Coupled optical absorption, charge carrier separation, and surface electrochemistry in surface disordered/hydrogenated TiO₂ for enhanced PEC water splitting reaction

Dilip Kumar Behara¹, Ashok Kumar Ummireddi¹, Vidyasagar Aragonda¹, Prashant Kumar

Gupta¹, Raj Ganesh S Pala^{1#*} and Sri Sivakumar^{1#†*}

¹Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, UP-208016, India

[#]Material Science Programme, Indian Institute of Technology Kanpur, UP-208016, India

[†]Centre for Environmental Science & Engineering, Thematic Unit of Excellence on Soft Nanofabrication, Indian Institute of Technology Kanpur, Kanpur, UP-208016, India

*Corresponding Authors: <u>rpala@iitk.ac.in</u>, <u>srisiva@iitk.ac.in</u>

Supplementary information

1.1 Materials and Methods

Titanium(IV) iso-propoxide (97%), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC.HCl, 98.0%), 4-pentynoic acid (95.0%), 3-bromopropyltrichlorosilane (96.0%), 3chloro-1-propanethiol (98.0%), 1,8-nonadiyne (98.0%), 3-aminopropyltriethoxysilane (APTES, 98.0%) were purchased from Sigma Aldrich and used without further purification. Tri sodium citrate and thiourea were purchased from Fisher Scientific and used without any further purification. Sodium borohydride (95.0%), copper sulfate pentahydrate (CuSO₄.5H₂O, 95.0%), ascorbic acid, dichloromethane (DCM, 99.5%), dimethyl sulfoxide (DMSO, 99.5%), toluene, methanol, acetonitrile and tetra hydro furan (THF, 99.5%), hydrogen peroxide (H₂O₂), isopropanol and absolute ethanol were purchased from Merck's chemicals. Fluorine doped titanium oxide (FTO) electrodes, tetrabutylammonium tetrafluroborate (TBA BF4, 99.8%) were purchased from Sinsil International and Sigma Aldrich respectively. Nafion solution (5%) and sodium azide (NaN₃) were purchased from DuPont and LOBA Chemie India respectively. Deionized water from Millipore water systems (Resistivity 18.2 M Ω .cm) was used in all experiments.

1.2 Azide surface functionalization of undoped/doped/hydrogenated doped TiO₂ nanoparticles

3-bromopropyltrichlorosilane (0.7 ml) dispersed in 1.3 ml of toluene was added to anatase TiO_2 (200 mg) in toluene (55 ml) and stirred for 18 h at 80 °C under inert atmosphere to yield bromofunctionalized nanoparticles. Bromo-functionalized anatase TiO_2 nanoparticles were centrifuged and washed thrice with toluene to remove unreacted silane followed by drying at 80 °C for 12 h. Sodium azide (0.32 g) dispersed in 16 ml of DMSO was added to 0.8 g of bromo-functionalized anatase TiO_2 nanoparticles under inert atmosphere and stirred at 80 °C for 18 h, which replaces the bromine group present on anatase TiO_2 nanoparticles with azide group of sodium azide. Finally, azide functionalized nanoparticles were centrifuged, washed with ethanol/water and dried at 80 °C overnight for further usage.

1.3 Alkyne functionalization of stainless steel (SS) substrate

1.3.1 Pre-treatment of substrates

SS substrates were cut into required size (1 cm \times 2 cm) and sonicated for 30 min in acetone followed by methanol. Cleaned substrates were washed with DI water and dried at room temperature for further usage.

1.3.2 Alkyne functionalization of SS substrate

Cleaned SS foils were treated with piranha solution to get hydroxyl group on to the surface. Piranha treated SS foils were immersed in 1% APTES solution in ethanol for 12 h to form a monolayer of amine group on the surface¹. Amino-functionalized SS substrates were washed with DI water and immersed in 1M PBS buffer solution containing 50 mM 4-pentynoic acid and 100 mM EDC for 7 h to form amide bond between amine and carboxylic group. Finally, alkyne functionalized SS substrates were washed with ethanol/water to remove any trace amounts of unreacted reactants and kept in desiccator for further usage.

