Electronic Supplementary Information
(ESI)

ESI: S-0

The thermal property and phase formation of as prepared BTZA sample was examined by TG-DTA (ESI S-0 Figure S-1). The TG-DTA curve shows that thermal decomposition occurs in three stages (ESI S-0 Table SI-1). In TG, the weight loss occurred below 185 °C is around ~23% and in temperature range 185-250 °C is 34%. The total weight loss up to 250 °C is due to the decomposition of BTZA complex followed by partial oxidation. The probable gaseous by-products may be CO, CO_2, NH_3, NO, CH_3, etc.[1,2,3] The exothermic peak at 250 °C is due to partial oxidation of decomposed BTZA. TG shows gradual weight loss around 11% from 300 to 700 °C, which is due to the removal of carbon, nitrogen and sulfur. The endothermic peak at 675 °C in DTA is due to complete decomposition of complex and formation of ZnO phase. Therefore, we have selected calcination temperature in the range of 500 to 700 °C, in order to obtain both mixed phases ZnO/ZnS and ZnO with maximum doping of carbon, nitrogen and sulfur elements.

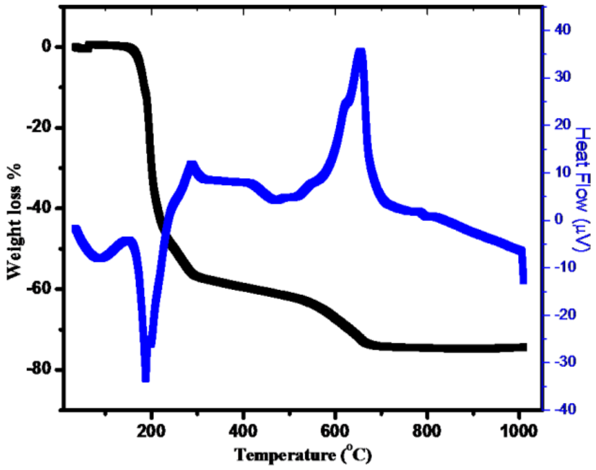


Figure S-1 TG-DTA curve for Bisthiourea zinc acetate intermediate (BTZA complex).

Table 1

Weight loss stages during calcination of BTZA sample from TG/DTA

Stages	Temperature range (°C)	Loss of molecules	% weight loss
I	60-200	NH_3 from excess thiourea and adsorbed H_2O molecules	29.0
II	200-500	NH_3, CO, CH_{4-x}	26.0
III	500-700	NO_2, CO_2, SO_{2-x}, CS_2	21.5

ESI: S-1

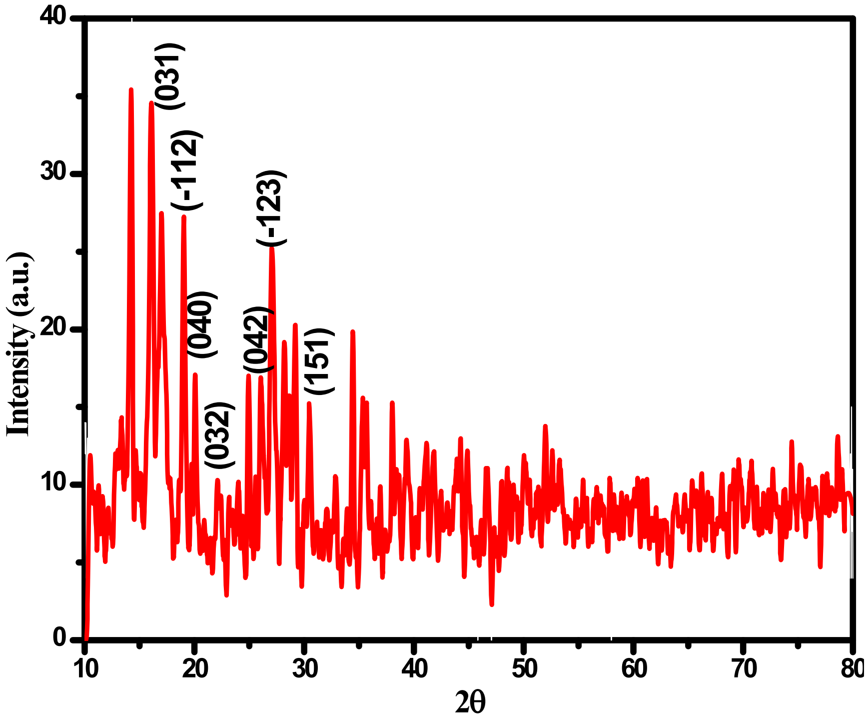


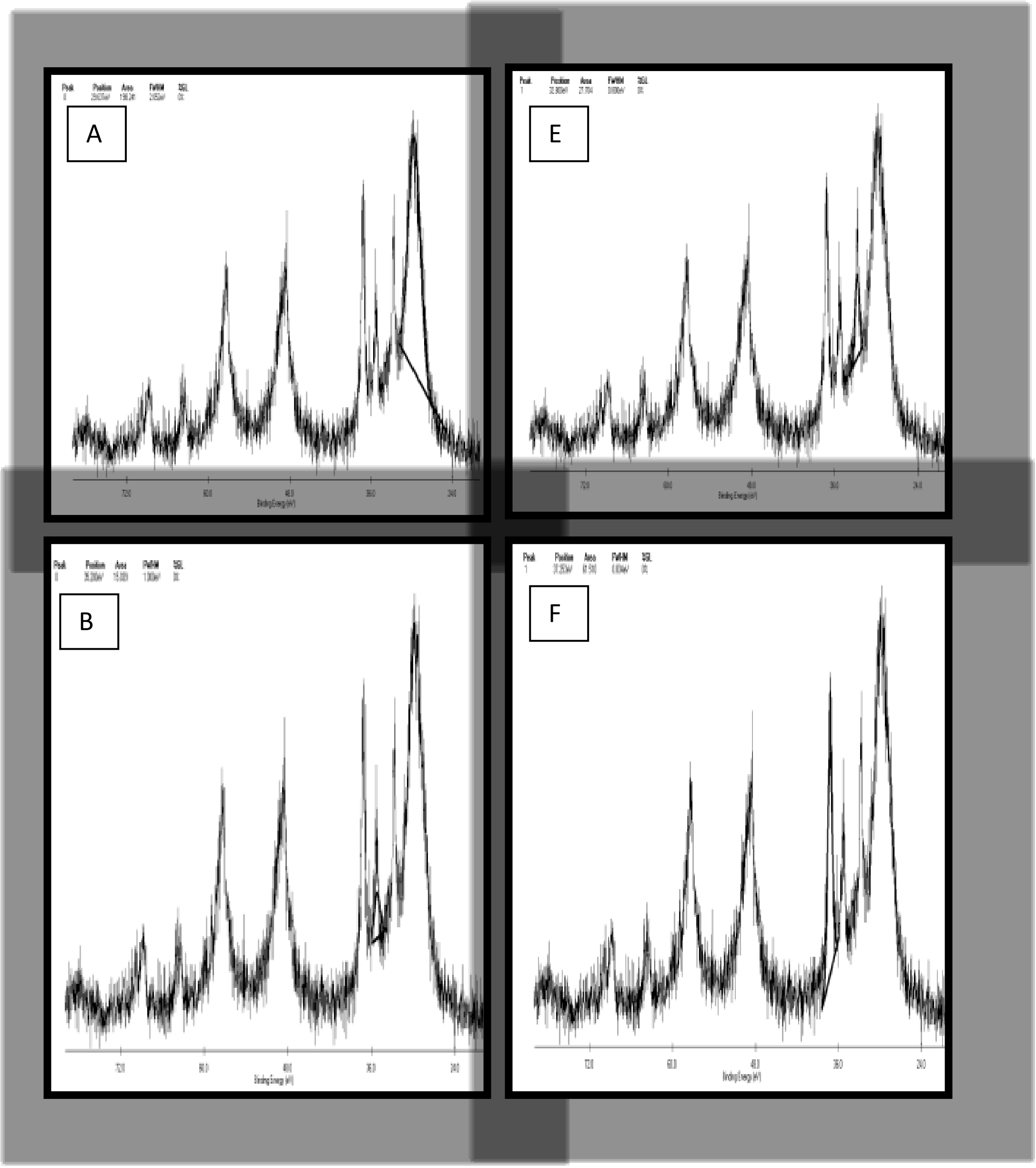
Figure S-1 XRD patterns of BTZA sample.

