Supplementary Information

Electroless Ni plated nanostructured TiO_2 as a photocatalyst for solar hydrogen production

Priyanka N. Birla, Sudhir Arbuj, Manish D. Shinde, Shany Joseph, Sunit Rane, Sulabha Kulkarni and Bharat Kale*

Centre for Materials for Electronics Technology (C-MET), Panchawati, Off Pashan Road, Pune: 411 008, India.

*Corresponding Author:

Dr. Bharat B. Kale

Director General

Centre for Materials for Electronics Technology (C-MET)

Panchawati, Off Pashan Road,

Pune: 411 008, India

Tel: + 91 020 25899273

Email: bbkale1@gmail.com

Keywords: Ni decorated TiO2, Sacrificial agent, Nanoparticles, Photocatalysis, Water Splitting

Nickel plating bath detail study

Cleaning solution

As mentioned under Materials and Methods section, For nickel loading commercial electrochemical bath was purchased from Grauer & Weil (India) Limited. Electrochemical commercial bath consisted of cleaning solution, mild etching solution, pre-activator, activator, Ni salt solution and reducing solution.

Table T1: Commercial electrochemical bath preparation process solutions and methods.

Sr. No.	Name of the process solution	Commercial Name	Preparation method
1.	Cleaning solution	Ginplate CC 50	**Ginplate CC-50** = 50% by volume **Distilled water** = Balance
2.	Mild Etching Solution	Ginplate AD 481	**Ginplate AD-481 SP** =100g/l in Distilled water **Sulphuric Acid, AR grade**=1% by volume
3.	Pre-activator	Ginplate PC 236	**Ginplate PC-236**=150 g/L in Distilled water **Hydrochloric Acid, AR Grade (37%)** = 2.5% by volume
4.	Activator	Ginplate Activator 444	**Deionized or distilled water** =66% by volume **Ginplate PC 236** = 150 g/l **Hydrochloric Acid, AR Grade (37%)** =1.5% by volume **Ginplate Additive 443** =1% by volume **Ginplate Activator 444** = 6.3% by volume
5.	Post Activator	Ginplate Post-Activator 493	**Ginplate PA 493** = 1 part by volume **Distilled water** = 5 parts by volume
6.	Ni salt solution	Ginplate 432A	**Ginplate Ni 432 A** = 80 ml/lit.
7.	Reducing solution	Ginplate 432B	**Ginplate Ni 432 B** = 150 ml/lit.

The above compositions are patented and the information provided above is as mentioned in their standard data sheet (www.growel.com). For the electroless Ni loading bath preparation above mentioned protocol is followed for the experiments in the present work.

Ref. Electroless nickel, alloy, composite and nano coatings - A critical review Sudagar, J., Lian, J., & Sha, W. (2013). Electroless nickel, alloy, composite and nano coatings - A critical review. Journal of Alloys and Compounds, 571, 183–204.

Ref. Laurence W. McKeen,4 - Binders, Editor(s): Laurence W. McKeen, In Plastics Design Library, Fluorinated Coatings and Finishes Handbook (Second Edition), William Andrew Publishing,2016, Pages 59-82, ISBN 9780323371261.

Ref. Electroless nickel, alloy, composite and nano coatings - A critical review Sudagar, J., Lian, J., & Sha, W. (2013). Electroless nickel, alloy, composite and nano coatings - A critical review. Journal of Alloys and Compounds, 571, 183–204.

Ref. Chapter 18 Electroless Deposition of Nickel, Mordechay Schlesinger, Modern Electroplating, Fifth Edition Edited by Mordechay Schlesinger and Milan Paunovic Copyright-2010 John Wiley & Sons, Inc.

Ref. Chapter No. 8. Electroless Plating Fundamentals and Applications, Glenn O. Mallory, Juan B. Hajdu, 1990, ISBN : 9780936569079, 0936569077

Table T2. Steps involved in surface activation and electroless Ni loading process over TiO_2 nanoparticles.