1.4 Fabrication of electrodes

Alkyne functionalized SS substrates were immersed in 3.5 wt% solution of azide terminated undoped/doped/hydrogenated doped TiO_2 nanostructures for 5 minutes. After 5 minutes, click solution (mixture of 1: 2 v/v ratios of CuSO₄.5H₂O and L-ascorbic acid) is added to above mixture and left for 12 h for click reaction. Ascorbic acid reduces the Cu(II) to Cu(I) which catalyzes click reaction between alkyne and azide moieties. The substrates were washed with DI water thrice and sonicated in water for 10 min to remove any physically attached nanoparticles. The fabricated electrodes were dried in room temperature for 5 minutes kept in desiccator for further electro/photoelectrochemical experiments.

For other electrochemical experiments like EIS measurements to determine charge carrier separation and charge space capacity versus potential measurements (Mott-Schottky plot), electrodes were fabricated in different way. In this procedure, 10 μ g of nanoparticles were dispersed in 0.5 mL of isopropanol, and two drops of nafion (5%) solution was added to the solution and sonication for 30 min. Uniform film of nanoparticles on FTO electrodes were fabricated by adding the above solution while

drying the FTO substrates at 60 °C.

1.5 Physicochemical characterization

Field Emission Scanning Electron Microscopy (FESEM-SUPRA 400VP Gemini, Zeiss, Germany) and Transmission Electron Microscopy (TEM; Tecnai G², U.S.A) has been used to investigate particle morphology, phase and size. X-ray Diffraction (XRD, X'Pert Pro, PAN Analytical, Netherlands, X-ray system with Cu K_{α} radiation) has been performed to identify crystal phases. Energy Dispersive X-ray Spectroscopy (EDX, Oxford instruments, SUPRA 40 VO Gemini, Zeiss, Germany), X-ray Fluorescence Spectroscopy (XRF, Rigaku ZSX Primus II), and X-ray photoelectron microscopy with auger electron spectroscopy (AES) module (PHI 5000 Versa Prob II, FEI Inc.) have been used to investigate composition of the materials under consideration. Optical spectra have been obtained using UV-Visible absorption spectra (Thermo Scientific Multiscan spectrum). Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer Spectrometer, U.S.A) and Raman spectral analysis (WiTec, Germany) using 532 nm wavelength of laser light have been performed to investigate surface functional groups and bond nature in the obtained samples. To determine the porosity and surface area BET surface area analyzer (Quanta chrome Autosorb 1C) is used. Focused Ion Beam (FIB, FEI Nova 600 Nanolab workstation (FIB/SEM) is employed for sputtering the sample to remove few atomic layers. Potentiostat (Autolab 302N, Metrohm India Ltd, Netherlands) and solar simulator (ORIEL, Sol3A, Newport suppliers, Netherlands) with AM 1.5G filter has been used for electro/photoelectrochemical measurements of prepared samples.

1.5.1 Focused Ion Beam (FIB) sputtering

Nova 600 Nanolab workstation (SEM/FIB) is used for sputtering hydrogenated samples clicked on SS substrate. This work station is equipped with a field emission gallium (Ga) ion source energies ranging from 2 kV to 30 kV, high resolution (up to 7 nm) ion optics, milling and gas chemistry functionalities along with EDX facility. The typical material removal rate is 1 μ m³/s. The ion beam voltage and current were set to 30 kV and 20 nA, respectively. The ion beam flux was changed from 0.61 to 18.82 ions per cm² per second. The dwell time of the ion beam at each spot or location is ranged from 1 μ s to 30 μ s. The ion beam incidence angle was changed from 0° to 52°.

1.5.2 Band edge calculations via XPS measurements

In order to find the VB edge shift after doping/hydrogenation, XPS measurements were carried out at lower binding energies (0 to 10 eV) for two control samples (anatase TiO₂, and hydrogenated N-S co-doped TiO₂@800°C/24h). An abrupt change in slope of the curve can be considered as an indicative of valence band edge maximum.

1.6 Electrochemical (EC) measurements

Charge space capacity vs. potential measurements (Mott-Schottky)

Since, Mott-Schottky plots give the information about the nature of charge carriers (donor density) as well as the change in the concentration of charge carriers in the semiconductor. The EIS measurements were carried out in 0.1M NaOH (13.6 pH) solution at DC potentials from -0.4 V to -1.0 V (step size of -0.05 V) with AC amplitude of 10 mV.