XRD patterns of BTZA sample shows peak at 2θ = 17.0 (031), 18.9 (-112), 19.9 (040), 22.0 (032), 25.9 (042), 26.9 (-123) and 30.3 (151) has been observed which is in good agreement with the reported BTZA complex.[4]

Table-1

Phase composition of ZnO: ZnS in S1 sample.

Sr. No	**Peak (2θ)**	**Area (a.u.)**	**ZnO/ZnS**	**Total Area composition**	**Ratio ofphase composition (ZnO:ZnS)**
1	28.7	198.2	ZnS	ZnO: 133.2	1:1.5
2	31.6	27	ZnO	ZnS: 198.2	
3	34.2	15	ZnO		
4	36.1	61.5	ZnO		
5	47.4	126.8	ZnS/ ZnO	Common peak	
6	56.4	92.9	ZnS/ ZnO	Common peak	
7	62.7	27	ZnS/ ZnO	Common peak	
8	67.7	29.7	ZnO		


A
E
B
F
Peak
Position
Area
FWHM
%GL
72.0
60.0
48.0
36.0
24.0
Binding Energy (eV)

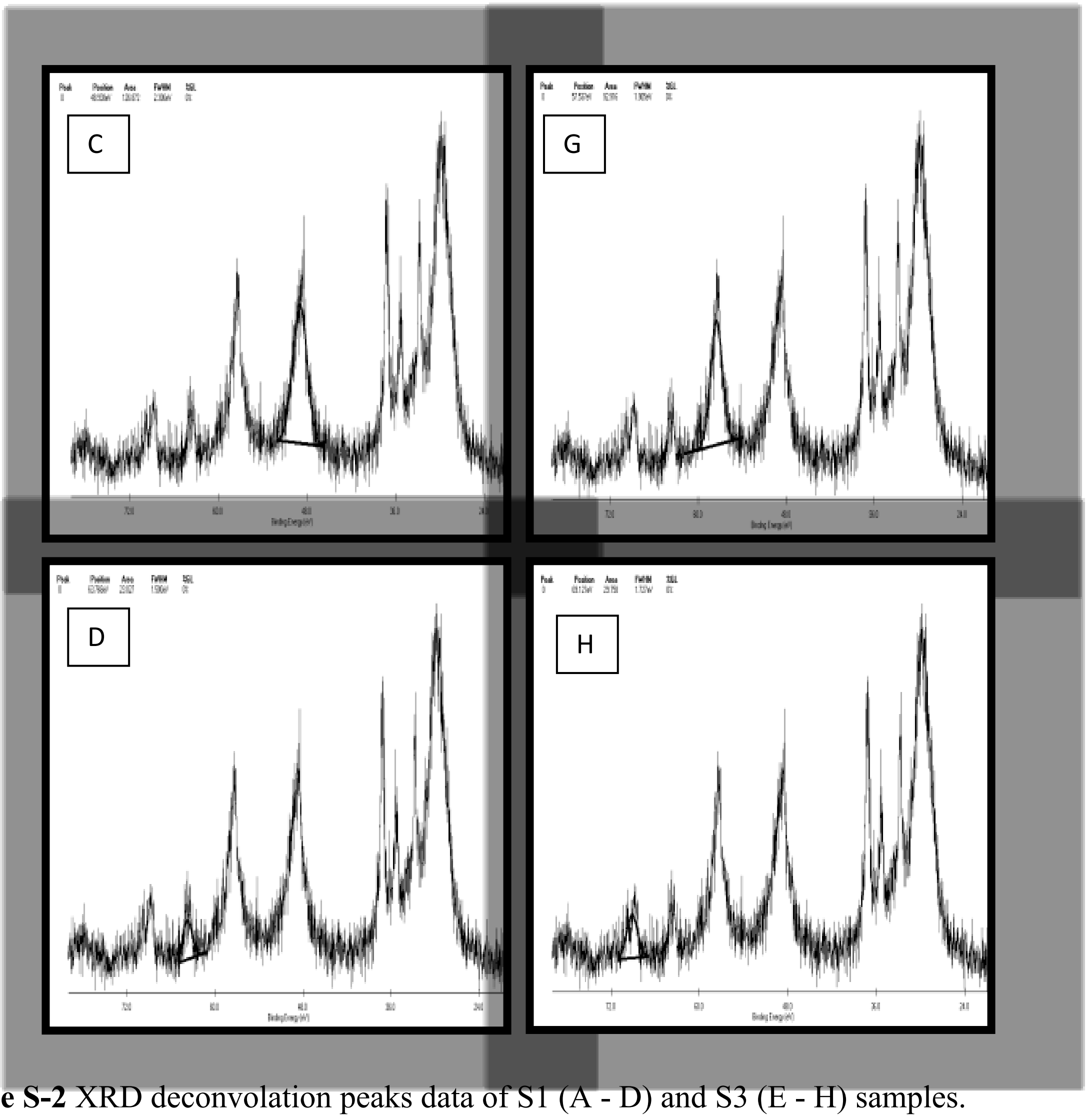


Figure S-2 XRD deconvolation peaks data of S1 (A - D) and S3 (E - H) samples.

