Electronic Supporting Information

Simultaneous cellulose conversion and hydrogen production assisted by cellulose decomposition under UV-light photocatalysis

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Experimental:

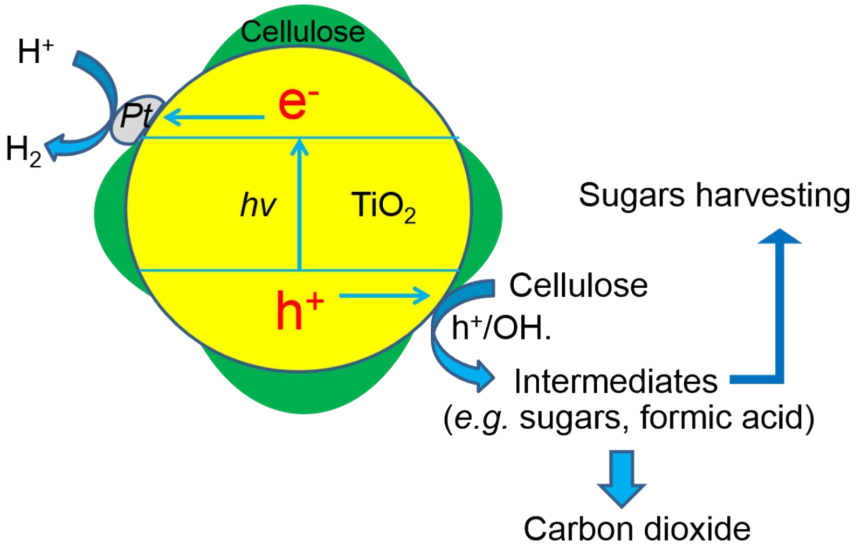
A cellulose colloid suspension was prepared by two-step ball-milling of 2 g of microcrystalline α-cellulose powder (Sigma-Aldrich) with zirconia ball size (10 mm and 1.0 mm). Cellulose powder was firstly milled with 10 mm zirconia ball for 60 min with a speed of 350 rpm and then milled with 1.0 mm zirconia ball for 60 min with a speed of 530 rpm. The ball-milled cellulose powder was collected by filtering with a steal mesh to remove the zirconia ball, and then dispersed in DI water in a big beaker. The big cellulose particles were settled down to the bottom of beaker, and the small cellulose nanoparticles were suspended well in water to form a white suspension overnight. Finally, the upper white cellulose suspension was separated and used as a stock. The ball-milled cellulose nanoparticles in water agglomerated together again after few days as observed from the particle size analysis (data not shown), thus the fresh ball-milled cellulose suspension was used for immobilization. Platinized TiO_2 (P25) with a typical Pt loading of 0.5 wt.% was firstly prepared by a photo-deposition method. A 500 ml TiO_2 (1.0 gL^{-1}) suspension with 50 ml methanol as electron donor and 6.5 ml of 1.0 gL^{-1} chloroplatinic acid ($H_2PtCl_6.6H_2O$) was irradiated with UV light (250 W iron-halide lamp) for 60 min. After irradiation, Pt-deposited TiO_2 (TiO_2(Pt)) powder was filtered, washed with D.I. water, and dried in air at room temperature.

Immobilizing cellulose nanoparticles onto TiO_2(Pt) nanoparticles was based on the condensation of their surface hydroxyl groups and formation of intra-molecular H-bonds. Different amounts of cellulose colloidal suspension (8 ml, 20 ml, 40 ml, 80 ml) were diluted with water to give a 250 ml aqueous suspension, then 0.1 g TiO_2(Pt) powder was added into the suspension. The mixed suspension was under sonication for 5 min by an ultrasonic probe and strongly stirred for 1 h to allow TiO_2(Pt) nanoparticles and cellulose particles evenly dispersed in water. Then the mixed TiO_2(Pt) and cellulose powders were collected by filtration and thoroughly washing with DI water to remove some weakly bound soluble sugars (glucose oligomers produced from ball-milling of bulk cellulose) onto the mixed solid powders. Finally, the collected mixed TiO_2(Pt) and cellulose powder was dried under room temperature and denoted as TC1, TC2, TC3, and TC4, for the samples prepared from 8 ml, 20 ml, 40 ml and 80ml cellulose suspension, respectively. Without mixing with the TiO_2 nanoparticles, pure cellulose polymer was obtained due to the condensation of hydroxyl groups and formation of H-bonds during drying.

