Green Synthesized ZnO Nanocatalysts for Rapid and Effective Visible-Light Degradation of Industrial Dyes

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Supplementary Information (SI)

Photocatalytic Studies

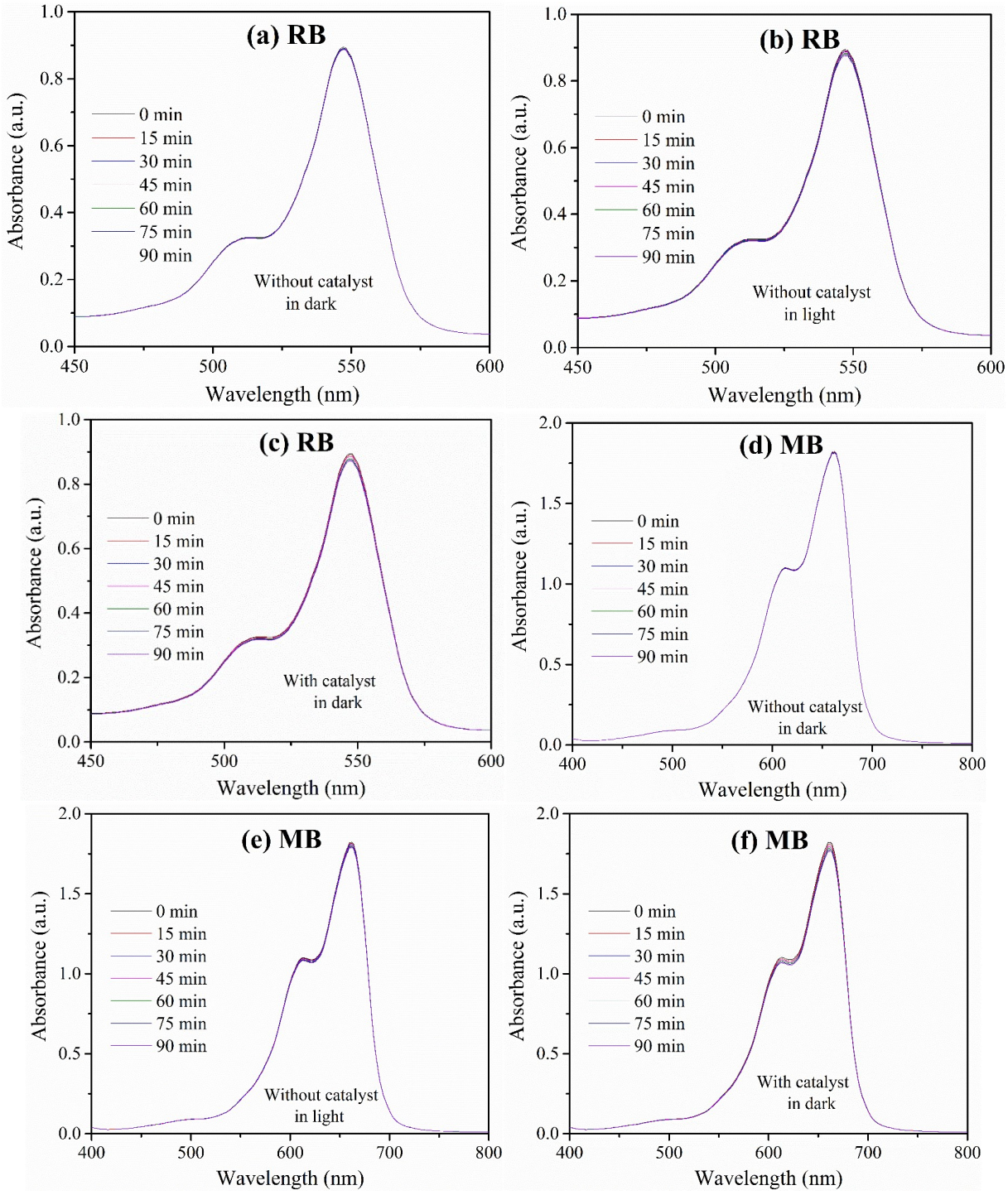

Figure S1 (a-f) Time-dependent absorption spectra of RB and MB recorded up to 90 mins under various experimental conditions.