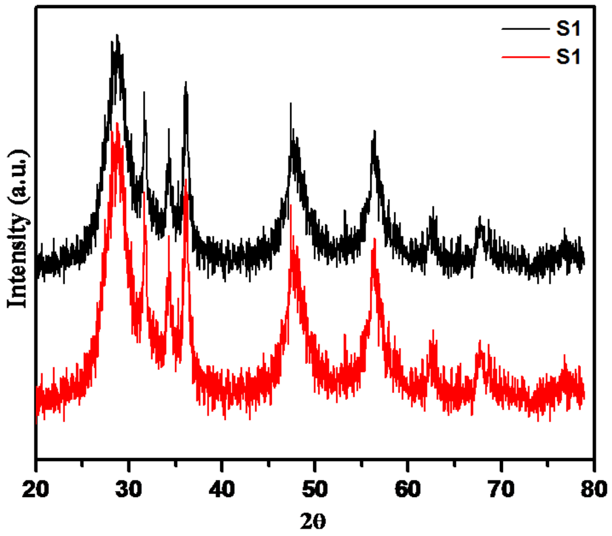
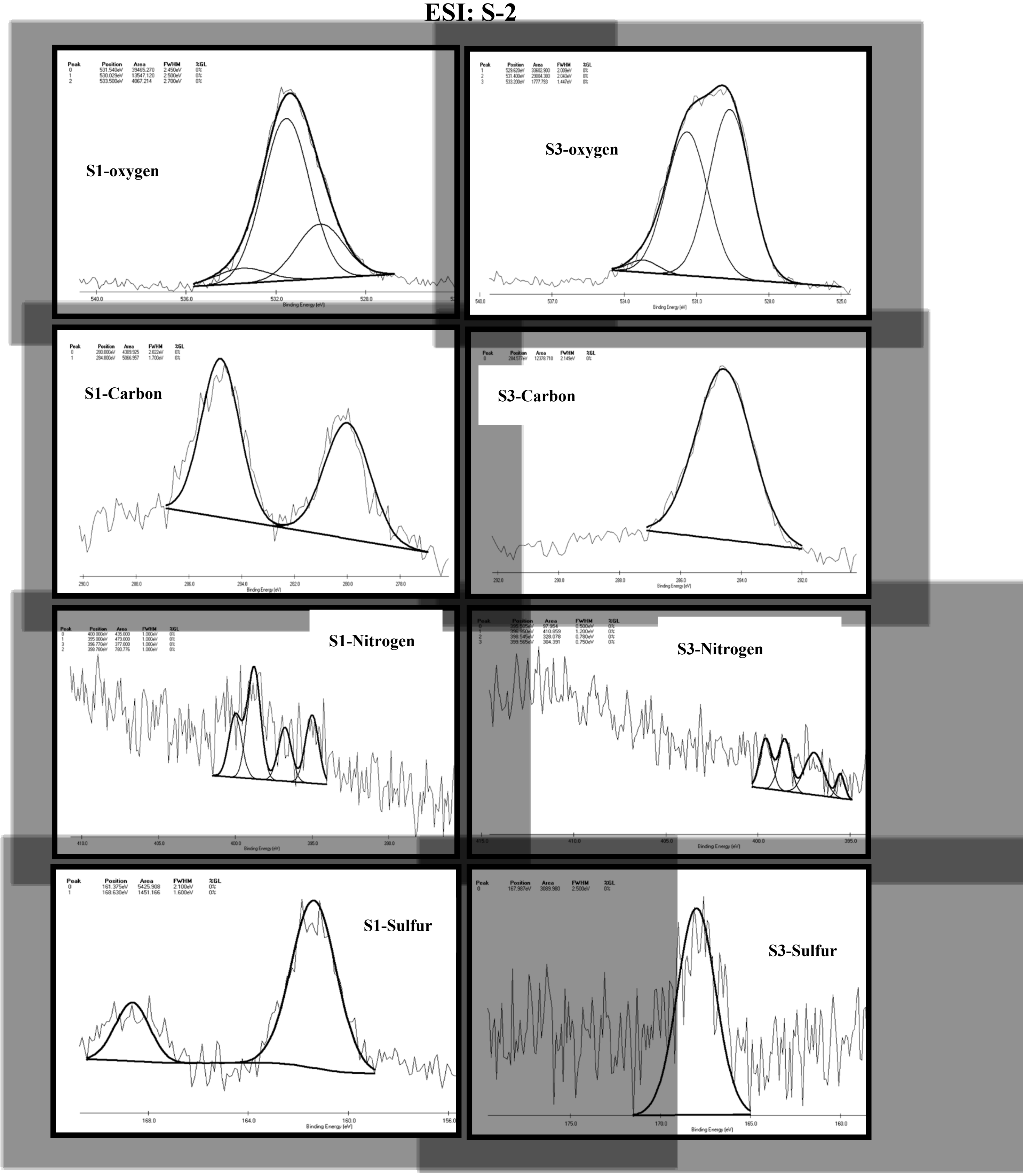


Figure S-3 XRD of sampleS1 reproducibility.



S1-oxygen

Peak	Position	Area	FWHM	%GL
0	531.540eV	39465.270	2.450eV	0%
1	530.029eV	13547.120	2.500eV	0%
2	533.500eV	4067.214	2.700eV	0%

S3-oxygen

Peak	Position	Area	FWHM	%GL
1	529.620eV	33602.900	2.009eV	0%
2	531.400eV	29004.380	2.040eV	0%
3	533.200eV	1777.793	1.447eV	0%

S1-Carbon

Peak	Position	Area	FWHM	%GL
0	280.000eV	4389.925	2.022eV	0%
1	284.800eV	5066.957	1.700eV	0%

S3-Carbon

Peak	Position	Area	FWHM	%GL
0	284.577eV	12378.710	2.149eV	0%

S1-Nitrogen

Peak	Position	Area	FWHM	%GL
0	400.000eV	435.000	1.000eV	0%
1	395.000eV	479.000	1.000eV	0%
3	396.770eV	377.000	1.000eV	0%
2	398.780eV	780.776	1.000eV	0%

S3-Nitrogen

Peak	Position	Area	FWHM	%GL
0	395.505eV	97.954	0.500eV	0%
1	396.950eV	410.859	1.200eV	0%
2	398.545eV	328.078	0.780eV	0%
3	399.565eV	304.391	0.750eV	0%

S1-Sulfur

Peak	Position	Area	FWHM	%GL
0	161.375eV	5425.908	2.100eV	0%
1	168.630eV	1451.166	1.600eV	0%

S3-Sulfur

Peak	Position	Area	FWHM	%GL
0	167.987eV	3089.980	2.500eV	0%

Figure S-1 XPS deconvolation peaks data of oxygen, carbon, nitrogen, sulfur for S1 and S3 sample.

Table 1

Surface composition of carbon, nitrogen, sulfur andoxygen elements

Samples	Element	Binding energy (eV)	Area (a.u.)	Sum	Total (CNS)	CNS doping	Ratio (%) (CNS)
S1	Carbon	280	4832	4832	14022	100%	34:17:49
		284	6380				
	Nitrogen	395	479	2307			
		396.7	377				
		398.8	1016				
		399.9	435				
	Sulfur	161.3	5426	6883			
		168	1457				
	Oxygen	531	39465	57079			
		530	13547				
		533	4067				
S3	Carbon	280	0	0	4291	30% with respective to S1 sample	0:28:72
		284	13016				
	Nitrogen	395	290	1202			
		396.7	412				
		398.8	280				
		399.9	220				
	Sulfur	161.3	0	3089			
		168	3089				
	Oxygen	531	28270	62920			
		530	33850				
		533	800				

ESI: S-3

The elemental composition is determined by EDS as shown in ESI S-3 Figure SI-1 and Table SI-1. This analysis shows presence of only C, N, S, O, Zn and absence of any other elements in all samples. These results are consistent with XPS results. However, with increase in calcination temperature from 500 to 700 °C, decrease in composition of the carbon, nitrogen and sulfur were observed which is quite obvious.