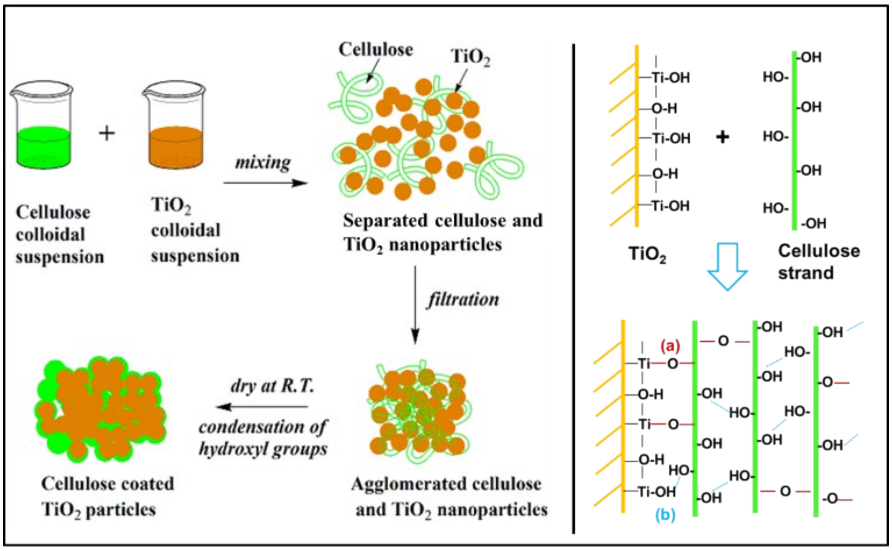
Cellulose conversion and H_2 production experiments were performed with 15 mg sample powder suspended in 50 ml DI water under UV-Visible light irradiation (250 W, iron doped halide lamp, emission spectrum of lamp is shown in Fig. S14). The suspension was sealed in a home-made photoreactor purged with pure Ar as a protective gas. Before photoirradiation, the sealed photoreactor was purged with Ar for 30 min to remove the O_2 and N_2. The amount of photogenerated H_2 and CO_2 (from cellulose decomposition) in the head-space (0.65 L) of photoreactor under irradiation were examined using an online gas chromatograph (Agilent 3000 Micro Gas chromatograph). The temperature of photoreactor was cooled down by continuous water flow, and the temperature of aqueous suspension increased from ~ 20 ^oC to ~ 40 ^oC during the light irradiation. Each photocatalysis run was performed for 6 h in one day, and then the suspension was purged with Ar for 30 min again prior to starting the second cycle to remove some accumulated H_2 that might be re-oxidized by holes. This process was repeated up to seven cycles until no significant amount of H_2 and CO_2 generated. The liquid products in the solution after each cycle test was measured using a high performance liquid chromatograph (HPLC, Agilent 1100 series, water as mobile phase, flow rate of 0.6 ml/min, column temperature at 79 ^oC) equipped with a refractive index detector and a Hi-plex column (4.6 mm× 150 mm) for sugar analysis. HPLC profiles from the commercial sugar molecules such as cellodextrins, glucose, arabinose, erythose, formic acid, gluconic acid were used to determine the cellulose decomposition products. The solid catalyst samples after photocatalysis were collected for further SEM and TGA characterizations. Outdoor tests for the simultaneous H_2 production and cellulose conversion under natural solar light irradiation. Pure TiO_2(Pt) and cellulose immobilized TiO_2(Pt) (TC4) powders were suspended in water in a sealed photoreactor purged Ar gas before light irradiation. (Experiments were performed outdoors in selected 3 days during July at St Andrews, Scotland; average temperature outdoors is 16 ^oC)

Characterization:

Particle size of cellulose was measured on a Mastersizer 2000 Particle Size Analyser (Malvern Instruments). Microstructure of samples was observed on a JEOL JSM-6700F Scanning Electron Microscope (SEM) at 5 kV. The SEM specimen was prepared by placing small amounts of sample powder onto a carbon plate attached to an Aluminum sample holder and gold powder was allowed to evaporate under vacuum at room temperature. Elemental analysis (CHN) was also performed for determination of compositions of cellulose loaded TiO_2 samples. Transmission electron microscope (TEM) was performed using a JEOL JEM-2011 electron microscope at 200 kV. Thermogravimetric and differential thermal analysis (TG-DTA) was measured on EX MOD Stanton Redcroft Thermal Analyser (STA-780). The measurements were carried out from 20 ^oC to 600 ^oC in air with a ramping rate of 4 ^oC/min.



Scheme S1. Illustration of photocatalytic H_2 production from water reduction and simultaneous cellulose decomposition to carbon dioxide upon immobilizing cellulose onto platinized TiO_2.



Scheme S2. Illustration of the procedure of immobilizing cellulose particles onto titania nanoparticles (left side) via the “mixing and drying” process and the possible pathways for binding TiO_2 with few cellulose strands: (a) condensation of their hydroxyl groups (b) formation of intra-molecular H-bonds.

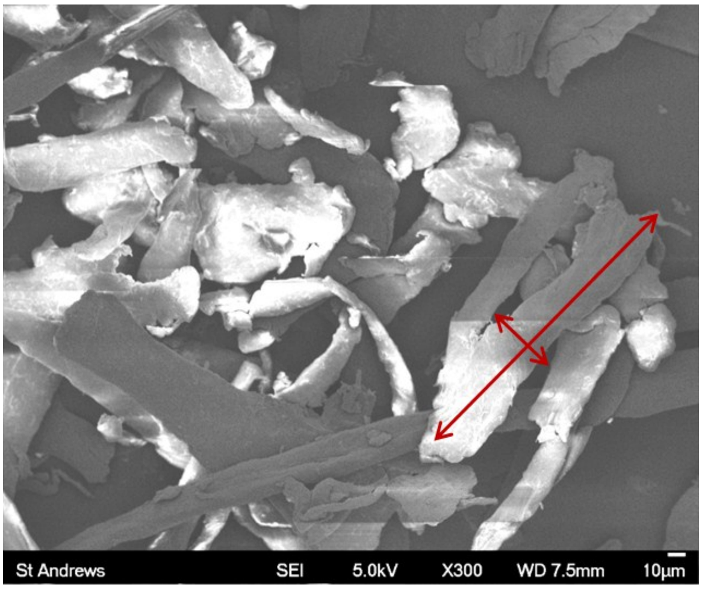


Fig. S1 SEM image of microcrystalline α-cellulose.

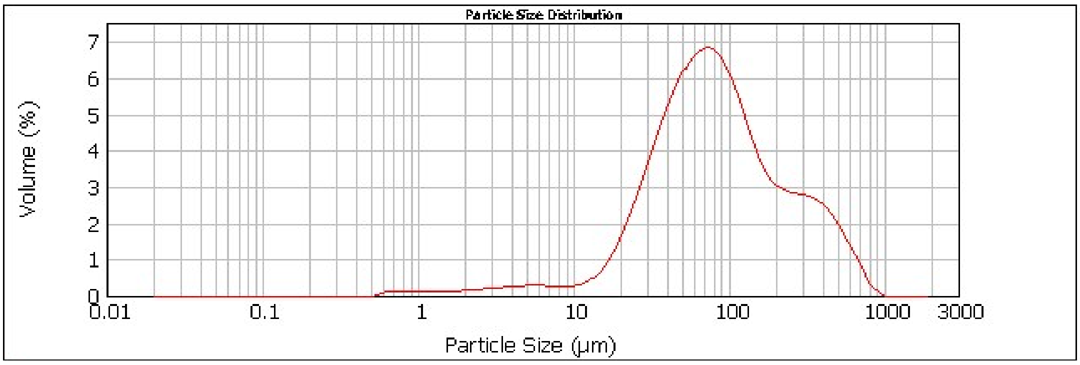


Fig. S2 Particle size distribution of original microcrystalline α-cellulose.