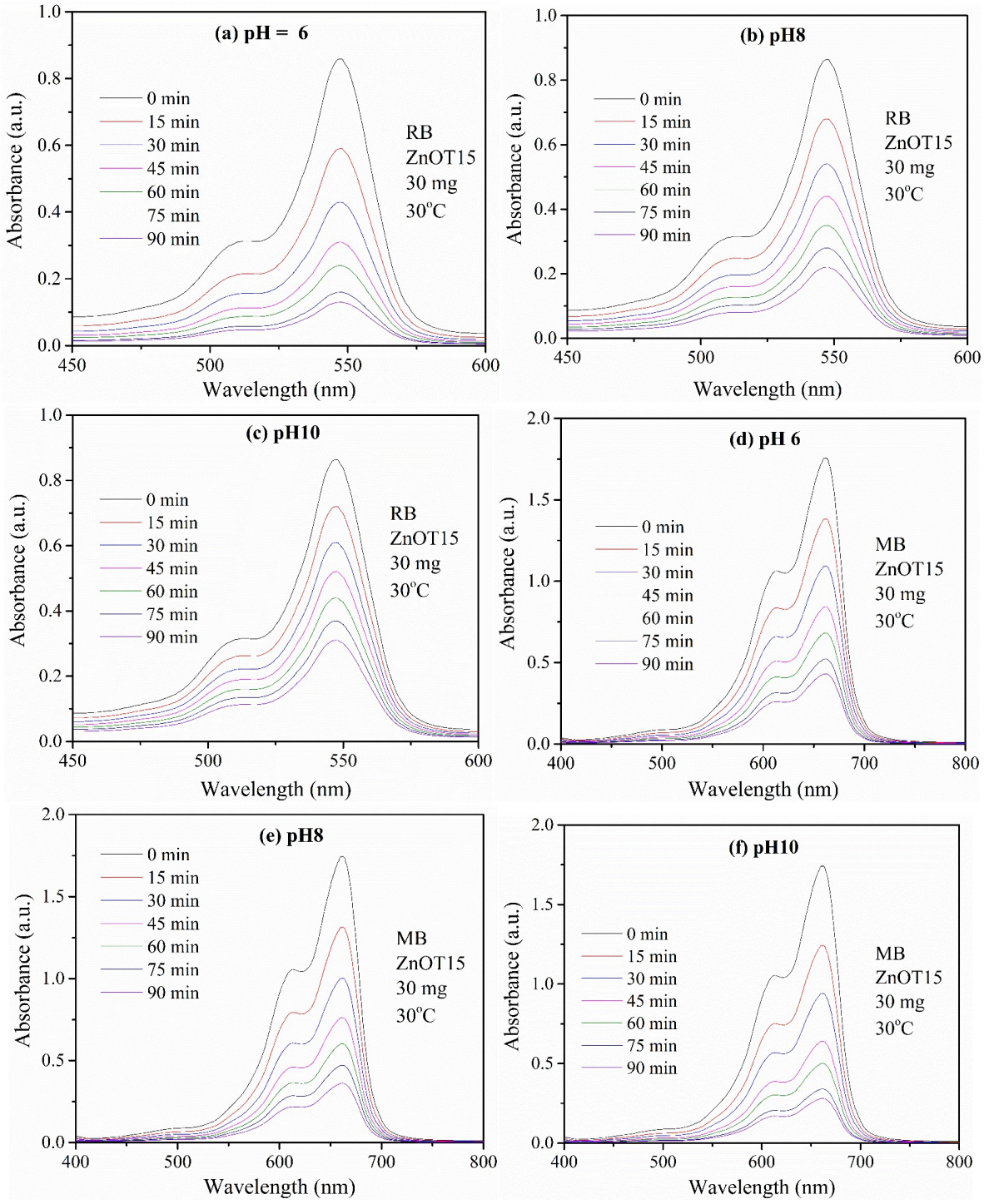

Figure S2 (a-c) and (d-f) Absorption spectra of RB and MB solutions in presence 30 mg of ZnOT15 for different solution pH after different duration of irradiation of light at room temperature.