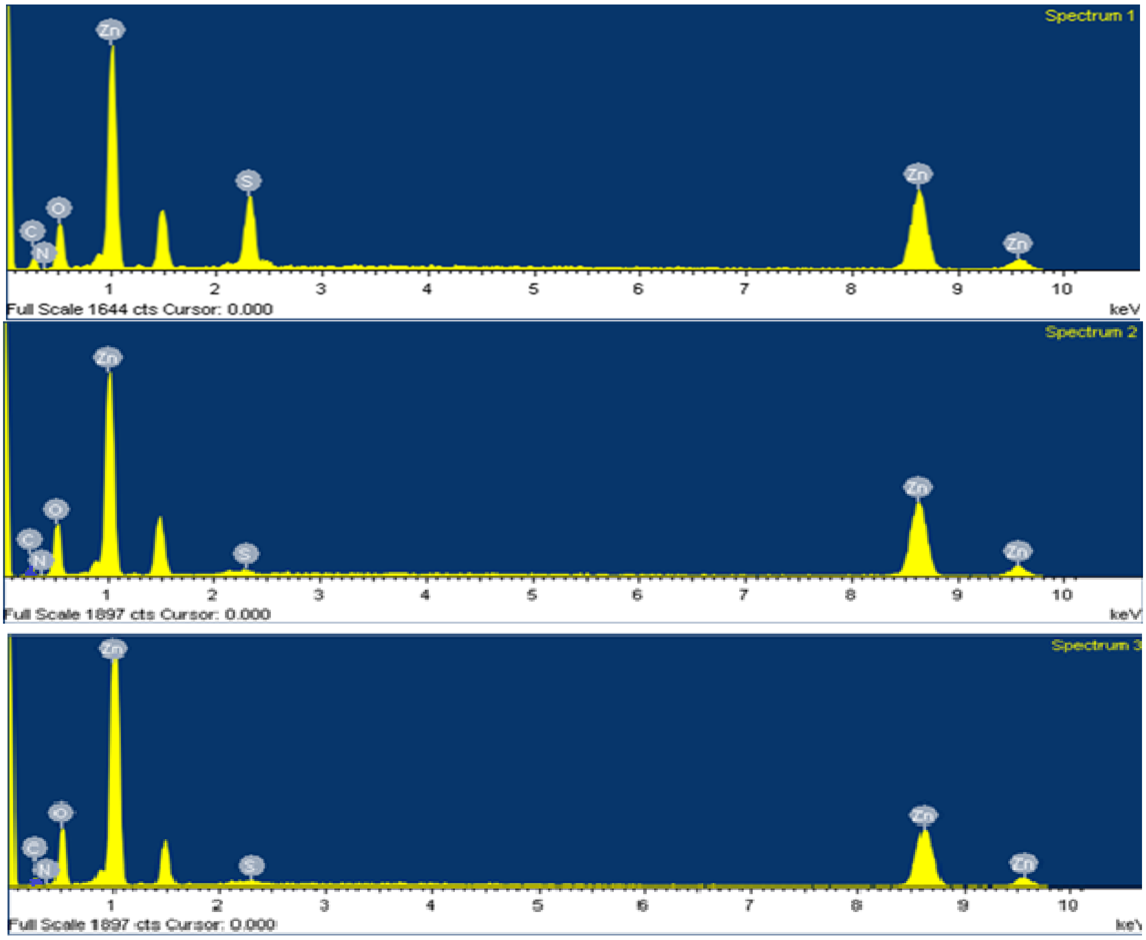


Figure S-1 E-DAX spectrum of sample A) S1, B) S3 and C) S4.

Table 1

Elemental analysis

Sr. No.	Catalysts	Calcination Temperature (°C)	Atomic (%)		
			S	N	C
2	S1	500	8.1	0.6	5.4
3	S3	600	0.4	1.1	0.5
4	S4	700	0.3	1.2	0.2

ESI: S-4

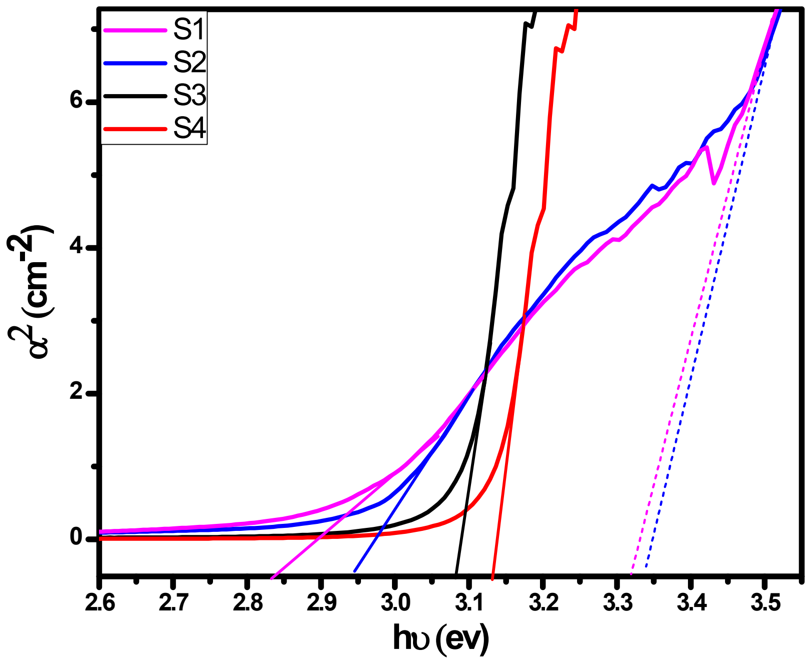


Figure S-1 Tauc plot of S1, S2, S3 and S4 samples.

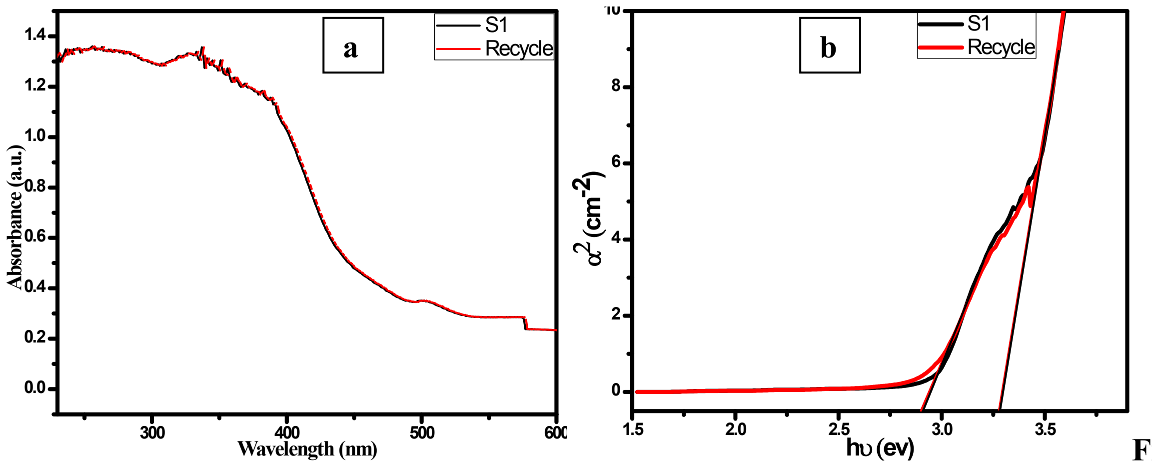


Figure S-2 (a) UV-DRS spectra of S1, and Recycle (fourth cycle) sample,

(b) Tauc plot of S1, and Recycle (fourth cycle) sample.

The band gap energy is determined by Tauc plot as shown insupporting informationESI S-4 Figure S-1. With increase in calcinations temperature from 500 to 700 ^{o}C shift in band gap from 2.83 to 3.13 eV was observed. This blue shift was might be due to the decrease in extent of nitrogen, carbon and sulfur from ZnO lattice due to calcinations this finding is consistent with XPS, Raman and EDX analysis.[1] The recovered catalyst shown 2.84 eV band gap which is equivalent to S1 sample, thus confirms stability of catalyst. While commercial samples of ZnO and ZnS showed 3.37 and 3.70 eV band gaps respectively, this is near to UV region and required higher energy than the prepared catalysts.