1.7 Photoelectrochemical (PEC) measurements

1.7.1 Current (I) vs. potential (V) measurements

The fabricated electrode, a platinum mesh (~1 cm²) and Ag/AgCl electrode were used as working, counter and reference electrodes respectively. The cells were illuminated through the glass substrate and illumination was provided by a solar simulator (ORIEL, Sol3A, Newport suppliers, Netherlands) with AM 1.5G filter with power intensity of 100 mW/cm². The cell was made up of quartz glass (Metrohm India Ltd) and 0.1M NaOH (pH 13.6) was used as an electrolyte. All the electro/photoelectrochemical measurements were done in 3-probe (half-cell studies) and 2-probe modes (full cell studies) and reported with reference to Ag/AgCl or RHE scale (Reversible Hydrogen Electrode). The conversion from Ag/AgCl scale to RHE scale is given below:

$$V_{RHE} = V_{Ag/AgCl} + 0.197 + 0.059 \text{ x pH} \dots (1)$$

1.7.2 Electrochemical Impedance spectroscopy (EIS) measurements

Electrochemical impedance spectroscopy (EIS) measurements were done in 0.1M NaOH (pH 13.6) with the amplitude of 10 mV of AC signal with a frequency range from 10 kHz to 0.1 Hz at different DC potential scans.

1.8 UV-Vis absorption measurements

UV–Vis spectra of diffuse reflectance (DRS) were measured by means of Agilent Technologies Cary 5000 UV–VIS–NIR spectrophotometer in DRA accessory with inbuilt spherical integrator facility with a spectral resolution of 1 nm. All samples are measured in diffuse reflectance mode and the corresponding absorbance (and reflectance) data were used for band-gap analysis of samples. **Table S1** Energy Dispersive X-ray (EDAX) analysis of doped TiO_2 samples

Sample	Ti (wt%)	O (wt%)	N (wt%)	S (wt%)
N doped TiO ₂	40.90	58.34	0.76	
S doped TiO ₂	27.46	68.57		3.96
N-S co-doped TiO ₂	40.27	53.01	4.01	2.71

S. No	Peak observed	Assigned to	Reference
	at wavenumber, cm ⁻¹		
1	~630	Ti-O-Ti	3
2	~3000-3600 and 1630	stretching and bending vibrations of	4
		hydroxyl (OH) groups	
3	~1138 and 1048	Ti-S	5
4	~1222	Ti-N	6
5	~3645, 3670, and 3685	Tetrahedral coordinated vacancies	6

Table S2 FTIR spectra data of undoped/doped/hydrogenated TiO_2 nanostructures

Table S3 Consolidated band-gap, and % applied bias to photo conversion efficiency (ABPE) data of	of
undoped, doped and hydrogenated doped TiO_2 samples	

S. No		Band gap, calculated, eV	% ABPE @ 0.628 V
	Sample name		applied bias
1		3.66	0.048
	Amorphous TiO ₂		
2		3.46	0.096
	Crystalline TiO ₂		
3	Hydrogenated TiO ₂	3.23	0.145
	@500°C/24h		
4		3.38	0.120
	N-doped TiO ₂		
5	Hydrogenated N doped TiO ₂	3.26	0.157
	@500°C/24h		
6	Hydrogenated N doped TiO ₂	3.14	0.181
	(a)700°C/24h		
7		3.37	0.101
	S-doped TiO ₂		
8	Hydrogenated S doped T_1O_2		0.111
	(a)500°C/24h	2.00	0.1.60
9		3.09	0.169
	N-S co-doped TiO ₂	2.10	
10	Hydrogenated N-S co-doped	3.19	0.205
	TiO ₂ @500°C/24h		0.205
11		3 12	
11	Hydrogenated N-S co-doped		0.235
	TiO ₂ @650°C/24h		
12	Hydrogenated N-S co-doped	2.95	0.270
	$\frac{1}{10000000000000000000000000000000000$		0.379
	110 ₂ (<i>u</i>)800 ⁺ C/24h	2.04	
13	Hydrogenated N-S co-doped	2.94	0.307
	TiO ₂ @800°C/72h		

Table S4 Consolidated PEC data (i.e. dark and photo current density at different applied bias potentials) of all TiO₂ samples (2-probe measurements)