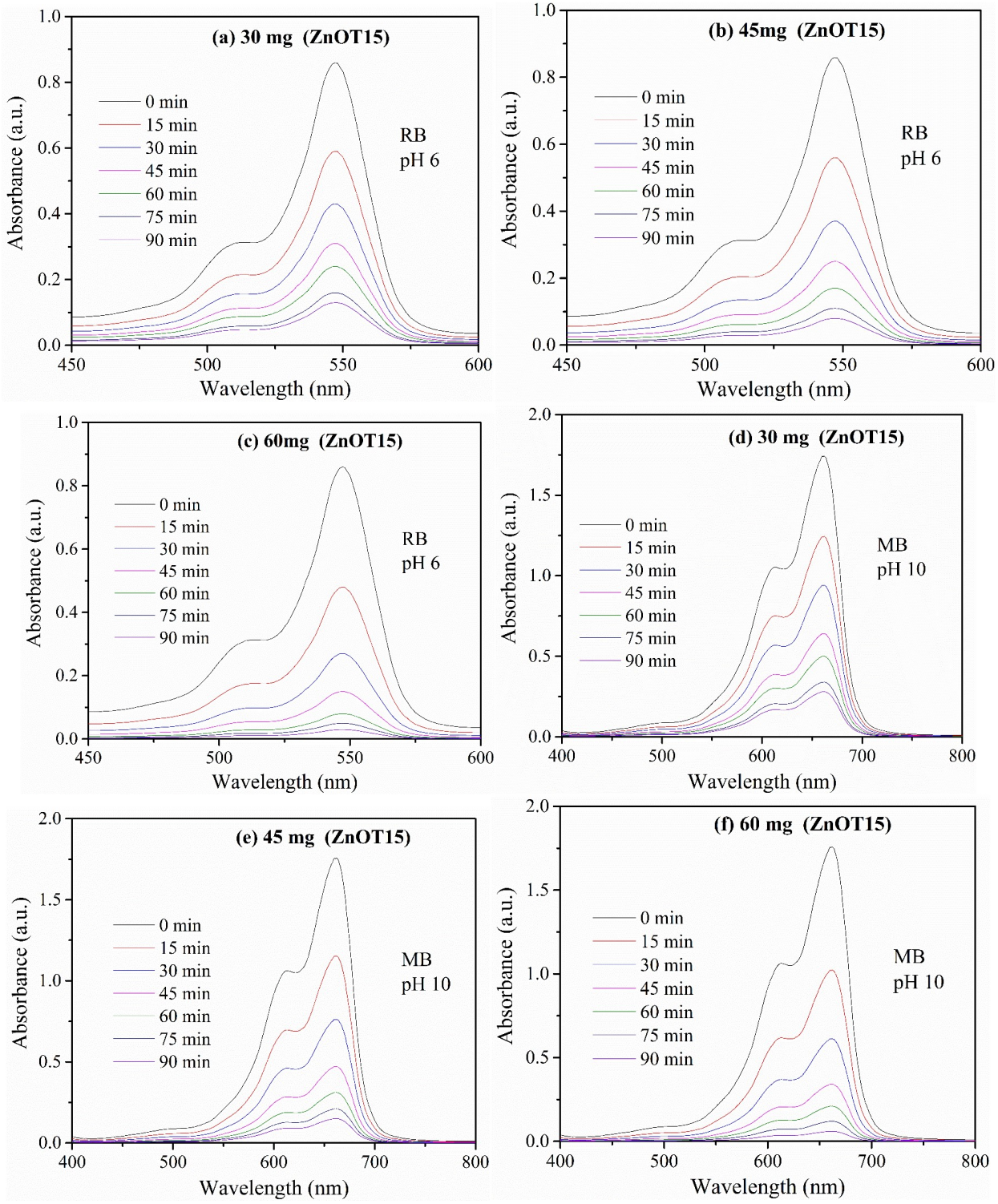

Figure S3 (a-c) and (d-f) Absorption spectra of RB and MB solutions in presence of different amount of ZnOT15 at room temperature, constant solution pH after different duration of irradiation of light.