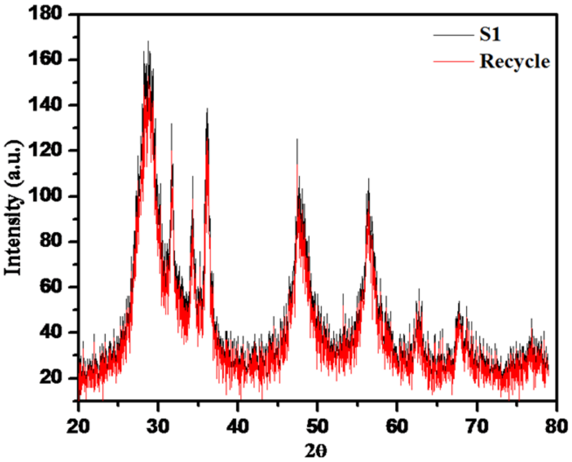


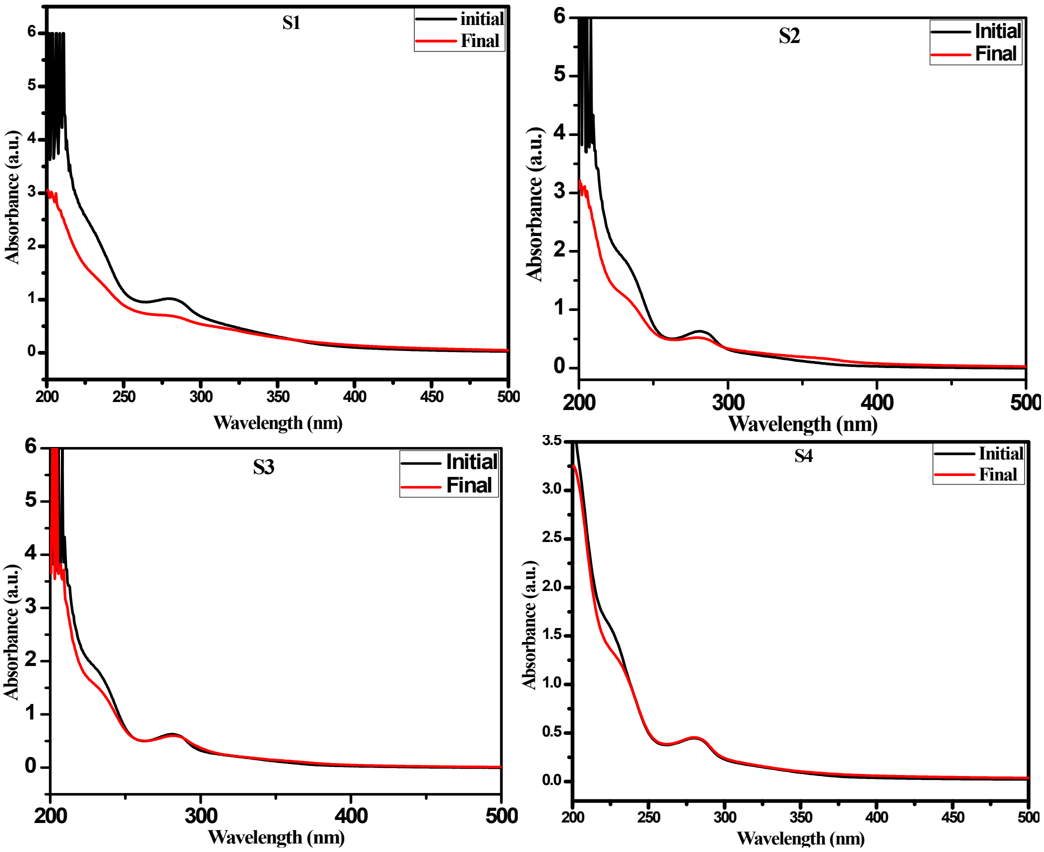
Figure S-3XRD of sample S1, and Recycle (fourth cycle) sample.

ESI: S-5

Table 1

Effect of catalyst loading on water splitting

Catalyst loading of S1 in mg	Average H_2 generation (μmol h^{-1})	Apparent quantum yield
100	580	14.1
200	892	23.9
500	223	5.4
1000	< 44.6	1.0



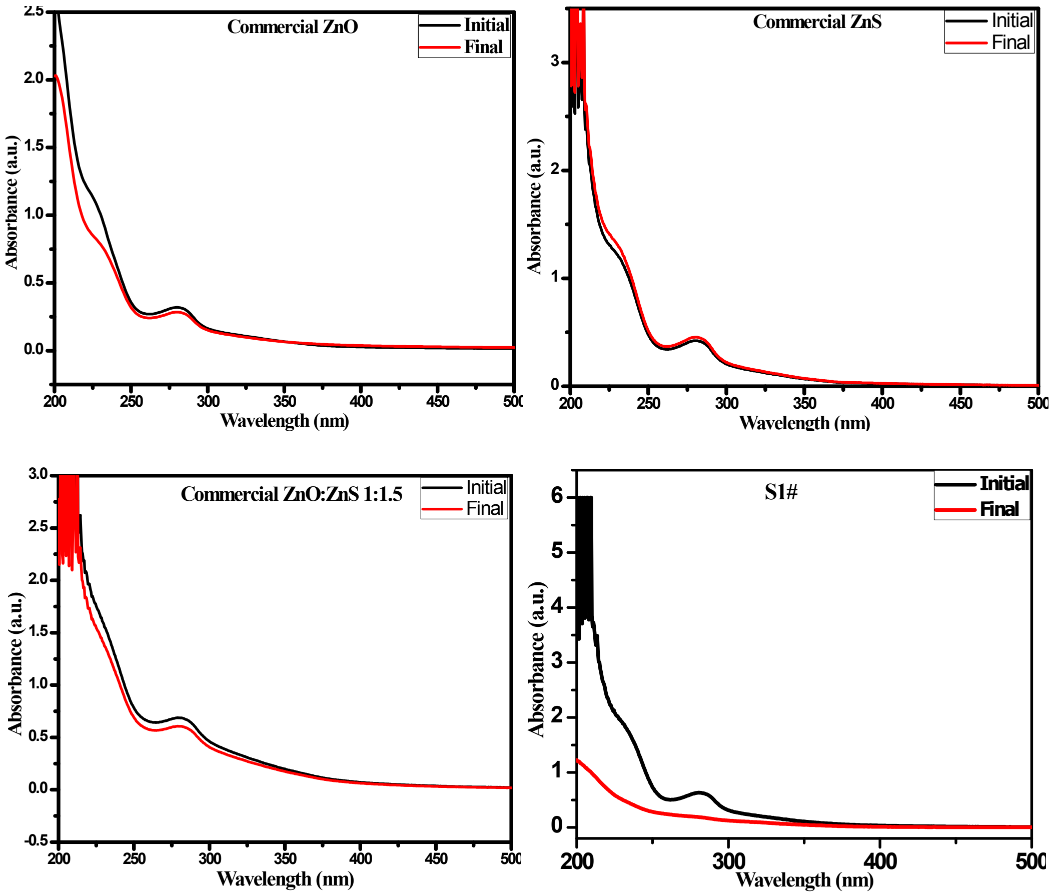


Figure S-1 Absorption spectra of lignin degradation using photocatalyst sample S1, S2, S3, S4, Commercial ZnO, Commercial ZnS, Commercial ZnO: ZnS 1:1.5, S1$^{\#}$ (S1 reusability)

