Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Data

Production of Phenolics via Photocatalysis of Ball Milled Lignin-TiO_2 Mixtures in Aqueous Suspension

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Table S1. SEM-EDS data of different wet milled TiO_2-lignin mixtures.

Sample	Carbon (%)	Oxygen (%)	Titanium (%)
WMH	36.65	48.24	18.67
WMA	37.25	48.99	13.61
WMW	37.40	48.69	15.52

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Figure S1. MALDI-TOF mass spectrum of lignin fully dissolved in NaOH at a pH of 12.

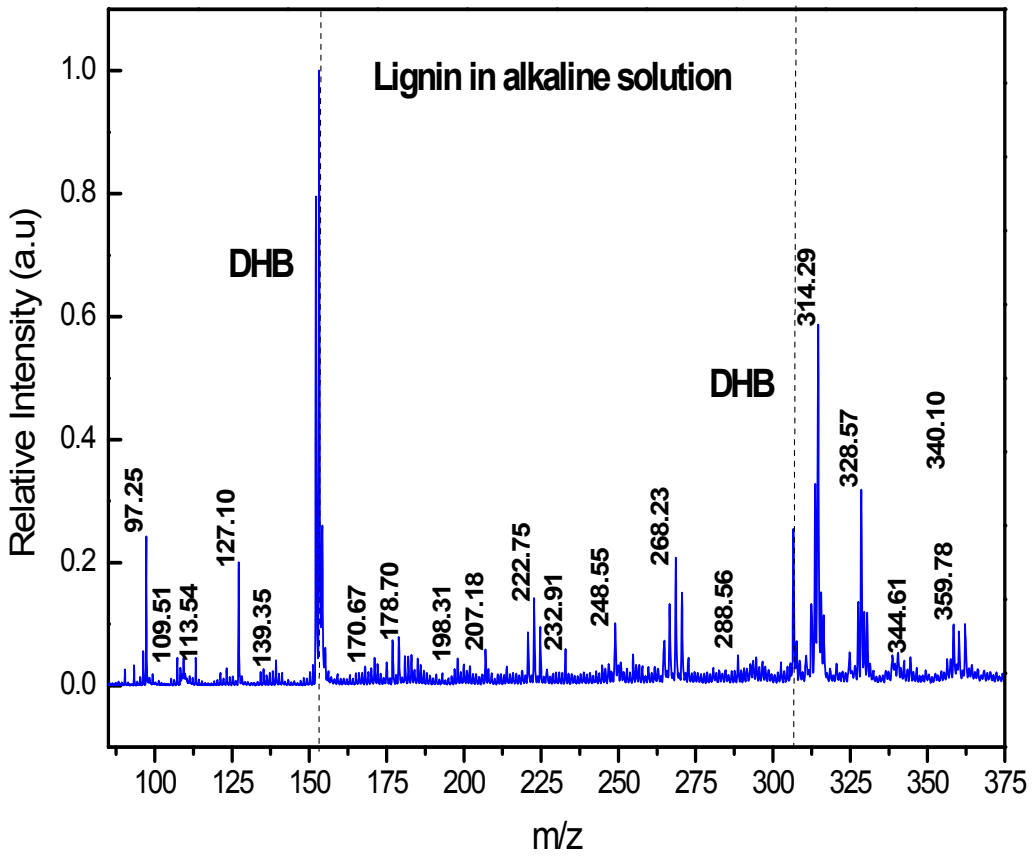

Figure S2. GPC calibration plot showing the variation of molecular weight of PMMA standards (M in Da) with elution volume (V in mL).