Sr. No.	Solution	Temperature (°C)	Time (min)	Water washing time (min)
1	Cleaning solution	60	10	1-2
2.	Mild etching solution	27	4	1-2
3.	Acid solution	27	2	1-2
4.	Pre-activator	27	2	0
5.	Activator	27	5	1-2
6.	Post activator	27	5	1-2
7.	Electroless Ni bath	85	15	5

XPS spectra of 0.1% Ni/TiO_2 powder for carbon, C1s

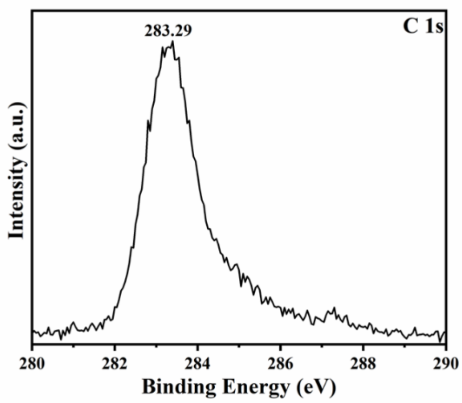

Fig. S1 XPS spectra of 0.1% Ni/TiO_2 powder corresponding to carbon, C1s.

FESEM images of 0.5%Ni/TiO_2 nanopowders

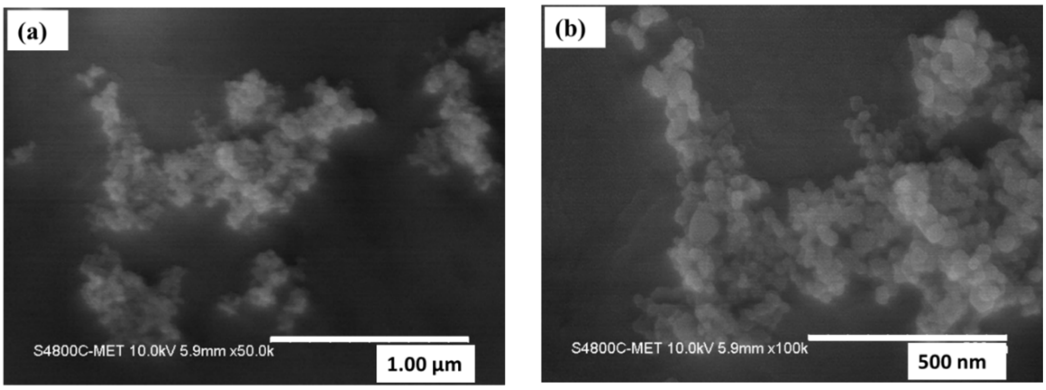

Fig. S2 FESEM images of 0.5%Ni/TiO_2 nanopowders at (a) low and (b) high magnification respectively.