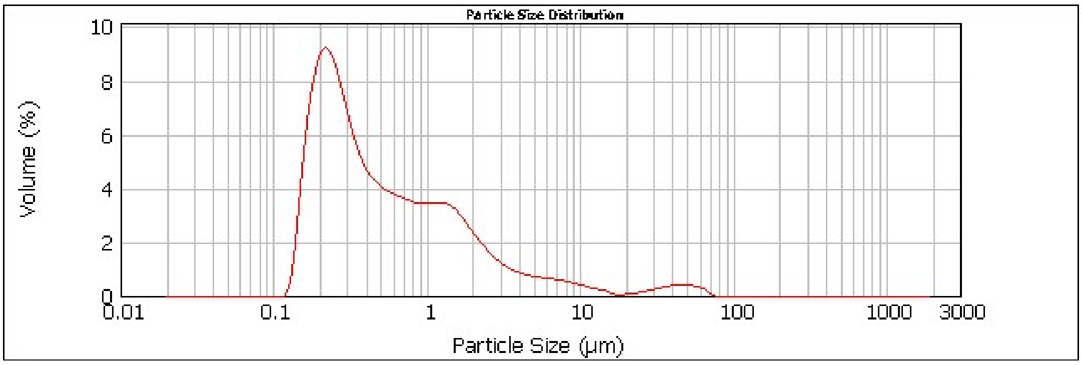


Fig. S3 Particle size distribution of ball-milled microcrystalline α-cellulose.

Fig. S4 Colloidal cellulose suspension in water prepared by ball-milling of microcrystalline α-cellulose

Fig. S5 Cellulose polymer obtained by drying the cellulose nanoparticles.

