Yadav^a, Vivek Kumar Agrahari^a, Yuriy Pihosh^b, Mamiko Nakabayashi^c, Wojciech Nogala^d Balendu Sekhar Giri^e, Kazunari Domen^{b, g}, Daya Shankar Pandey^a*, Bhavana Gupta^{d, f}*, Subha Sadhu^a*

^aDepartment of Chemistry, Institute of Science, Banaras Hindu University, Varanasi, India

^bOffice of University Professors, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

^cInstitute of Engineering Innovation, The University of Tokyo, 7-3-1 Hongo, Tokyo, 113-8656, Japan

^dInstitute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

^eSustainability Cluster, School of Advanced Engineering, UPES, Dehradun, India.

^fDepartment of Chemistry, Applied Sciences Cluster, School of Advanced Engineering, UPES, Dehradun, India

^gResearch Initiative for Supra-Materials (RISM), Shinshu University, 4-17-1 Wakasato, Nagano 380-8533, Japan

*Email: <u>subha@bhu.ac.in; bhavana.gupta@ddn.upes.ac.in; dspbhu@bhu.ac.in</u>



Figure S1: TEM images of (a) anatase granular and (b) rutile TiO₂ nanorod.



Figure S2: Nitrogen adsorption and desorption isotherm of (a) anatase granular and (b) rutile TiO₂ nanorod.



Figure S3: FT-IR of (1) anatase granular and (2) rutile TiO_2 nanorod



Figure S4: a) SEM image of anatase granular TiO_2 and corresponding EDAX mapping for b) Ti and c) O



Figure S5: High resolution XPS spectra of anatase granular. (a) Ti 2p and (b) O 1s.



Figure S6: High resolution XPS spectra of rutile nanorod. (a) Ti 2p and (b) O 1s.

Table S1: XPS composition analysis of O and Ti and O: Ti ratio of anatase granular and rutile TiO₂ nanorod

Nanoparticle	Signal	ASF	ТА	TA/ASF	Ratio of elements	O : Ti Ratio
Anatase TiO ₂	O1s	0.711	16561.10	23292.69	0.669	1:2.04
	T12p	2.001	23096.82	11542.64	0.331	
Rutile TiO ₂	O1s	0.711	16503.48	23211.65	0.701	1 : 2.40
	Ti2p	2.001	19720.28	9855.21	0.298	



Figure S7: Photocatalytic H_2 generation was conducted using anatase granular under a 300 W Xe-lamp. The experiments involved three consecutive runs, during which we observed the maximum rate of H_2 generation.



Figure S8: Band structure of a) anatase granular and b) rutile TiO_2 -Pt nanorod for charge separation (inset shows the trend and maximum rate of hydrogen generation). Mechanism of H₂ generation on c) rutile TiO_2 nanorod and d) rutile TiO_2 -Pt nanorod, respectively.



Figure S9: TEM image of TiO₂-Pt (0.1 wt. %) after photo-deposition induced H_2 production.



Figure S10: SEM image of TiO_2 -Pt (0.1 wt. %) after photo-deposition induced H₂ production. Pt deposition present within circle.

AQE calculation formula:

$$AQE = \frac{number \ of \ reacted \ electrons}{number \ of \ incident \ photons} * 100\%$$
$$= \frac{2 * number \ of \ evolved \ H^2 \ molecules}{number \ of \ incident \ photons} * 100\%$$

$$E = \frac{nhc}{\lambda}$$

- n = number of incident photon per second
- h= Planck's constant
- c= velocity of light
- λ = wavelength