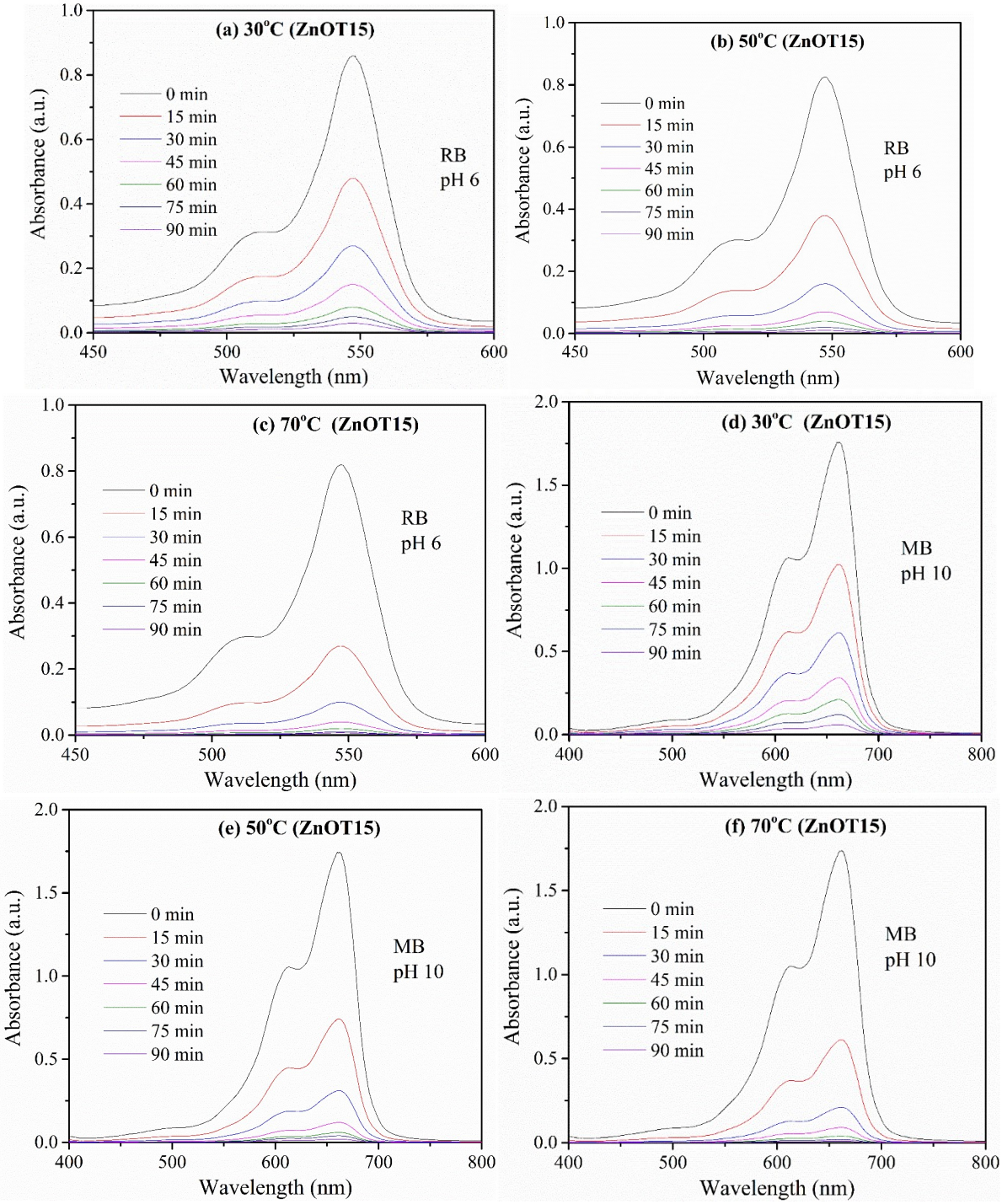

Figure S4 (a-c) and (d-f) Absorption spectra of RB and MB solutions in presence 60 mg of ZnOT15 at constant solution pH at different temperatures after different duration of irradiation of light.