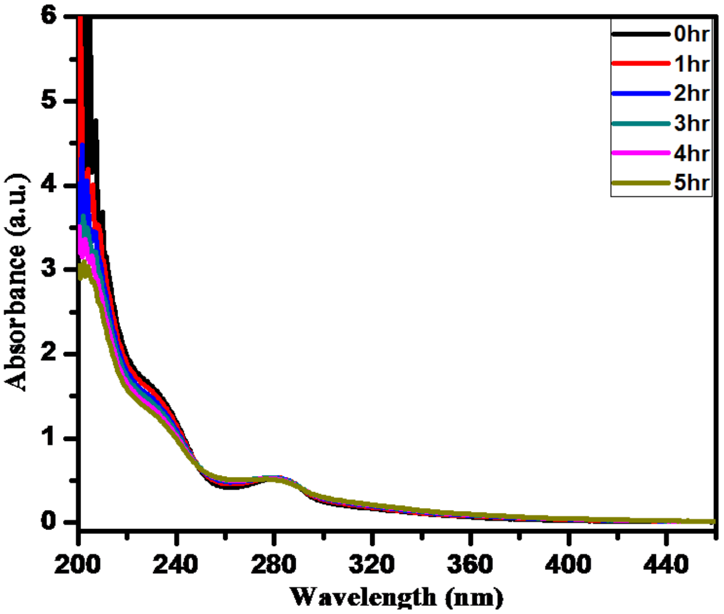
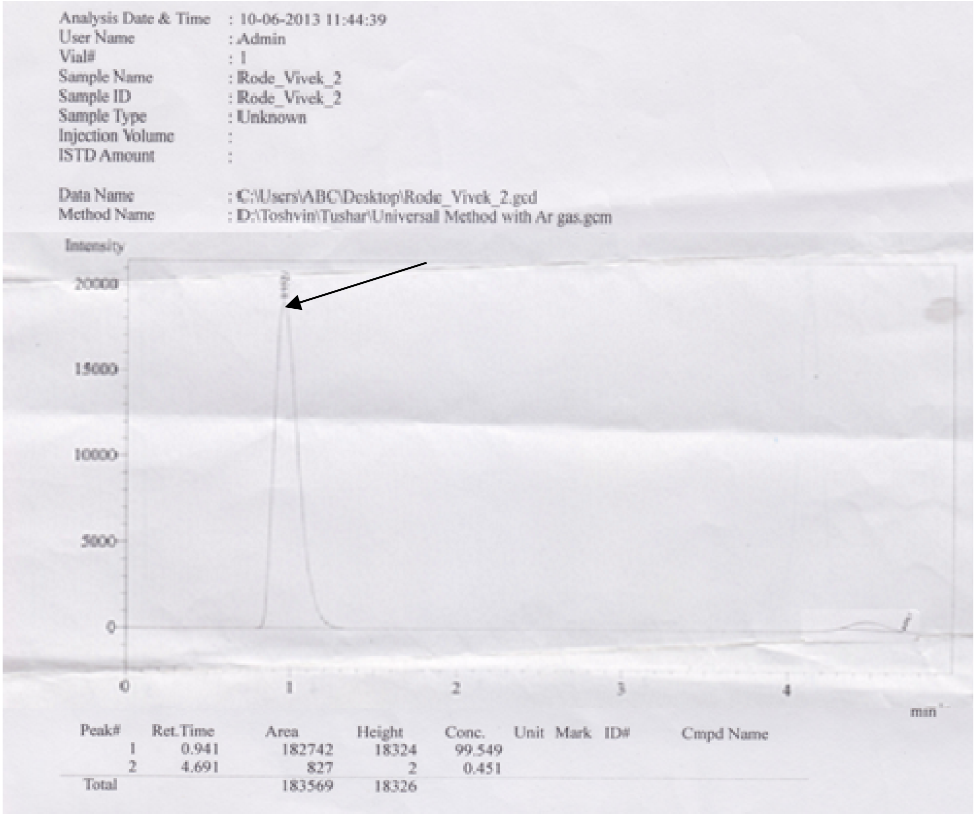


Figure S-2 Absorption spectra of lignin degradation without catalyst.

ESI: S-6

Analysis of hydrogen by GC

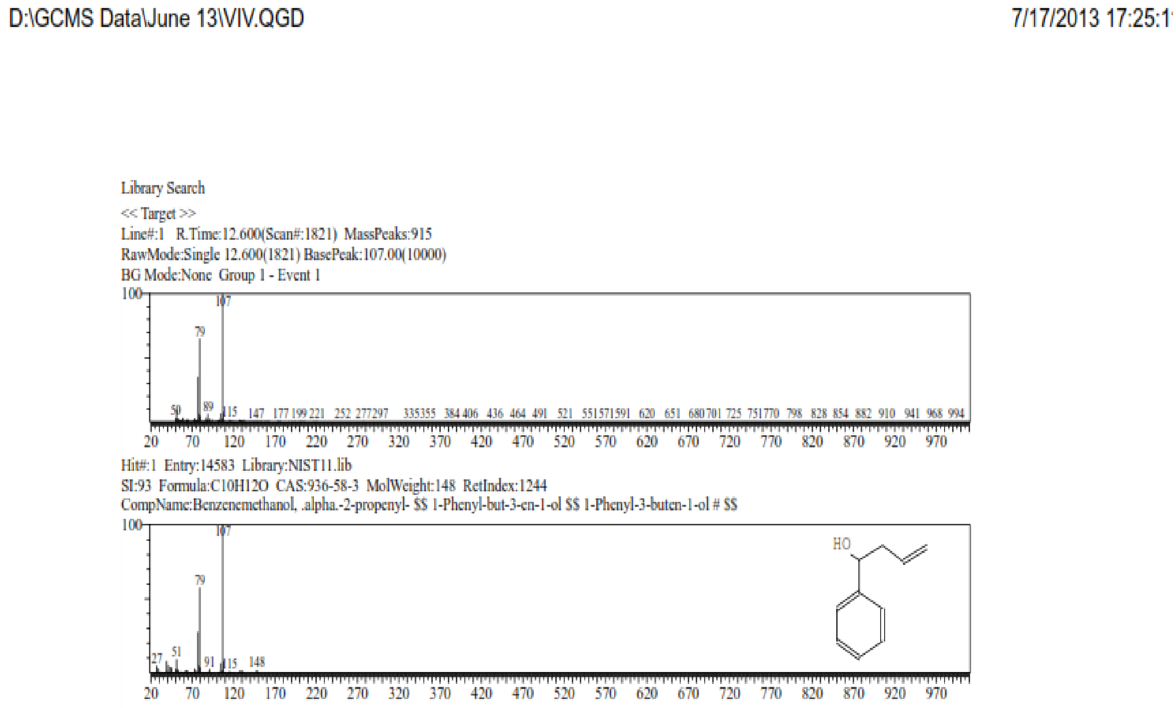


Analysis Date & Time : 10-06-2013 11:44:39
User Name : Admin
Vial# : 1
Sample Name : Rode_Vivek_2
Sample ID : Rode_Vivek_2
Sample Type : Unknown
Injection Volume :
ISTD Amount :

Data Name : C:\Users\ABC\Desktop\Rode_Vivek_2.gcd
Method Name : D:\Toshvin\Tushar\Universal Method with Ar gas.gcm

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	0.941	182742	18324	99.549				
2	4.691	827	2	0.451				
Total		183569	18326					

Figure S-1 GC of collected gas sample.



