Supporting Information

Recent Advances and Strategies Applied to Tailor Energy levels, Active Sites and Electron Mobility in Titania and its Doped/Composite Analogues for Hydrogen Evolution in Sunlight

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Table S1 Different methods of hydrogen generation.[1]

H_2 production process	Advantages	Drawback
Steam reforming of methane	Least expensive (48 % of world hydrogen produced by this route)	Generation of greenhouse gases.
Gasification of coal	Only competitive with methane reforming where natural gas is expensive.	Generation of CO_2; Less efficient
Gasoline and methanol reforming	Not mentioned. Requirement of pure oxygen;	Generation of more CO_2 than steam reforming.
From biomass	Less expensive raw materials.	Little contribution (4%) towards world H2 production.
Electrolysis	Cost effective for production of extremely pure hydrogen in small amount.	Electrolysis is very much expensive at large scale.
Solar and wind power based electrolysis	Less expensive than conventional electrolysis	Still in developing stage

Table S2 Crystal phase/structure dependent H2 evolution of TiO_2 photocatalyst

Photocatalyst	**Crystal structure**	**Band gap (eV)**	**Co-catalyst**	**Light source**	**Reactant solution**	**Sacrificial agents**	**H_2 evolution**	**Year**	**Ref**
TiO_2	Anatase: Rutile (87:13)	3.24	No co-catalyst used	415W Philips CLEO florescent tubes	Water	Methanol	10.74 µmol/h	2013	[2]
Cu-doped TiO_2 film	Anatase	Not mentioned	No co-catalyst used	300-W Xe lamp	Water	Methanol	810 µmol/h/g	2014	[3]
TiO_2 nanofiber	Anatase and Rutile	3.0	Pt	350 W Xe arc lamp	Water	Methanol	324 µmol/g/h	2014	[4]
Pt/TiO_2	Anatase/Rutile	3.1	No co-catalyst used	100 Watt ultraviolet lamp (H-144GC-100, Sylvania par 38)	Water	Ethanol	2000 µmol/m^2	2015	[5]
Ti^{3+}-doped TiO_2 (Sheets)	Anatase	3	Pt	300 W xenon lamp	Water	Methanol	46 µmol/g	2013	[6]
Au/$HTiNbO_5$	Orthorhombic	2.1	No co-catalyst used	400 W halide lamp	Water	Methanol	100 µmol/h	2014	[7]

Table S3 H_2 evolution efficiency of the porous structured TiO_2 composites

Photocatalyst	Porosity	Crystal structure	Band gap (eV)	Co-catalyst	Light source	Reactant solution	Sacrificial agents	H_2 evolution	Year	Ref
N-doped mesoporous TiO_2	**Mesoporous**	Anatase	2.4	No co-catalyst used	450W Xe lamp	Water	Methanol	14.9 µmol/g/h	2012	[8]
Hierarchical and fibrous meso-macroporous N-doped TiO_2	**Meso-macroporous**	Anatase	2.3	Pt	125 W Hg visible lamp	Water	Methanol	380 µmol/g/h	2013	[9]
Mesoporous TiO_2-SiO_2	**Mesoporous**	Anatase	3.2	No co-catalyst used	300 W Xenon arc lamp	Water	Methanol	0.08805 mmol/h	2014	[10]
Three-dimensionally ordered macroporous N-dopedTiO_2	**Macroporous**	Anatase	~2.4	No co-catalyst used	300 W xenon lamp	Water	0.25 M Na_2S and 0.35 M Na_2SO_3,	29 µmol/g/h	2014	[11]
g-C_3N_4 nanosheets hybridized N-TiO_2 nanofibers	**Mesoporous**	Anatase	2.8	Pt	300 W xenon arc lamp	Water	Methanol	8931 µmol/g/h	2014	[12]

Table S4 Particle shape/morphology dependent H_2 evolution efficiency of TiO_2 photocatalyst.

Photocatalyst	**Morphology**	**Crystal structure**	**Band gap (eV)**	**Co-catalyst**	**Light source**	**Reactant solution**	**Sacrificial agents**	**H_2 evolution**	**Year**	**Ref**
Pt@CuO/TiO_2	**Nanorods and Nanosheets**	Anatase	2.9	Pt	500 W high-pressure Xe lamp	Water	Methanol	200 µL/h	2014	[13]
Pt-TiO_2 nanotube arrays	**Nanotube arrays**	Not mentioned	3.2	No co-catalyst used	300 W Xe lamp	Water	Na_2SO_4 & ethylene Glycol	135 µmol/h	2014	[14]
Titanium phosphate	**Layered hexagonal shape**	Anatase	3.2	No co-catalyst used	300 W Xenon lamp	Water	Methanol	286 µmol/h	2014	[15]
Hierarchical nanstructured TiO_2	**3D urchin**	Anatase	3.17	Pt	300 W Xe lamp	Water	Methanol	1310 µmol/h/g	2014	[16]