S. No	Sample Name	Current @0.628 applied mA/cm ²	density V bias,	Current density @1.23 V applied bias, mA/cm ²		Current density @1.565 V applied bias, mA/cm ²		Current density @1.8 V applied bias, mA/cm ²	
		Under dark	Under light	Under dark	Under light	Under dark	Under light	Under dark	Under light
1	Crystalline TiO ₂	0.06	0.22	0.078	0.85	1.9	2.9	4	5.3
2	Hydrogenated								
	TiO ₂ @500°C/24h	0.08	0.34	0.09	0.89	2.9	4.1	4.4	6.1
3	N-doped TiO ₂	0.05	0.25	0.07	0.9	3.1	4.4	4.1	6
4	Hydrogenated N doped TiO ₂ @500°C/24h	0.08	0.36	0.09	1.1	3.2	4.5	4.2	7.3
5	Hydrogenated N doped TiO ₂ $@700^{\circ}C/24h$	0.07	0.37	0.09	11	3.8	49	5.1	79
6	S-doped TiO ₂	0.192	0.36	0.54	1.1	3.1	4.3	4.2	7
7	Hydrogenated S doped TiO ₂ @500°C/24h	0.06	0.245	0.08	0.9	3.15	4.35	4.3	7.1
8	N-S co-doped TiO ₂	0.07	0.35	0.085	0.9	3.4	4.5	3.7	5.7
9	Hydrogenated N-S co-doped TiO ₂ @500°C/24h	0.06	0.4	0.08	0.98	3.9	5	5.2	8.1
10	Hydrogenated N-S co-doped TiO ₂ @650°C/24h	0.09	0.49	0.098	1.3	4.2	5.3	5.5	8.2
11	Hydrogenated N-S co-doped TiO ₂ @800°C/24h	0.21	0.84	0.48	1.7	4.7	6.3	6.5	9.9
12	Hydrogenated N-S co-doped TiO ₂ @800°C/72h	0.08	0.59	0.095	1.28	4.4	5.8	5.8	9

S. No	Sample Name	Current densi	Current density		
		@1.2 V vs. A	g/AgCl		
		(2.2 V vs. RH	E)		
		applied potent	tial, mA/cm ²		
		Under dark	Under light		
1	Crystalline TiO ₂	22.4	25.4		
2	Hydrogenated TiO ₂	23.6	27.9		
	@500°C/24h				
3	N-doped TiO ₂	23.1	27		
4	Hydrogenated N doped TiO ₂ @500°C/24h	24.3	28.6		
5	Hydrogenated N doped TiO ₂ @700°C/24h	24.5	28.9		
6	S-doped TiO ₂	22	24.6		
7	Hydrogenated S doped TiO ₂	23	26.5		
	@500°C/24h				
8	N-S co-doped TiO ₂	23.4	27.5		
9	Hydrogenated N-S co-doped	24.9	29.1		
	TiO ₂ @500°C/24h				
10	Hydrogenated N-S co-doped	25.1	30.4		
	TiO ₂ @650°C/24h				
11	Hydrogenated N-S co-doped	25.6	31.4		
	TiO ₂ @800°C/24h				
12	Hydrogenated N-S co-doped	25.3	30.5		
	TiO ₂ @800°C/72h				

Table S5 Consolidated cyclic voltammetry (CV) data of all TiO₂ samples (3-probe measurements)

Table S6a Double layer capacitance data of hydrogenated N-S co-doped TiO_2@800°C/24h

from fitted EIS circuit

S. No	Applied Potential,	Double layer	Double layer
	V vs. RHE	capacitance	capacitance
		$(C_{dl}), \mu F, dark$	$(C_{dl}), \mu F, light$
1	1.2	26.57	26.10
2	1.4	27.15	142.61
3	1.6	137.46	116.37
4	1.8	912.57	909.99
5	2.0	622.24	514.24
6	2.2	779.25	92.28

Table S6b: Film resistance (R_f) , charge transfer resistance (R_{ct}) , and capacitance (C_{dl}) data of anatase TiO₂, hydrogenated N-S co-doped TiO₂@800°C/24h, and hydrogenated N-S co-doped TiO₂@800°C/72h under light conditions calculated via EIS measurements