D:\GCMS Data\June 13\VIV.QGD 7/17/2013 17:25:1

Library Search
<< Target >>
Line#:1 R.Time:12.600(Scan#:1821) MassPeaks:915
RawMode:Single 12.600(1821) BasePeak:107.00(10000)
BG Mode:None Group 1 - Event 1

Hit#:1 Entry:14583 Library:NIST11.lib
SI:93 Formula:C10H12O CAS:936-58-3 MolWeight:148 RetIndex:1244
CompName:Benzenemethanol, .alpha.-2-propenyl- $$ 1-Phenyl-but-3-en-1-ol $$ 1-Phenyl-3-buten-1-ol # $$

Figure S-2 GCMS of intermediate (1-Phenyl-3-buten-1-ol) step sample.

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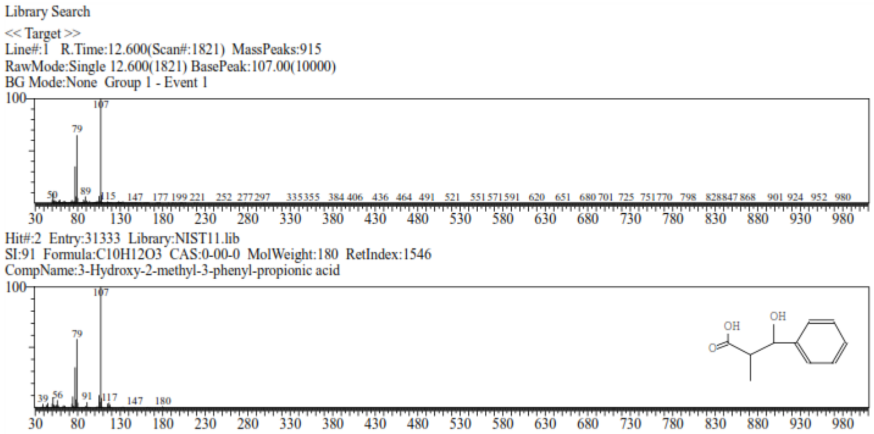

Library Search

<< Target >>

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RawMode:Single 12.600(1821) BasePeak:107.00(10000)

BG Mode:None Group 1 - Event 1

Hit#:2 Entry:31333 Library:NIST11.lib

SI:91 Formula:C10H12O3 CAS:0-00-0 MolWeight:180 RetIndex:1546

CompName:3-Hydroxy-2-methyl-3-phenyl-propionic acid

Figure S-3 GCMS of intermediate (3-Hydroxy-2-methyl-3-phenyl-propionic acid) step sample.

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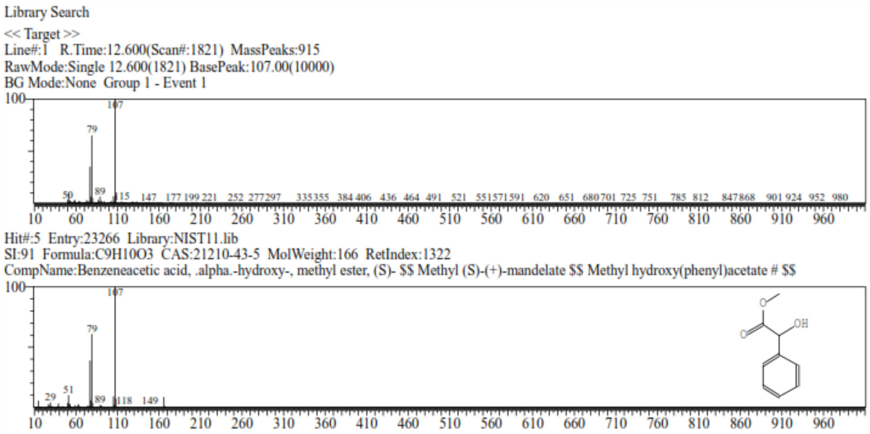

Library Search

<< Target >>

Line#:1 R.Time:12.600(Scan#:1821) MassPeaks:915

RawMode:Single 12.600(1821) BasePeak:107.00(10000)

BG Mode:None Group 1 - Event 1

Hit#:5 Entry:23266 Library:NIST11.lib

SI:91 Formula:C9H10O3 CAS:21210-43-5 MolWeight:166 RetIndex:1322

CompName:Benzeneacetic acid, .alpha.-hydroxy-, methyl ester, (S)- $$ Methyl (S)-(+)-mandelate $$ Methyl hydroxy(phenyl)acetate # $$

Figure S-4 GCMS of intermediate (Methyl hydroxyl (phenyl)acetate) step sample.

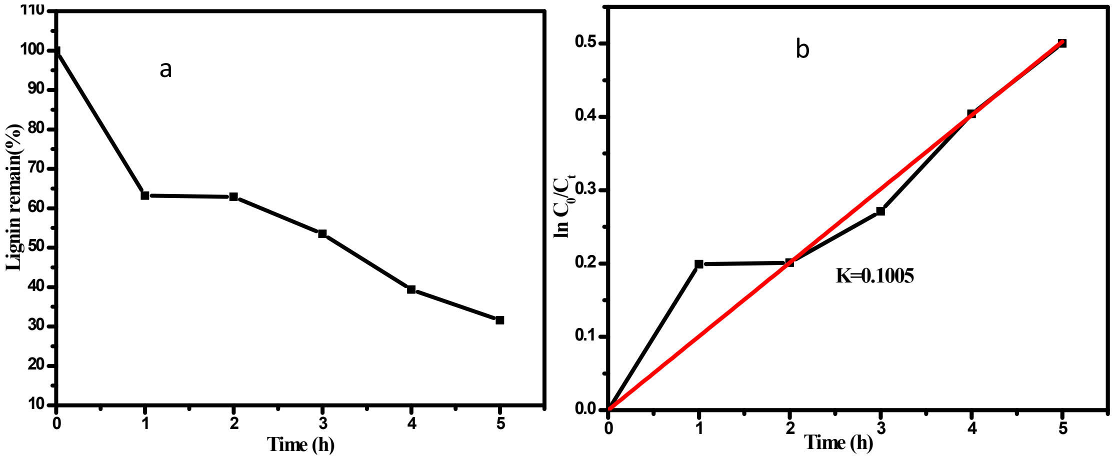

Figure S-1. Photocatalytic degradation of Lignin (100 ppm) by using S1 catalyst. Reaction conditions: catalyst, 0.1 g; water, 200 ml; Lignin, 100 ppm, Xe lamp, 300 W (Oriel).

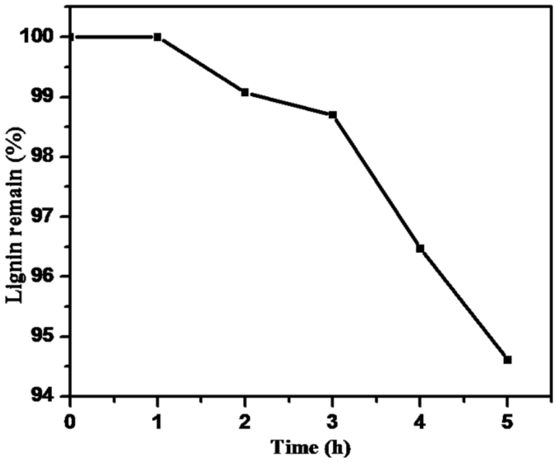

Figure S-2. Photocatalytic degradation of Lignin (100 ppm) by using without catalyst. Reaction conditions: Lignin, 100 ppm 200 ml, Xe lamp, 300 W (Oriel).