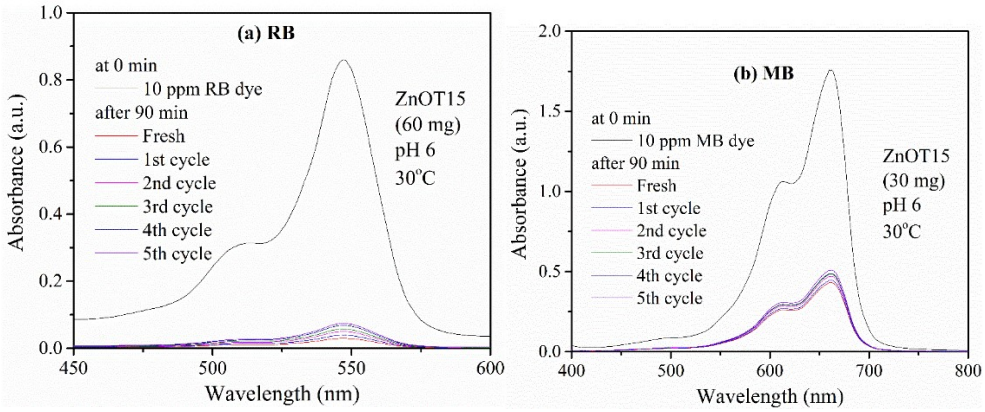

Figure S5 (a) and (b) Absorption spectra after 90 mins light irradiation of RB and MB solution for five recycle with ZnOT15 at room temperature.