S.	Potential	tential Film resistance (\mathbf{R}_{f}), Ω			Charge transfer resistance (R_{ct}), Ω			Сарасіtance (С _{dl}), µF		
No	(V vs. RHE)	Anatase TiO ₂	Hydrogenat ed N-S co- doped TiO ₂ @800°C /24h	Hydrogen ated N-S co-doped TiO ₂ @800° C/72h	Anatase TiO ₂	Hydrogena ted N-S co- doped TiO ₂ @800° C/24h	Hydrogen ated N-S co-doped TiO ₂ @800° C/72h	Anatase TiO ₂	Hydrogen ated N-S co-doped TiO ₂ @800° C/24h	Hydrogen ated N-S co-doped TiO ₂ @800° C/72h
1	1.5	3840	1080	3950	73300	28000	137000	21.7	9.21	7.16
2	1.6	2720	530	2850	35400	3540	32300	21.2	10	7.27
3	1.7	919	205	754	4120	502	1680	22.6	11.7	7.87
4	1.8	247	98.4	325	603	224	532	24.9	12.2	8.95

Table S7 XPS data of FIB sputtered and unsputtered portions of hydrogenated N doped TiO₂ $@500^{\circ}C/24h$ sample

S. No	XPS peaks information	Binding energy, eV				
		Unsputtered portion	FIB sputtered portion			
1	Addition of new peaks	No peak	42.42, 69.65, 112.7,			
			154.39, 176.89, 200.74			
			216.6, 237.55, 256.81,			
			266.38, 396.1, 664.59			
2	Shift in peaks	21.725, 27.95	20.03, 29.61, 61.57,			
		63.16, 315.94	317.52, 973.81			
		975.11				
3	Disappearance	60.05, 107.85, 554.4,	No peak			
	of original peaks	938.54, 954.29, 1085				

Table S8 Double layer capacitance data of hydrogenated N doped $TiO_2@500^{\circ}C/24h$ sample calculatedfrom differential capacitance measurements (through CV) for FIB sputtered and unsputtered portions at1.1 and 1.2 V (vs. RHE) applied potential

S. No	Applied Potential, V	Double layer capacitance (C_{dl}), μF		
	vs. RHE	unsputtered portion	FIB sputtered portion	
1	1.1	12.9	10.4	
2	1.2	28.36	17.28	



Fig. S1 (a) Hydrogenation chamber used for hydrogenation; and (b-n) digital images of undoped/doped/hydrogenated doped TiO_2 samples.



Fig. S2 XRD of (a) un-hydrogenated doped, un-doped TiO₂ samples; (b) hydrogenated un-doped and doped TiO₂ samples; and (c) hydrogenated N-S co-doped TiO₂@700°C/24h, hydrogenated N-S co-doped TiO₂@800°C/24h, hydrogenated N-S co-doped TiO₂@800°C/72h samples showing anatase and rutile phases.



Fig. S3 SEM images of (a) amorphous TiO₂; (b) calcined TiO₂; (c) N doped TiO₂; (d) S- doped TiO₂; (e) N-S co-doped TiO₂; and (f) EDAX of figure **e**.



Fig. S4 SEM images of TiO₂ samples hydrogenated at 500 °C for 24 h (a) crystalline TiO₂; (b) N doped TiO₂; (c) S doped TiO₂; and (d) N doped TiO₂ clicked on SS substrate.



Fig. S5 TEM images of (a) hydrogenated TiO₂@500°C/24h; (c) hydrogenated N doped TiO₂@500°C/24h;
(b) SAED pattern corresponds to figure a; and (d) SAED pattern corresponds to figure c.



Fig. S6 Raman spectra of (a) un-hydrogenated TiO_2 samples; (b) hydrogenated TiO_2 samples; broadening of Raman peaks before and after hydrogenation of (c) N doped TiO_2 ; and (d) N-S co-doped TiO_2 .



Fig. S7 FTIR spectra of (a) un-hydrogenated TiO_2 samples; (b) hydrogenated N-S doped and functionalized TiO_2 samples; FTIR spectra of crystalline TiO_2 and N-S co-doped TiO_2 ; (c) whole wavenumber range (0 to 4000 cm⁻¹); and (d) wavenumber range from 1000 cm⁻¹ to 1500 cm⁻¹.



Fig. S8 (a) FTIR spectra showing tetrahedral coordinated vacancies in hydrogenated S doped $TiO_2@500^{\circ}C/24h$ sample; (b) alkyne functionalized stainless steel substrate; and (c) contact angle measurements of alkyne functionalized SS substrate.