ESI: S-8

FTIR of BTZA complex and CNS-ZnO

The FTIR spectrum of as prepared (BTZA complex) and its calcined samples are shown in Figure S-1. The FTIR spectrum of as prepared samples showed peaks at 412, 478, 661, 778, 981, 1018, 1128, 1317, 1405, 1587, 1639, 2354, 2769, 3054, 3302 and 3382 cm^{-1} are originating from bisthiourea zinc acetate complex (BTZA) which is in agreement with literature.[1] However, after calcinations of this complex at various temperature showed intensities of some peaks (1018, 1128, 1317, 1405, 1587, 1639and 3054cm^{-1}) decreased and some of are disappeared.[4,5] The absorption peak observed at 1590 cm^{-1} is due to -C=O bond in carbonyl acetate ion (–C(=O)-O-) in salt.[6]

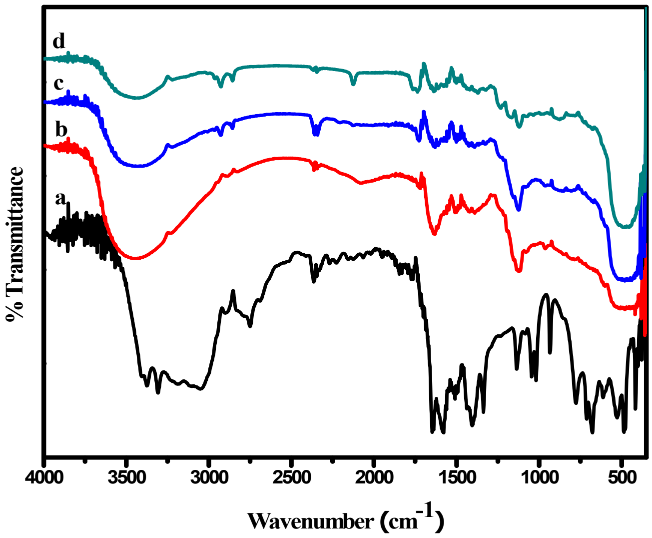

Figure S-1 FTIR of the A) BTZA complex, B) S1, C) S3 and D) S4 samples.

The FTIR spectrum of Industrial and Aldrich lignin samples are given away in Figure S-2. The peaks at 1035, 1172, 1417, 1453, 1509, 1589, 2939, 2845 and 3372$cm^{-1}$are due to stretching frequenciesmode of aromatic functional groups such as C-S-, -C=S, -CH, -OMe, -C=O, -CH_3 and -$CH_2$$cm^{-1}$respectively originate from sodium salt of lignosulfonate (Figure S-2, black line).However, almost all FTIR of industrial sample is very well matched with the Aldrich sample (Figure S-2, red line). Hence it is proved that industrial sample is also of sodium salt of lignosulfonate.

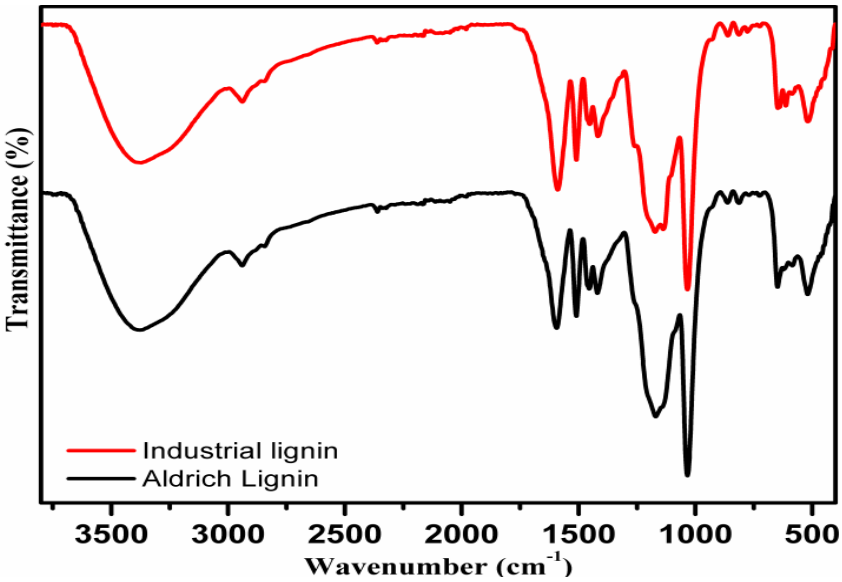

Figure S-2 FTIR of the Industrial lignin and Aldrich lignin sample.

ESI: S-9

ED pattern of C, N, S-ZnO/ZnS and N, S-ZnO

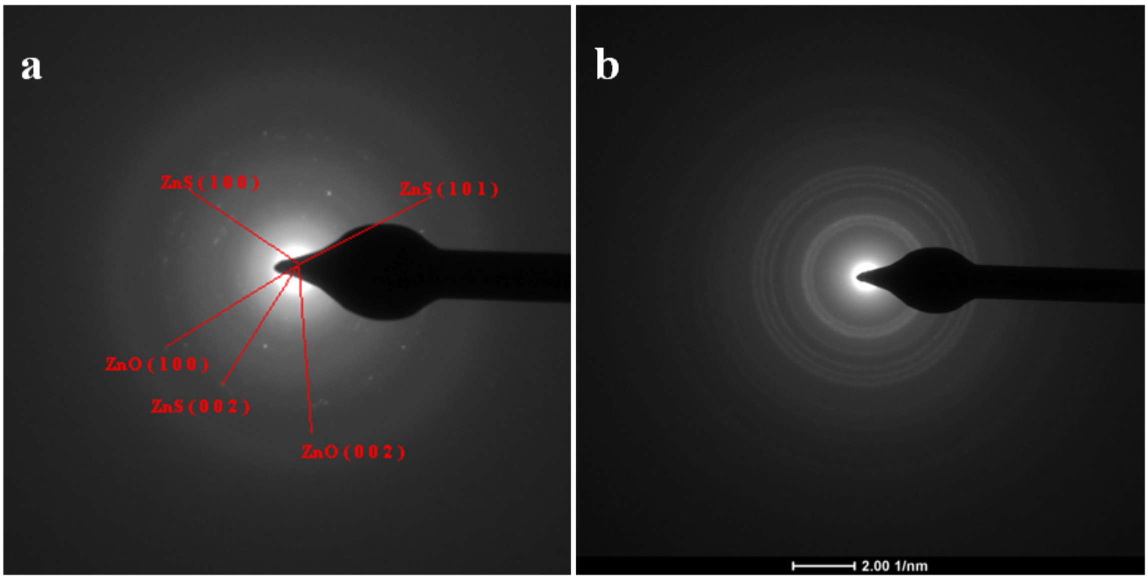

Figure S-1.ED pattern a) sample S1 and b) samplesS3.

References

1. S. K. Apte, S. N. Garaje, S. S. Arbuj, B. B. Kale, J. O. Baeg, U. P. Mulik, S. D. Naik, D. P. Amalnerkar and S. W. Gosavi, *J. Mater. Chem.***2011,** 21, 19241-19248.
2. A. P. Bhirud, S. D. Sathaye, R. P. Waichal, L. K. Nikam and B. B. Kale, *Green Chem.***2012**, 14,2790-2798.
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6. M. Samadi, H. A. Shivaee, M. Zanetti, A. Pourjavadi and A. Moshfegh, *J. Mol. Catal. A: Chem.***2012**, *359*, 42-48.