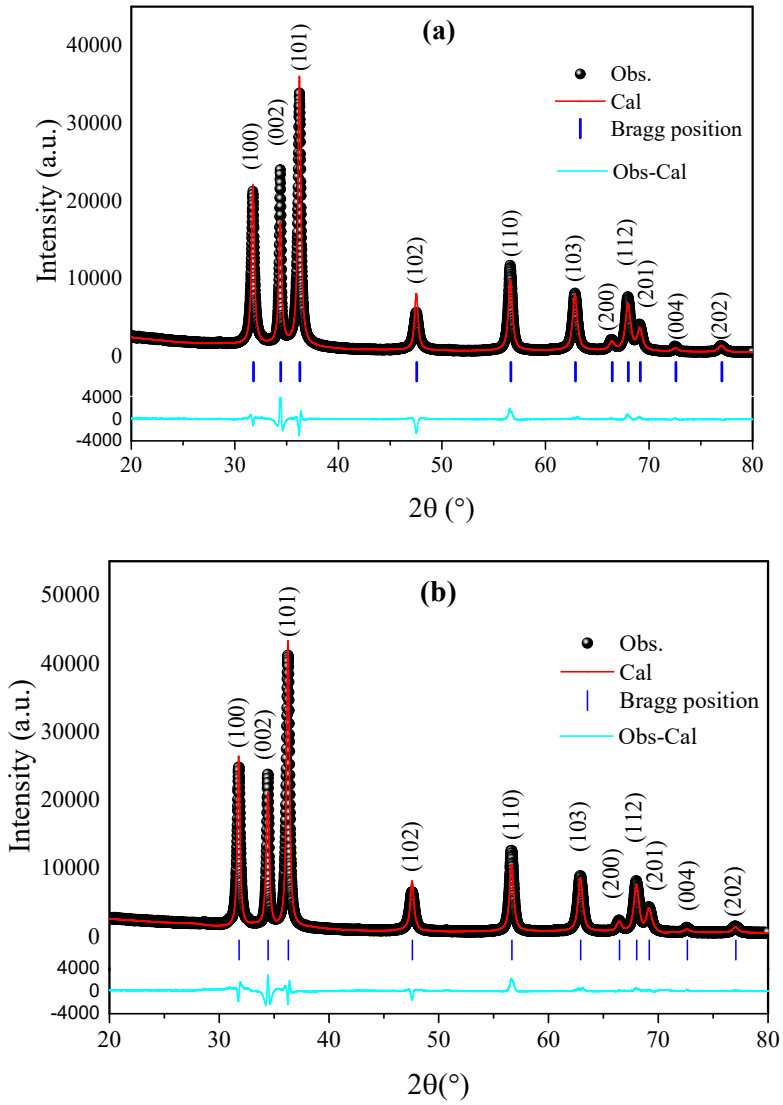

Figure S6 Powder XRD patterns of ZnO samples: (a) as-grown and (b) recycled

Supplementary Table 1 Powder XRD analysis data of green-synthesized ZnO materials: as grown sample and recycle sample.

Sample		Composition	Space group	Lattice parameters			*D* (nm)
				a (Å)	c (Å)	*V* (Å^3)	
ZnOT15	As grown sample	ZnO (100%)	*p63 mc*	*3.247*	*5.206*	*47.557*	23.3
	recycled sample	ZnO (100%)	*p63 mc*	3.245	5.201	47.459	23.9

Synthesis & Characterization of Materials

Synthesis of Materials

Zinc acetate dihydrate, $Zn(CH_3COO)_2$. $2H_2O$ was used as zinc source while KOH was used to control pH. All chemicals were purchased from Merck L Sc. Pvt. Ltd. (India). These were of high purity and used without any further purification. Fresh *T. divarricata* flowers were collected.

Fresh and clean *T. divaricata* flower were dried in sunlight for four days. Then these dried flowers were finely powdered using grinder. 10 g of such fine powders were heated at 80^{o}C in 100 ml of distilled water for 15 minutes under constant stirring. The solution was then cooled down to room temperature and filtered repeatedly to remove any particulate matter. A light brown solution was obtained as the *T. divaricata* flower extract (hereafter denoted as TFE) which kept refrigerated for further synthesis. To prepare the ZnO, following literature method, firstly 0.01M zinc acetate dihydrate was dissolved into 100 mL of distilled water and the solution (*A*) was kept under continuous stirring for 30 minutes. Another solution (*B*) was prepared by dissolving 0.2M KOH in 100 mL distilled water. For the synthesis of pure ZnO, solution *B* was added dropwise to solution *A*, which immediately resulted in to a white-colored solution. This solution was then heated at 80^{o}C for 1 hr. which ultimately gave rise to a white precipitate. This precipitate was collected, filtered and washed with water and acetone repeatedly. Finally, the filtrate was dried in air at 80^{o}C for 4 hrs. giving rise to the pure ZnO sample (say, ZnO0). For the green synthesis of TFE-capped ZnO, solutions *A* and *B* were separately prepared as discussed above. In the typical synthesis of TFE-capped ZnO sample, 5mL of TFE was initially added to *A*. The rest of the synthesis remained the same as described for ZnO0. The sample thus produced was termed ZnO5. Similarly, other TFE-capped samples were synthesized by varying the amount of TFE (10 mL for ZnO10 and 15 mL for ZnO15). For all synthesis, pH of the reaction medium was maintained at 11. All dried samples were finely powdered by mortar and pestle for characterization studies.

Characterization of Materials

The synthesized materials were used for physical characterization – FTIR, powder XRD, UV-Vis, photoluminescence (PL), Raman, SEM, EDX and TEM studies. FTIR study was done with BRUKER INVENIO R. Powder XRD study was carried out with Rigaku Smart Lab X-RAY diffractometer with wavelength of 1.5405Å. The UV-Vis spectra were taken with a Cary-5000 UV-VIS-NIR spectrometer in diffused reflectance spectra (DRS) mode. PL and Raman spectroscopy were done with Confocal Raman Microscope of HORIBA Scientific (Lab RAM HR Evolution). Field emission scanning electron microscope (FE-SEM) images were obtained using ZEISS Gemini instrument with 30 kV accelerating voltage. Atomic percentage and elemental information from Energy Dispersive X-ray Spectroscopy (EDS) were collected using Octane Elect EDS system with Silicon Drift Detector (SDD) technology attached to the FE-SEM system and using analysis APEX^{TM} software. Transmission electron microscope (TEM) images were obtained using JEM-F200 F2 Multipurpose Analytical S/TEM.