FETEM images of 0.1%Ni/TiO_2 nanopowders

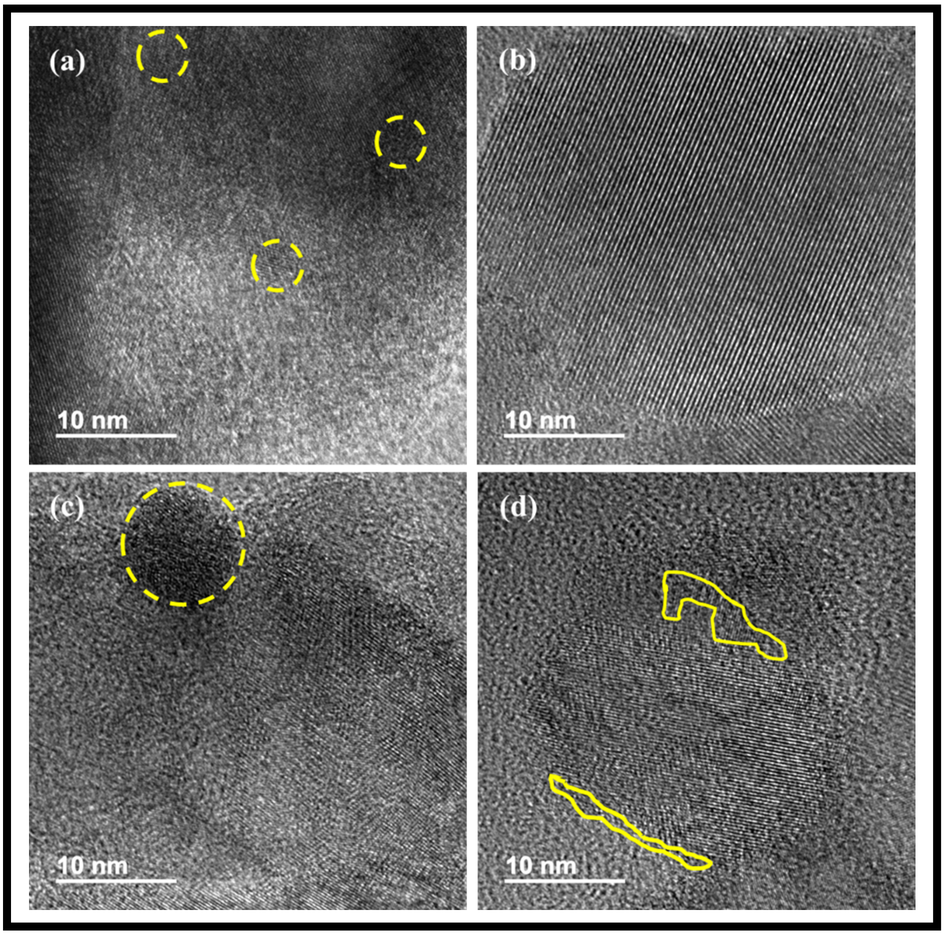

Fig. S3 FETEM images of 0.1%Ni/TiO_2 nanopowders. Yellow highlighted regions show nanoclusters (dotted circles) and nanofilms (irregular shapes) deposited over TiO_2 surfaces.

FETEM images of 0.5 %Ni/TiO_2 nanopowder

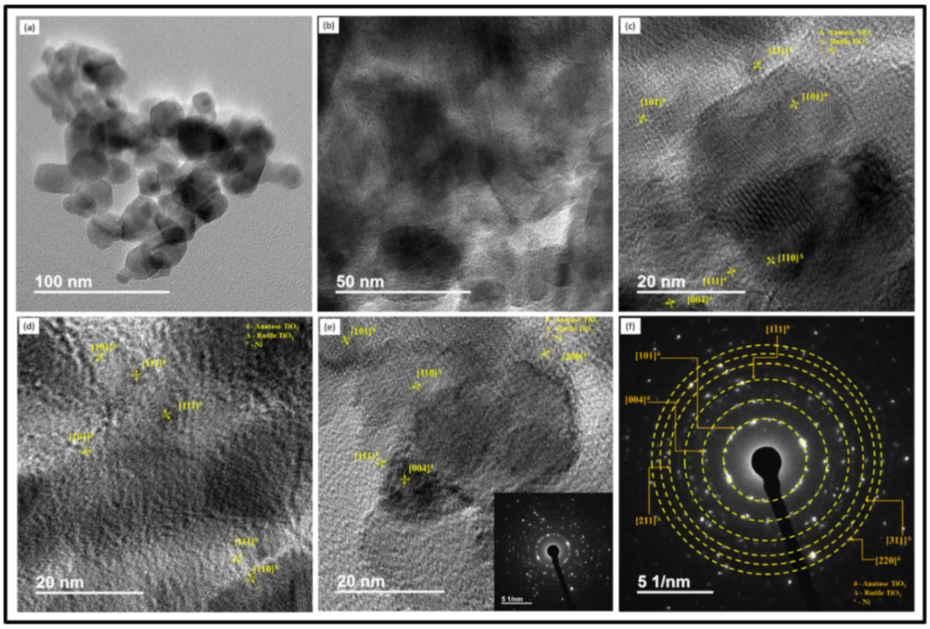

Fig. S4 FETEM images of 0.5 %Ni/TiO_2 nanopowder photocatalyst.