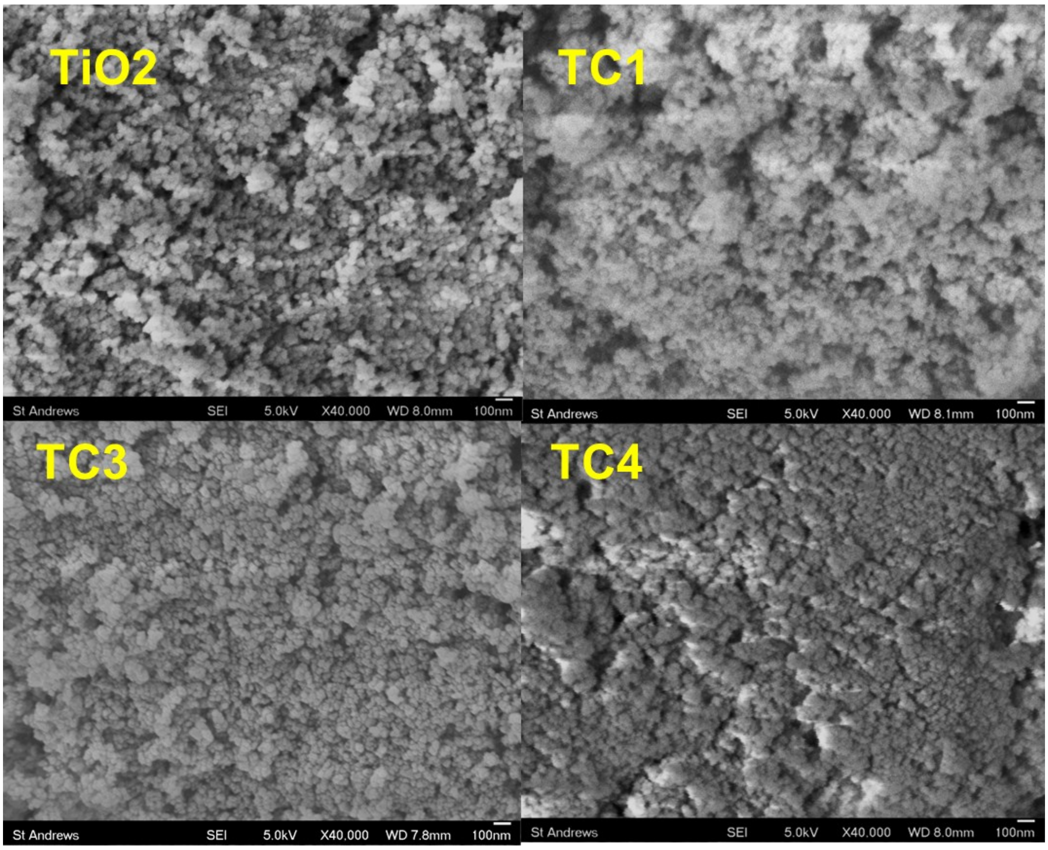


Fig. S6 SEM images of pure TiO_2 nanoparticles and cellulose immobilized TiO_2 nanoparticles

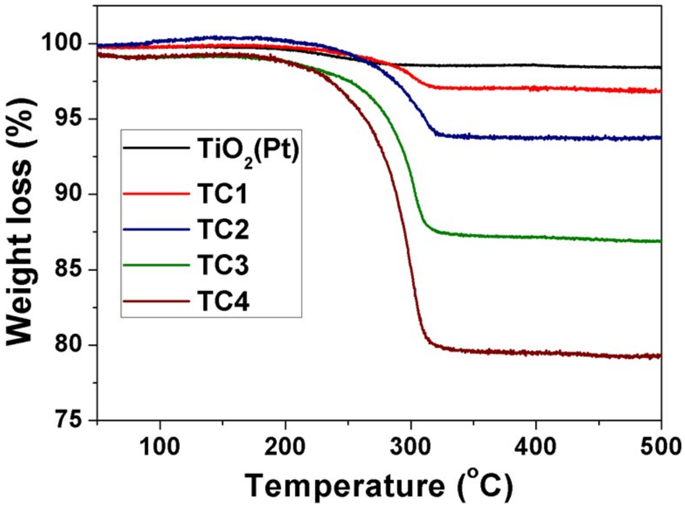


Fig. S7 Thermo-gravimetric analysis (TGA) of pure TiO_2(Pt) and cellulose immobilized TiO_2 samples.

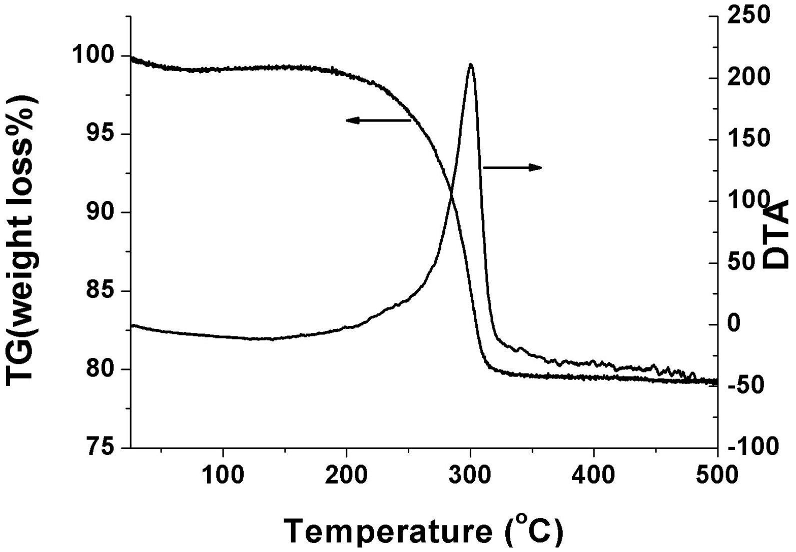


Fig. S8 TG-DTA analysis of TC4 sample in the air with a ramping rate of 4 °C/min.

Table S1 Elemental analysis of cellulose immobilized TiO_2 samples.