Characterization Results

X-ray Diffraction (XRD) Analysis

Powder XRD patterns of ZnO0, ZnO5, ZnO10 and ZnO15 confirm the formation of single-phase hexagonal wurtzite ZnO (JCPDS 36-1451; space group $P6_3mc$). The main reflections indexed to the (100), (002), (101), (102), (110) and (103) planes show no evidence of impurity phases. With increasing extract concentration, slight variations in peak broadening and position are observed, indicating subtle modifications in crystallite growth. Crystallite size shows a gradual increase, while both dislocation density and lattice strain decrease, suggesting improved crystallinity and reduced defect levels in the extract-assisted samples.

FTIR Analysis

FTIR spectra of all samples show characteristic Zn–O stretching vibrations near 376 and 669 cm^{-1}, confirming ZnO lattice formation. A broad O–H stretching band around 3392 cm^{-1} corresponds to surface-adsorbed moisture or hydroxyls. Additional features associated with amines, CO_2, phenolic C=O, C–O–C and C=C stretching originate from phytochemicals extract. These functional groups indicate their role as reducing and capping agents during ZnO nanoparticle synthesis.

UV–Visible Optical Properties

UV–Vis DRS spectra show the absorption edges of the samples in the 388–395 nm region. A modest red-shift with increasing extract concentration suggests modification of surface states and particle growth. The calculated direct optical band gap decreases slightly from 3.20 eV (ZnO0) to 3.14 eV (ZnO15), consistent with larger crystallite sizes and reduced quantum confinement. Tauc plot analyses for direct and indirect transitions confirm the trend in band gap narrowing and highlight the influence of extract-mediated defect states.

Photoluminescence (PL) Characteristics

PL spectra recorded at 350 nm excitation display multiple emissions extending from the violet to the near-infrared region. For the ZnO0 sample, visible emission bands are attributed to intrinsic point defects such as zinc interstitials (Zn_i), zinc vacancies (V_{Zn}), oxygen interstitials (O_i) and oxygen vacancies (V_O). Changes in emission intensity and peak position across the sample series indicate variations in defect population with increasing extract concentration. These observations support the construction of a defect-level energy diagram illustrating the recombination pathways in the materials.

Raman Spectroscopy

Raman spectra of the synthesized ZnO nanoparticles exhibit the characteristic phonon modes of the wurtzite phase, including the prominent E_2(high) mode at 431–436 cm^{-1} and the $A_{1\text{-}TO}$, $A_{1\text{-}T}$ and $E_{1\text{-}LO}$ modes near 322–330, ~380 and 573–578 cm^{-1}, respectively. The dominance of

the $E_{2(high)}$ mode reflects good crystallinity. Slight peak shifts and broadening with increasing extract concentration suggest mild variations in lattice order attributable to interactions between ZnO surfaces and phytochemicals during growth.

Morphological and Elemental Characterisation

FESEM Analysis: FESEM images reveal quasi-spherical ZnO nanoparticles with noticeable agglomeration, which is typical for ZnO due to its high surface energy. The particle size increases from ~52 nm to ~62 nm with increasing extract concentration, indicating controlled grain growth facilitated by biomolecules from the extract.

EDX Composition Analysis: EDX spectra display only Zn and O signals, confirming the purity of the samples. The atomic percentage of Zn shows a slight increase while that of O decreases with extract concentration, suggesting generation of oxygen vacancies under the reducing environment provided by the extract.

TEM and HRTEM Analysis: TEM images reveal small, agglomerated nanoparticles consistent with FESEM observations. HRTEM micrographs exhibit clear lattice fringes, indicating the crystalline nature of the particles. The interplanar spacing measured as 2.59 Å corresponds to the (002) plane of wurtzite ZnO. SAED patterns show distinct diffraction rings indexed to the (110) and (002) planes, confirming the polycrystalline wurtzite structure.