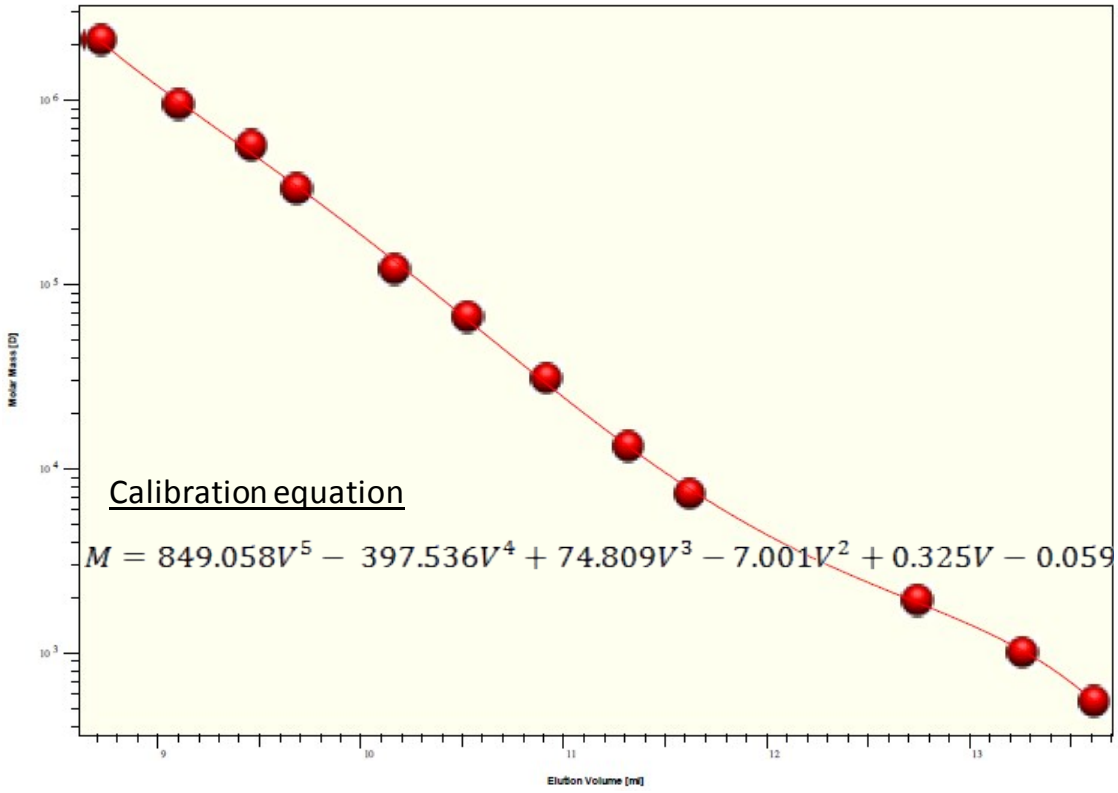

Figure S3. FT-IR spectra of lignin, TiO_2 and various ball milled mixtures of lignin and TiO_2 in the absence of presence of solvents. It is important to note that the C=O stretching vibration (1720 cm^{-1}) is absent in the case of WMA and WMW mixtures. Similarly, phenolic O-H bending vibration (1364 cm^{-1}) is also absent in both the mixtures. Other mixtures, DM and WMH, exhibit all the signature peaks of lignin.