Table S5 H_2 evolution efficiency of the doped-TiO_2 photocatalyst

Photocatalyst	Dopant	Crystal structure	Band gap (eV)	Co-catalyst	Light source	Reactant solution	Sacrificial agents	H_2 evolution	Year	Ref
Nitrogen doped TiO_2	N	Anatase	3.08	-	400 W medium pressure halide lamp UV / 500 W halogen Lamp-Visible	Water	Methanol	4386 µmol/g/h 185 µmol/g/h	2012	[17]
C,N-TiO_2	C, N	Anatase	2.92	-	Xe-lamp	Water	Methanol	81.8 µmol/h	2013	[18]
Carbon coated N-TiO_2 nanotube films	C, N	Rutile and Anatase	2	-	500 W high-pressure ball-shaped Xe lamp	Water	Na_2S (0.1 M) and Na_2SO_3 (0.02 M)	400 µmol/g/h	2012	[19]
TiO_2 functionalized N- graphene (NGR)	N and graphene	Anatase	-	-	150 W GY-10 xenon lamp	Water	triethanol amine	13.3 µmol/h	2014	[20]
N-TiO_2/graphene oxide	N and graphene	Anatase	2.69	-	500Whigh-pressure Hg lamp	Water	Methanol	250 µmol/h	2012	[21]
Self doped TiO_2–graphene nanoplatelets	Ti^{3+} and graphene	Anatase	-	Pd	day-light fluorescent lamps	Water	Methanol	288 µmol/h	2014	[22]
N-TiO_2	N	Anatase	2.9	Pd	day-light fluorescent lamps (Wipro, 36 W each)	Water	Methanol	12 µmol/2 h/50 mg	2012	[23]
N-TiO_2	N	Anatase	2.4	Pt	Xe lamp (300 W)	Water	Na_2SO_3	310 µmol/h	2006	[24]

S- and C-codoped TiO_2	S, C	Anatase	3.1	Pt	400 W high pressure Hg lamp	Water	Methanol	70000 µmol/h	2013	[25]
TiO_2 was co-doped with P and N	P,N	Rutile	2.0	-	300-W Xe lamp	Water	-	11.2 µmol/g/h	2014	[26]
Pt-N $La_2Ti_2O_7$	Pt, N	-	1.56	-	Luzchem LZC-UVA, centered at 360 nm	Deionize d water	-	200 µmol/h	2013	[27]
Indium and nitrogen co-doped TiO_2	In, N	Anatase	3.0	-	Ordinary day light fluorescent lamps (Wipro, 36W	Water	Methanol	13.9 µmol/h	2010	[28]
Ga-N co-doped TiO_2	Ga, N	Anatase	3	-	125 W mercury lamp with a 400 nm cut-off filter	Water	Methanol	5 µmol/g/h	2012	[29]
Ce/N-Codoped TiO_2	Ce, N	Anatase	2.52	-	500W medium pressure mercury lamp	Water	Methanol	100 µmol/h	2010	[30]

Table S6 H_2 evolution of the TiO_2 composite photocatalyst

Photocatalyst	Composite material	Crystal structure	Band gap (eV)	Co-catalyst	Light source	Reactant solution	Sacrificial agents	H_2 evolution	Ref
Eosin -sensitized CuO incorporated TiO_2	Eosin dye and CuO	-	-	-	200 W halogen lamp	Water	diethanolamine	10.56 µmol/h	[31]
CuO/TiO_2	CuO	Anatase: Rutile	2.61	-	SB-100P/F lamp (100 W, 365 nm)	Water	Ethanol	21300 µmol/h	[32]
$Cu(OH)_2/TiO_2$ nanotube arrays	$Cu(OH)_2$	Anatase	3.2	-	PLS-SXE300UV Xe lamp	Water	ethylene glycol	6.5 µmol/h/cm^{-2}	[33]
TiO_2/CuO composite nanofibers	CuO	Anatase	2.6	-	400 W Hg lamp and 360 W Na lamp as the UV–vis light source	Water	Methanol	5500 µmol/h	[34]
ZnO/TiO_2 composite	ZnO	Anatase/Crystalline /Amorphous	-	-	300 W xenon lamp	Water	Methanol	865 µmol/h	[35]
Ta_2O_5-TiO_2 / S doped TiO_2 / S doped Ta_2O_5	Ta_2O_5, S	Anatase	3.09 / 2.9 / 2.9	Pt	visible and UV irradiation (>300 nm) applying four 300W Vitalux bulbs	Water	Methanol	0.14 mmol / 4.55 mmol / 0.24mmol	[36]
Core-shell $CuS@TiO_2$	CuS	Anatase	CuS 1.35 / TiO2 3.19	-	UV-lamps (18Wcm−2)	Water	Methanol	1.2 mmol/h	[37]
Copper oxide incorporated indium Titanium oxide	Cu_2O, In_2O_3	cubic In_2O_3 and Anatase TiO_2 structure	2.01	-	500 W tungsten halogen lamp	Water	Methanol	2149 µmol/g/h	[38]