Sample	Cellulose (ml)	C (wt.%)	H (wt.%)	O (wt.%)	Total (wt.%) (CHN)	Total (wt.%) (TGA)
TC1	8	1.71	<0.1	1.9	3.61	3.0
TC2	20	3.15	0.36	3.5	7.11	6.5
TC3	40	5..86	0.71	6.5	13.07	13.0
TC4	80	9.68	1.23	10.75	21.66	20.5

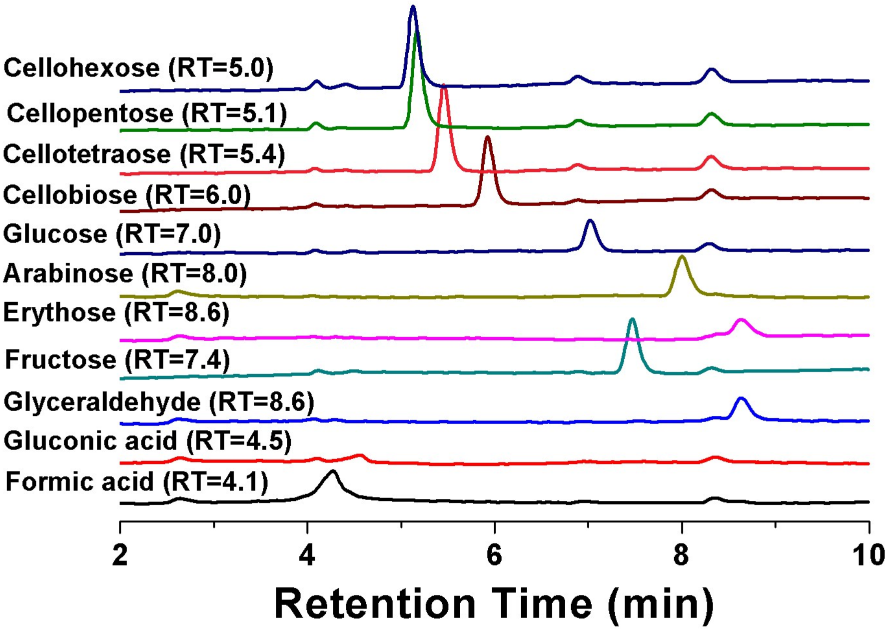


Fig. S9 HPLC profiles of standard sugars and organic acids.

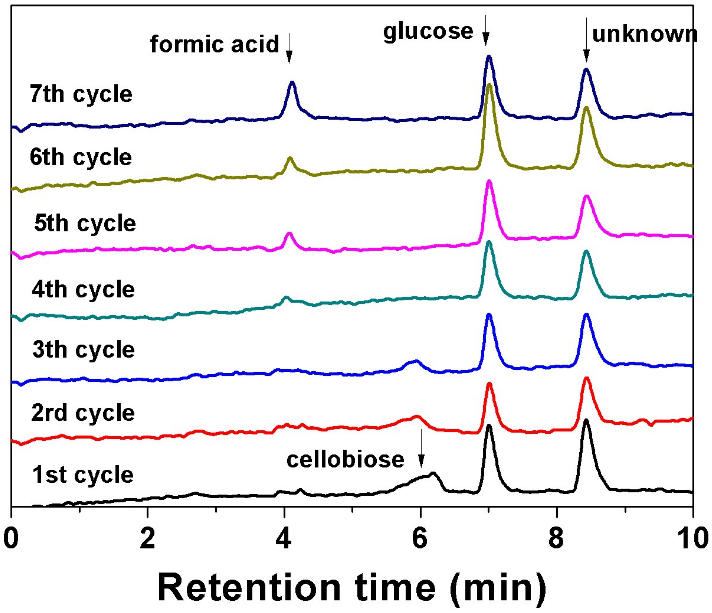


Fig. S10 HPLC measurements of aqueous solution from TC4 sample during the repeated cycles.