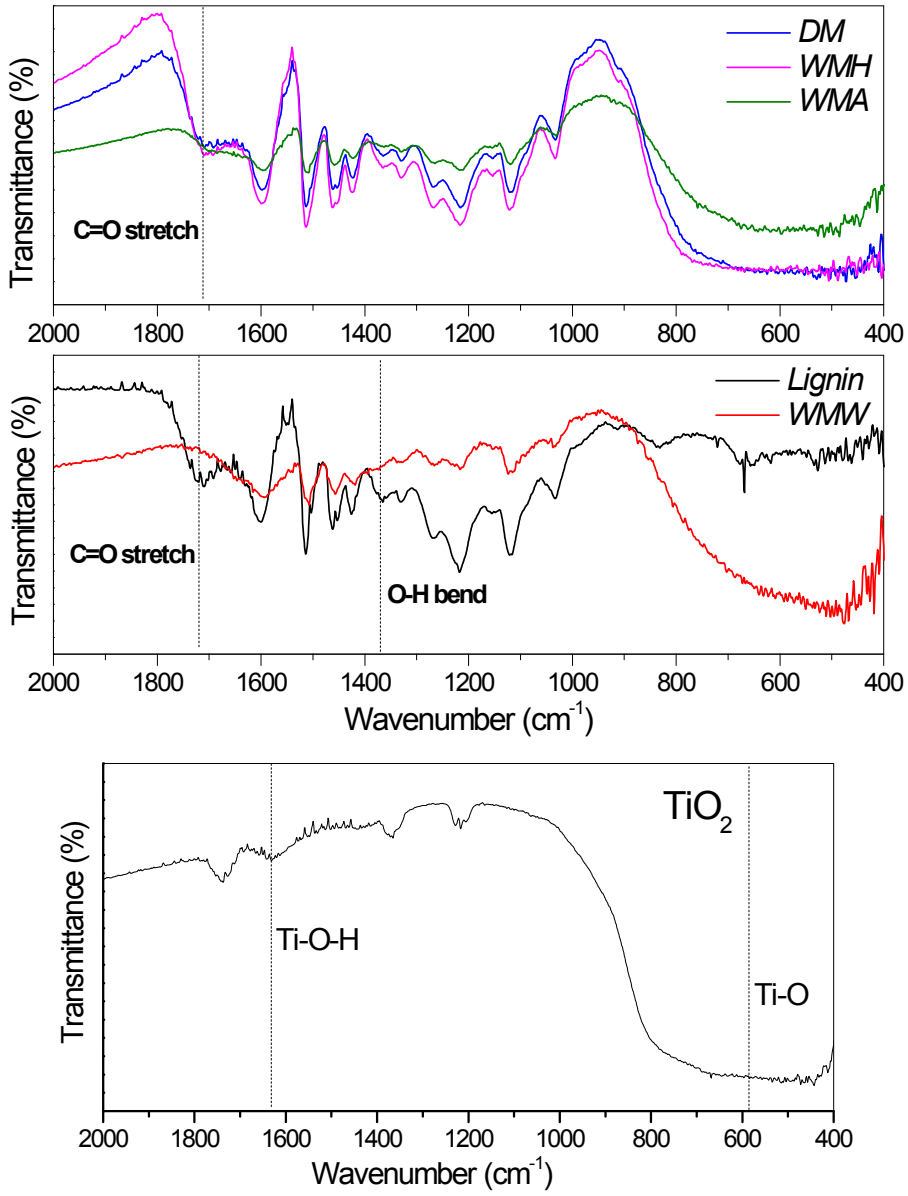

Figure S4. UV-visible spectra of Aeroxide® TiO_2 and various lignin-TiO_2 mixtures.