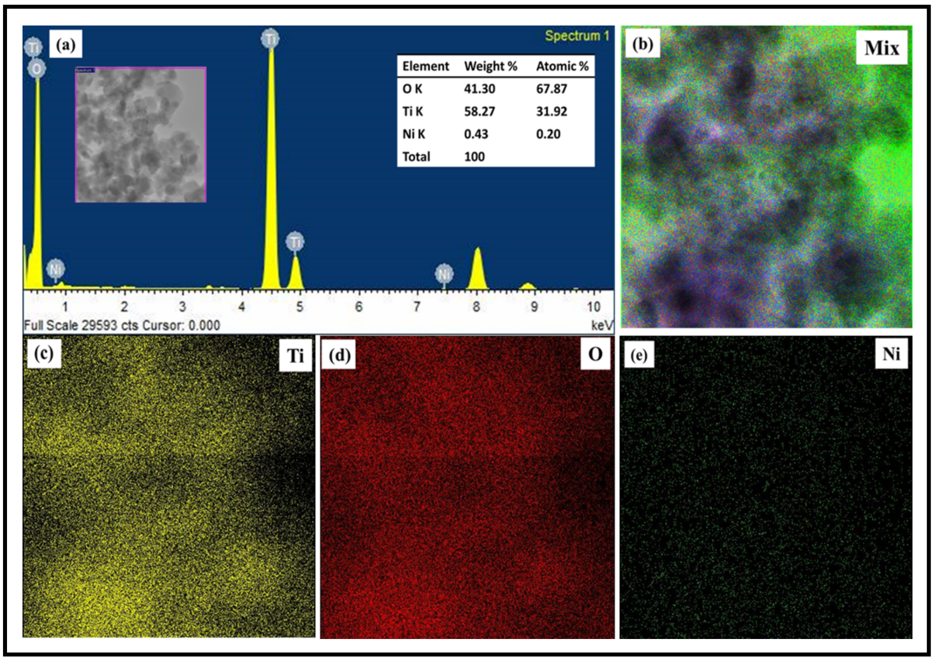

Fig. S5 FETEM-STEM-EDS elemental mapping images of 0.5% Ni/TiO_2 nanopowders: (a) EDS spectra (Inset: electron image of selected region and its quantitative EDS data) and its elemental mapping images for (b) their elemental mix (c) Ti, (d) O and (e) Ni.

FETEM images of 0.1%Ni/TiO_2 nanopowder photocatalyst after recycling

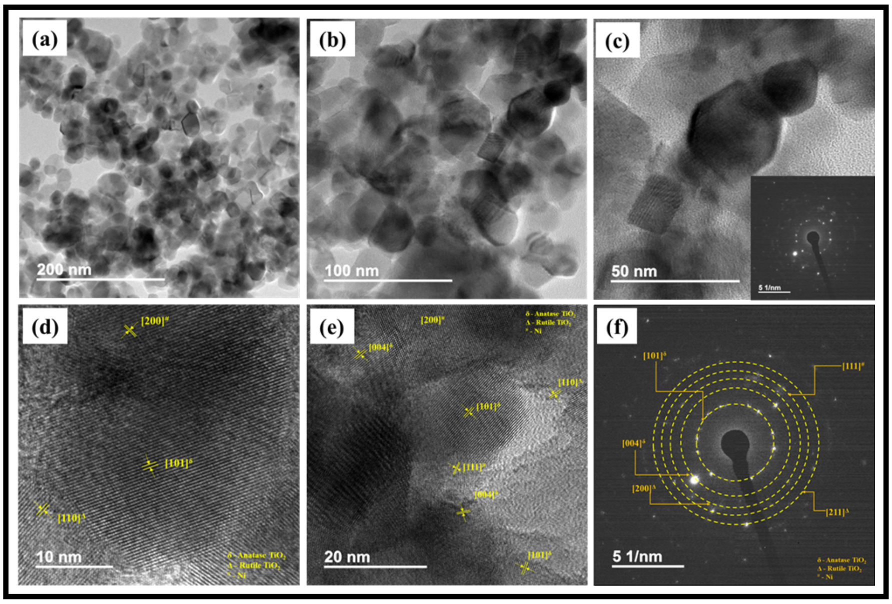

Fig. S6 FETEM images of recycled 0.1%Ni/TiO_2 nanopowder photocatalyst.

Section S1: Apparent Quantum Efficiency (AQE)

The apparent quantum efficiency for a particular wavelength is calculated using equation (I)(57),(77)

$$Apparent\ Quantum\ Efficiency = \frac{(number\ of\ photo\ Hydrogen\ molecule)\ x\ 2}{number\ of\ incident\ photons} \qquad (I)$$

The value of number of incident photons was obtained using the parameters of wavelength and intensity of incident light as well as irradiation area as given below:

$$Number\ of\ incident\ photons\ per\ second = \frac{Light\ intensity\ x\ irradiation\ area\ x\ lightwavelength}{Planck's\ constant\ x\ light\ speed} \qquad (II)$$