Fig. S9 UV-Vis spectra of (a) N-S co-doped TiO₂ sample hydrogenated at different temperature (500 °C, 650 °C and 800 °C) for 24 h and 72 h; (c) undoped and N doped TiO₂ samples hydrogenated at 500 °C and 700 °C for 24 h; (e) unhydrogenated doped/undoped TiO₂ nanostructures; (b) tauc plot corresponds to figure **a**; (d) tauc plot corresponds to figure **c**; and (f) tauc plot corresponds to figure **e**.



Fig. S10 EPR spectra of (a) crystalline (un-hydrogenated) TiO_2), (b) hydrogenated N-S co-doped $TiO_2@800^{\circ}C/24h$, c) N-S co-doped TiO_2 , d) enlarged part of fig c, e) hydrogenated N-S co-doped $TiO_2@500^{\circ}C/24h$, and f) hydrogenated N-S co-doped $TiO_2@650^{\circ}C/24h$ sample.



Fig. S11 Mott-Schottky plot for anatase TiO_2 , hydrogenated N-S co-doped $TiO_2@800^{\circ}C/24h$, and hydrogenated N-S co-doped $TiO_2@800^{\circ}C/72h$.



Fig. S12 XPS spectra of a) survey scan of hydrogenated N-S co-doped $TiO_2@650°C/24h$, b) Ti 2p spectra, c) O 1s spectra, and d) survey scan of focused ion beam (FIB) sputtered, unsputtered hydrogenated N-S co-doped $TiO_2@500°C/24h$ sample.



Fig. S13 Valence band XPS spectra of anatase TiO₂ and hydrogenated N-S co-doped TiO₂@800°C/24h.



Fig. S14 Current vs. applied bias plots of (a) amorphous TiO₂; (b) crystalline TiO₂; (c) N doped TiO₂; and

(d) S doped TiO₂; two-probe measurements performed in 0.1M NaOH solution.



Fig. S15 Current vs. applied bias plots of (a) hydrogenated $TiO_2@500^{\circ}C/24h$; (b) hydrogenated N doped $TiO_2@500^{\circ}C/24h$; (c) hydrogenated N doped $TiO_2@700^{\circ}C/24h$; and (d) hydrogenated S doped $TiO_2@500^{\circ}C/24h$; two-probe measurements performed in 0.1M NaOH solution.



Fig. S16 Applied bias photon to current conversion efficiency (ABPE) of (a) doped un-hydrogenated samples; and (b) N doped and S doped TiO_2 samples hydrogenated at 500 °C and 700 °C for 24 h time period.



Fig. S17 Electrochemical Impedance Spectroscopy (EIS) of hydrogenated N-S co-doped $TiO_2@800^{\circ}C/24h$ sample: a) Nyquist plot in dark, and b) under dark and light conditions at a particular potential of 0.8 V.



Fig. S18 Hydrogenated N-doped TiO₂@500°C/24h sputtered and un-sputtered portions; (a) Raman spectra taken at two different locations; (b) enlarged window 1100 to 1730 cm⁻¹; (c) FTIR; and (d) XRD.



Fig. S19 Setup for collection of evolved gases from working and counter electrode.

References

- 1. Howarter, J. A.; Youngblood, J. P. Langmuir 2006, 22, 11142-11147.
- Zhang, W.; Shi, J.; Wang, X.; Jiang, Z.; Song, X.; Ai, Q. J. Mater. Chem. B 2014, 2, 1371-1378.
- Shunhang Wei, R. W., Jikang Jian, Fengjuan Chen and Yanfei Sun Dalton Trans., 2015, 44, 1534–1538.
- 4. Li, H.; Zhang, X.; Huo, Y.; Zhu, J. Environ Sci. Technol 2007, 41, 4410-4414.
- 5. Yang, G.; Jiang, Z.; Shi, H.; Xiao, T.; Yan, Z. J. Mater. Chem. 2010, 20, 5301-5309.
- Wang, Z.; Yang, C.; Lin, T.; Yin, H.; Chen, P.; Wan, D.; Xu, F.; Huang, F.; Lin, J.; Xie, X. Adv. Funct. Mater. 2013, 23, 5444-5450.