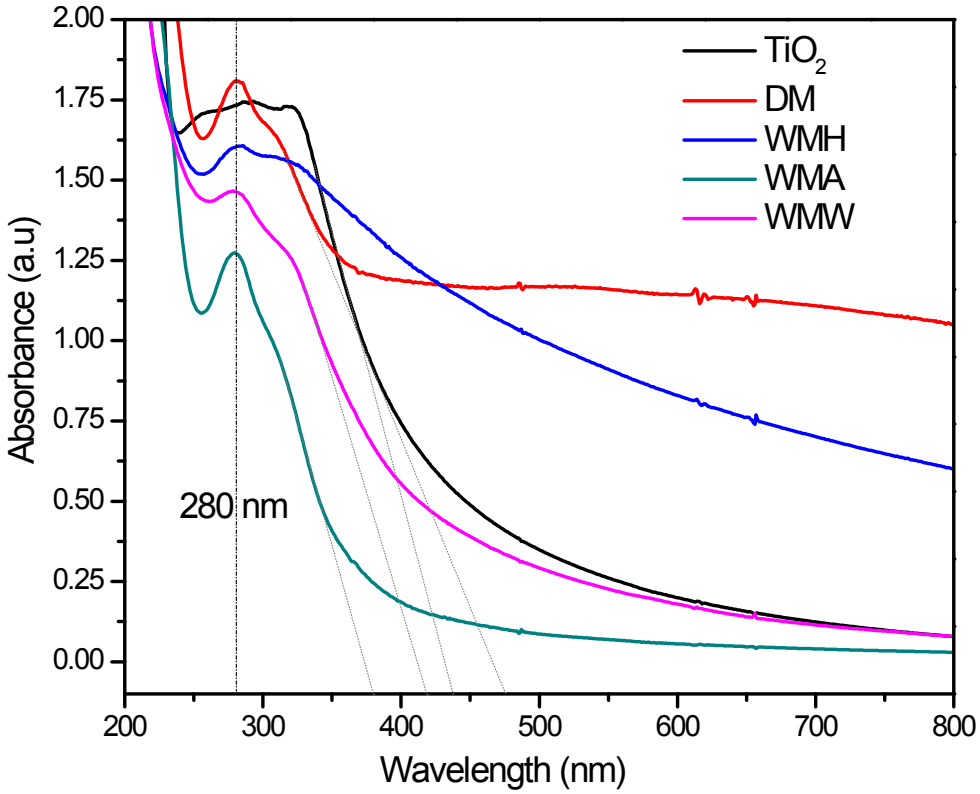

Figure S5. Particle size distribution of lignin and ball milled lignin

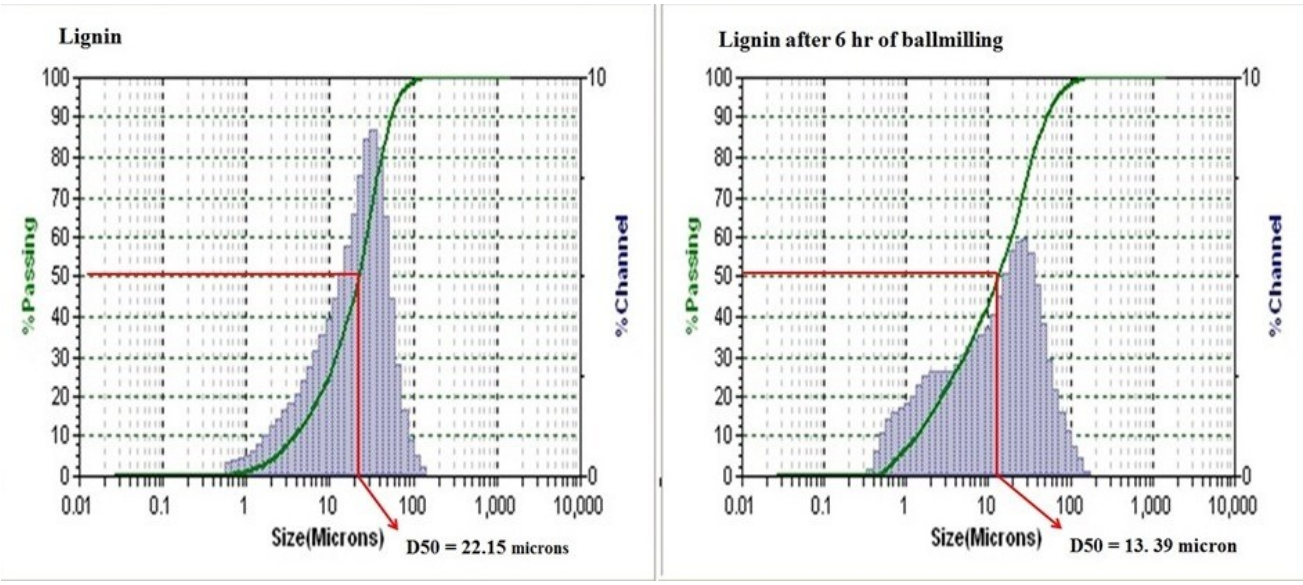

Figure S6. Molecular weight distribution of untreated lignin and after different treatments including wet milling with water, dark stirring and UV irradiation. The decrease in mass fraction of high molecular weight components of lignin with UV treatment is evident.