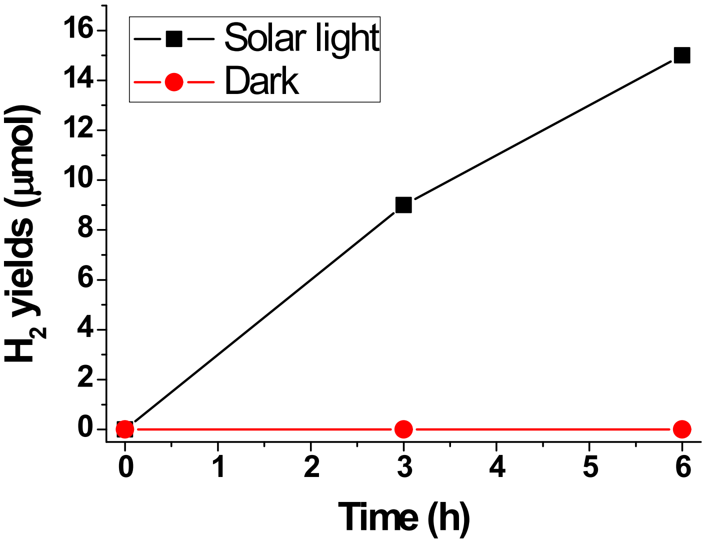


Fig. S11 Photocatalytic H_2 production from TC4 sample under natural solar light irradiation and in dark.

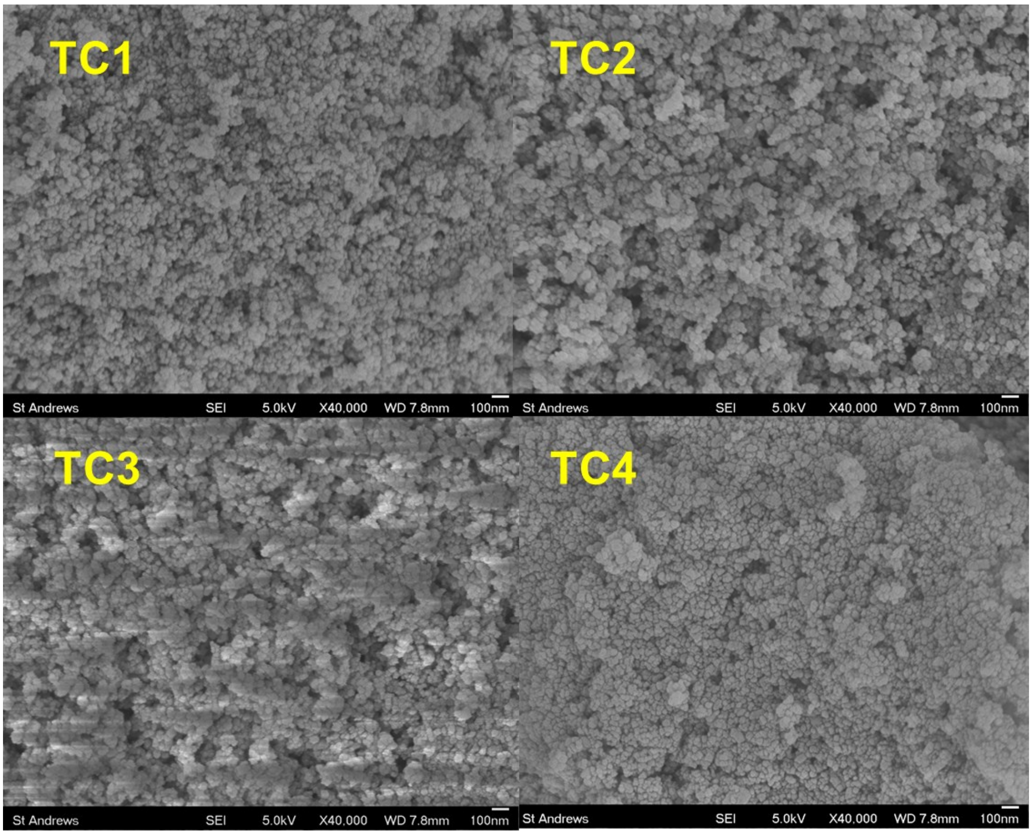


Fig. S12 SEM images of cellulose immobilized samples after photocatalytic tests.