Pt-Sr($Zr_{1-x}Y_x$)$O_{3-\delta}$-TiO_2 (Pt-SZYT)	Pt,Sr, Zr, Y	Anatase, Rutile	-	-	250 W xenon lamp	Water	oxalic acid	1.68 mmol/h	[39]
Ni/NiO/N-TiO_{2-x}	Ni, NiO,N	Anatase	~3.0-2.4	-	110-W high-pressure sodium lamp with UV cutoff filter (l > 420 nm)	Water	Methanol	1210 µmol/g/h	[40]
Ti^{3+}-doped TiO_2 (Sheets)	Ti^{3+}	Anatase	3	Pt	300 W xenon lamp	Water	Methanol	46 µmol/g	[41]
CdS decorated Au@TiO_2 core-shell	CdS, Au	Anatase	-	-	300-W Xenon lamp	Water	Na_2S and Na_2SO_3	3.94 µmol/h	[42]
CdS/TiO_2	CdS	Anatase	2.2	-	Hg-Arc lamp (500 W)	Water	Na_2S and Na_2SO_3	422.4 µmol/h	[43]
CdS-trititanate nanotube	CdS	Hexagonal	2.4	-	300 W Xenon lamp	Water	Ethanol	10 µmol/h	[44]
TiO_2/Fe_2O_3	Fe_2O_3	-	-	Pt	300 W xenon lamp	Water	Methanol	1.5 mmol/h	[45]
Nanocomposite of MWCNTs and TiO_2 nanoparticles	MWCNTs	-	~ 3	-	500 W Hg-lamp	Water	triethanolamine	8 mmol/g/h	[46]
Carbon/TiO_2/carbon nanotubes	Carbon	Anatase	~ 0.88	-	Solar simulator (Newport, 94023 A)	Water	Ethanol	37.6 mmol/h/g	[47]
TiO_2-RGO	RGO	Anatase	2.9	-	300 W xenon/mercury lamp	Water	Ethanol	1.125 mmol/g/h	[48]

CuO/TiO_2-GR	CuO, GR	Anatase: Rutile	2.8	-	500 W Xe arc lamp	Water	Methanol	2905.60 µmol/h	[49]
Pt/TiO_2/activated carbon	Pt, activated carbon	Anatase	3.1	-	250 W Hg lamp	Water	Methanol	650 µmol/h	[50]
Three-dimensionally ordered macroporous (3DOM) N-doped TiO_2	N	Anatase	~ 2.4	-	300 W xenon lamp	Water	0.25 M Na_2S and 0.35 M Na_2SO_3	29 µmol/g/h	[51]
CuO/Carbon Fiber/TiO_2	CuO, Carbon Fiber	80:20 A:R	2.85	-	Xenon lamp	Water	Ethanol	2000 µmol/h	[52]

Table S7 Noble metal supported TiO_2 photocatalyst and their hydrogen evolution

Photocatalyst	**Crystal structure**	**Band gap (eV)**	**Co-catalyst**	**Light source**	**Reactant solution**	**Sacrificial agents**	**H_2 evolution**	**Year**	**Ref**
Au/TiO_2	-	3.2	-	UV-PC mercury lamp	**Water**	Methanol	1866 μmol/h	2013	[53]
Au/TiO_2	Anatase	2.29	-	Solar simulator (Thermo Oriel 1000 W)	**Water**	Methanol	45 μmol/h	2013	[54]
Pt/TiO_2	Anatase and Rutile	3.19	-	150 W mercury lamp	**Water**	Methanol	220 μmol/h	2014	[55]
Pt/TiO_2	Anatase/ Rutile	3.1	-	350 W high-pressure mercury lamp	**Water**	Methanol	2100 μmol/h	2012	[56]
Pt/TiO_2	Anatase	-	-	300W Xe lamp	**Water**	Methanol	739.94 μmol/h	2010	[57]
Pt/TiO_2	Rutile	3.0	-	300 W xenon lamp	**Water**	-	33 μmol/h	2014	[58]

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