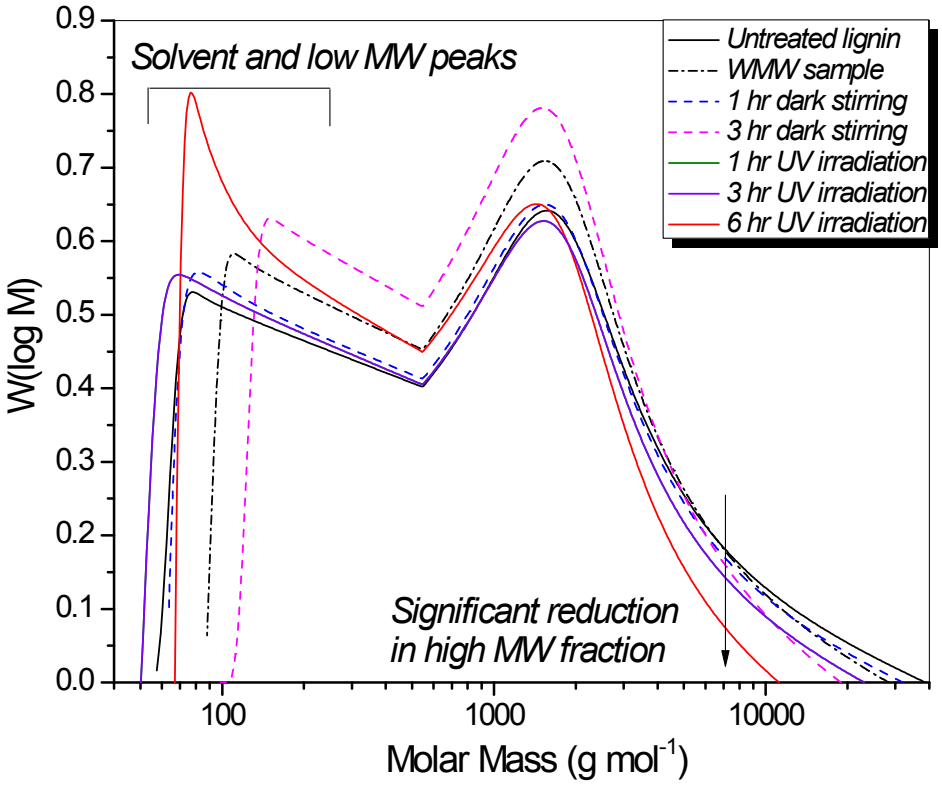

Figure S7. Concentration profiles of phenolic compounds formed during dark mixing and photocatalysis from different WMW lignin-TiO_2 mixtures containing different amounts of TiO_2. The total concentration of the mixture in water was 2 g L^{-1}.