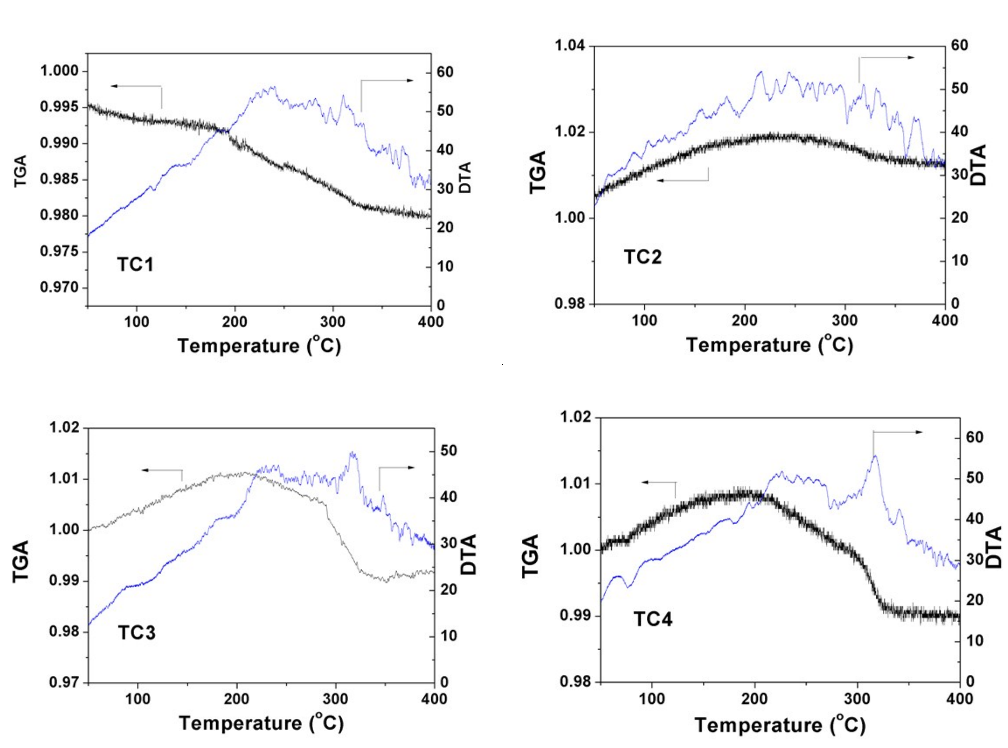


Fig. S13 TG-DTA curves of cellulose immobilized samples after photocatalytic tests.

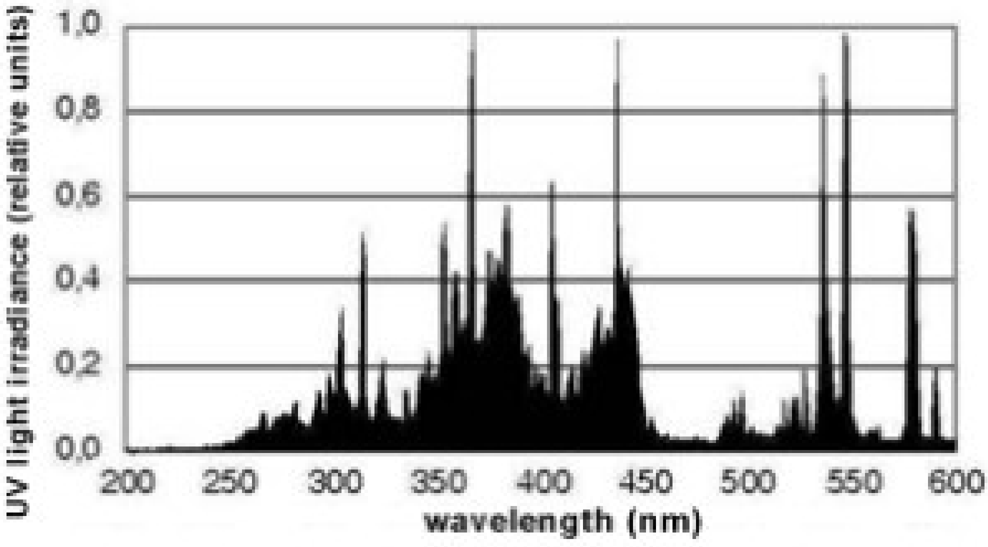


Fig. S14 Emission spectrum for Iron doped metal halide UV lamp (Source from google photos)