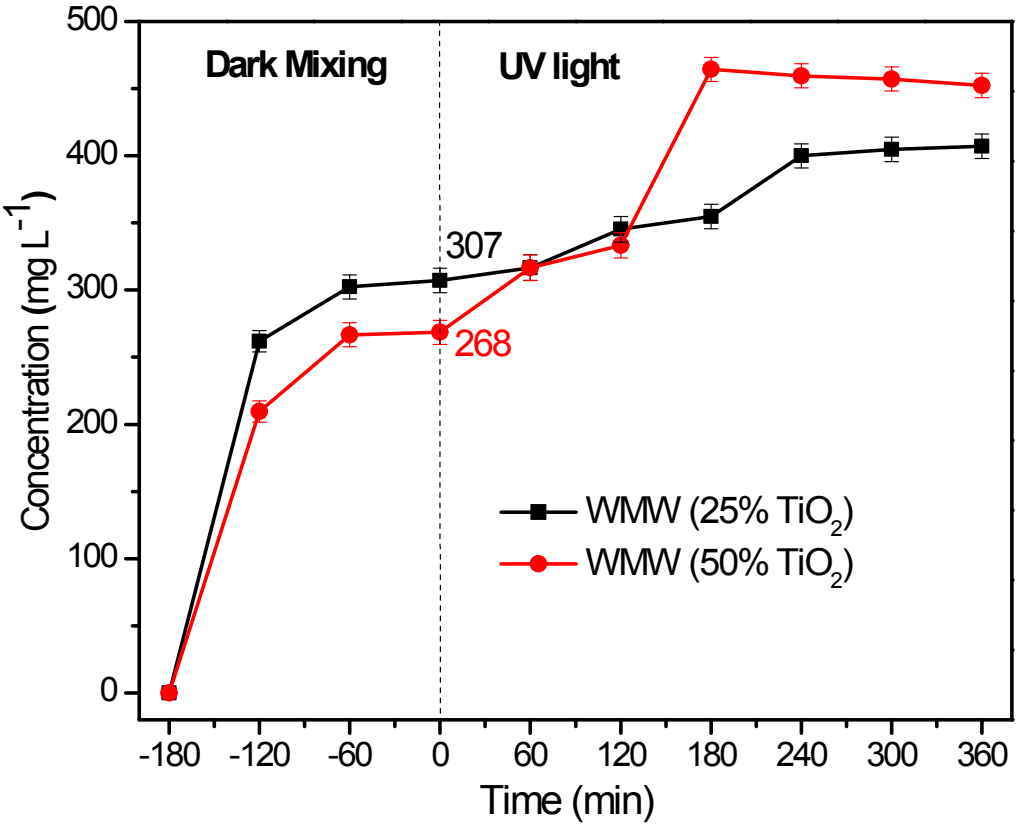

Table S2. List of products obtained when lignin was fast pyrolyzed at 500 ^{o}C in a micropyrolyzer (Frontier Laboratories, Japan) coupled with GC/MS. (G - guaiacol and its intermediates, H - simple phenol /hydroxy methyl and its intermediates, S - syringol and its intermediates)

Compound	Area%	Phenol type
2-Methoxy-4-vinyl phenol (or) Vinyl guaiacol	13.09	G
Phenol, 2-methoxy-4-methyl-	6.91	G
2-Methoxyphenol	5.65	G
Guaiacol, 4-ethyl-	4.47	G
Isoeugenol	3.43	G
1,2-Benzenediol, 3-methoxy-	2.53	G
Acetovanillone	1.22	G
Isovanillin	0.77	G
4-Vinyl phenol	6.59	H
Phenol, 4-ethyl-	1.74	H
Phenol	1.39	H
Phenol, 4-methyl-	1.25	H
Phenol, 2,6-dimethoxy- (or) Syringol	5.94	S
Phenol, 2,6-dimethoxy-4-(2-propenyl)- (or) Methoxy eugenol	3.33	S
Acetosyringone	9.11	S
Syringaldehyde	0.7	S
Carbon dioxide	15.25	
n-Hexadecanoic acid	5.51	
Squalene	4.65	

Methanethiol	3.1	
1-Nonadecene	1.8	
Tetradecanoic acid	0.81	
2-Propanone	0.76	
TOTAL	**100**	

Analysis conditions: mass of lignin sample = 300±20 μg; pyrolysis temperature = 500 ^{o}C; flow rate of He gas = 1.59 mL min^{-1}; GC column (UA-5; 30 m×0.25 mm; 0.25 μm film thickness); GC oven program - 40 ^{o}C for 1 min, heating at a rate of 10 ^{o}C min^{-1} to 300 ^{o}C, and finally held at 300 ^{o}C for 15 min. Other conditions were similar as outlined in section 2.5.