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Electronic Supplementary information:

Physicochemical Insights of Irradiation-Enhanced Hydroxyl Radical Generation from ZnO Nanoparticles

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Figure S1-a

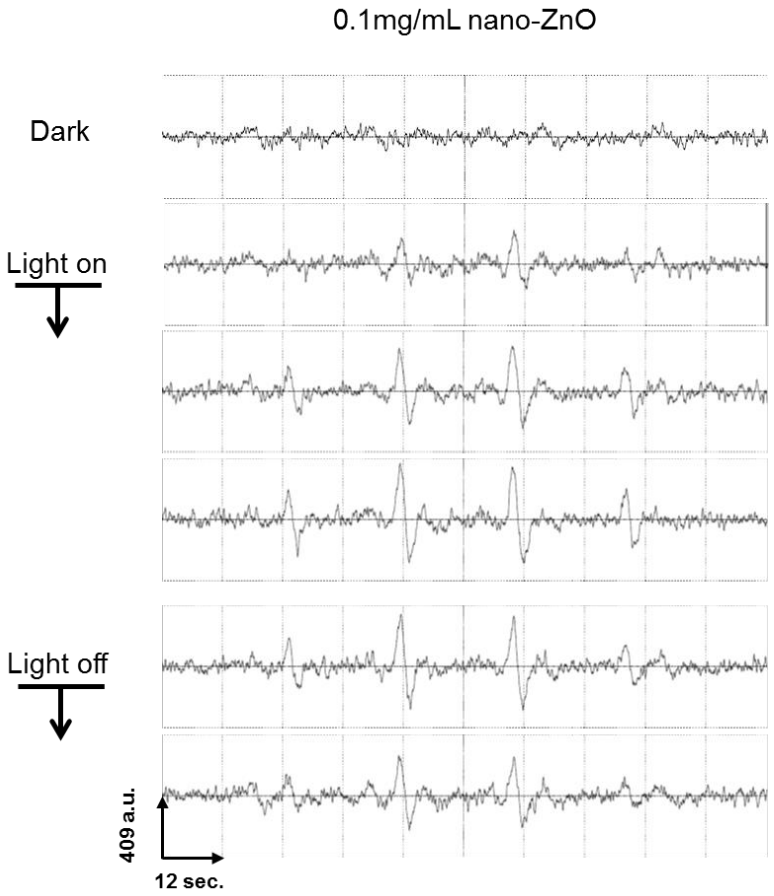

Figure S1-b

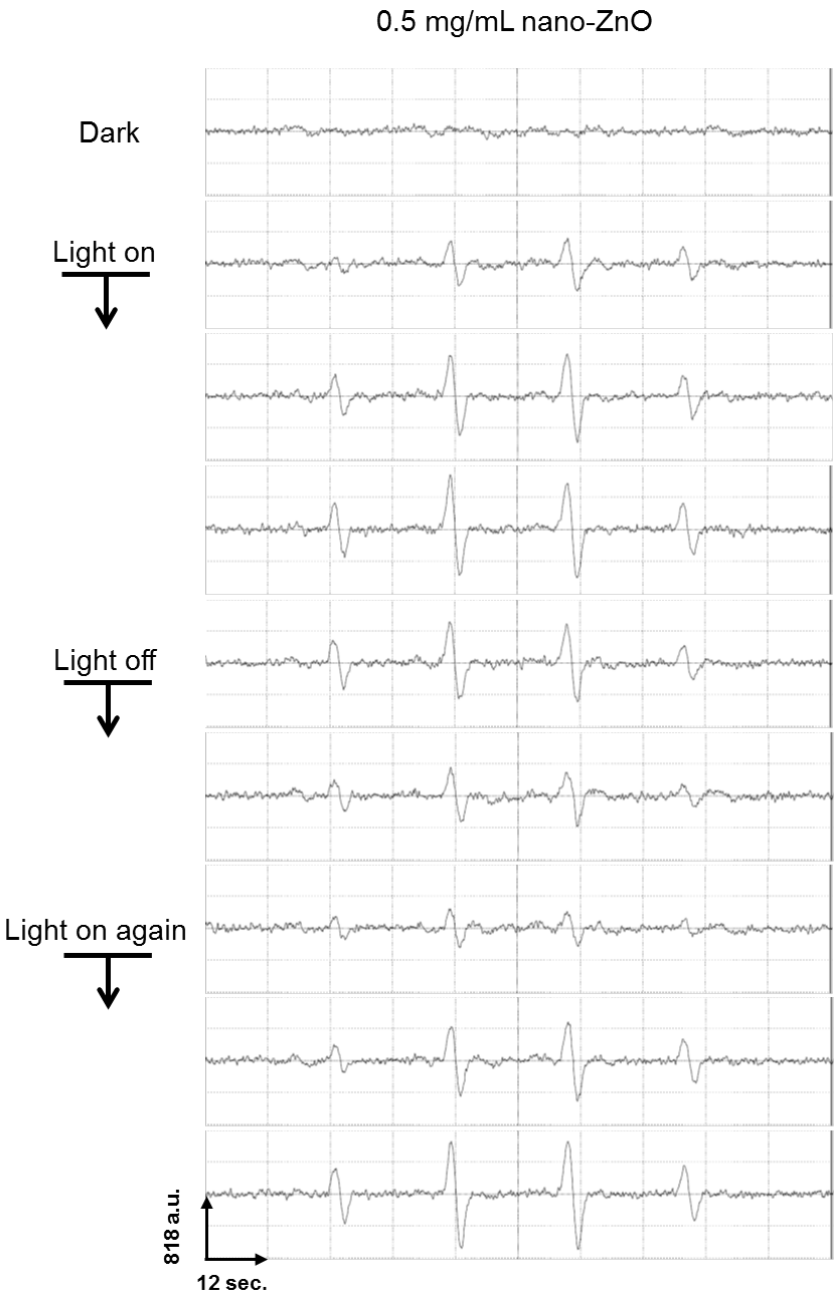
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Figure S1-c

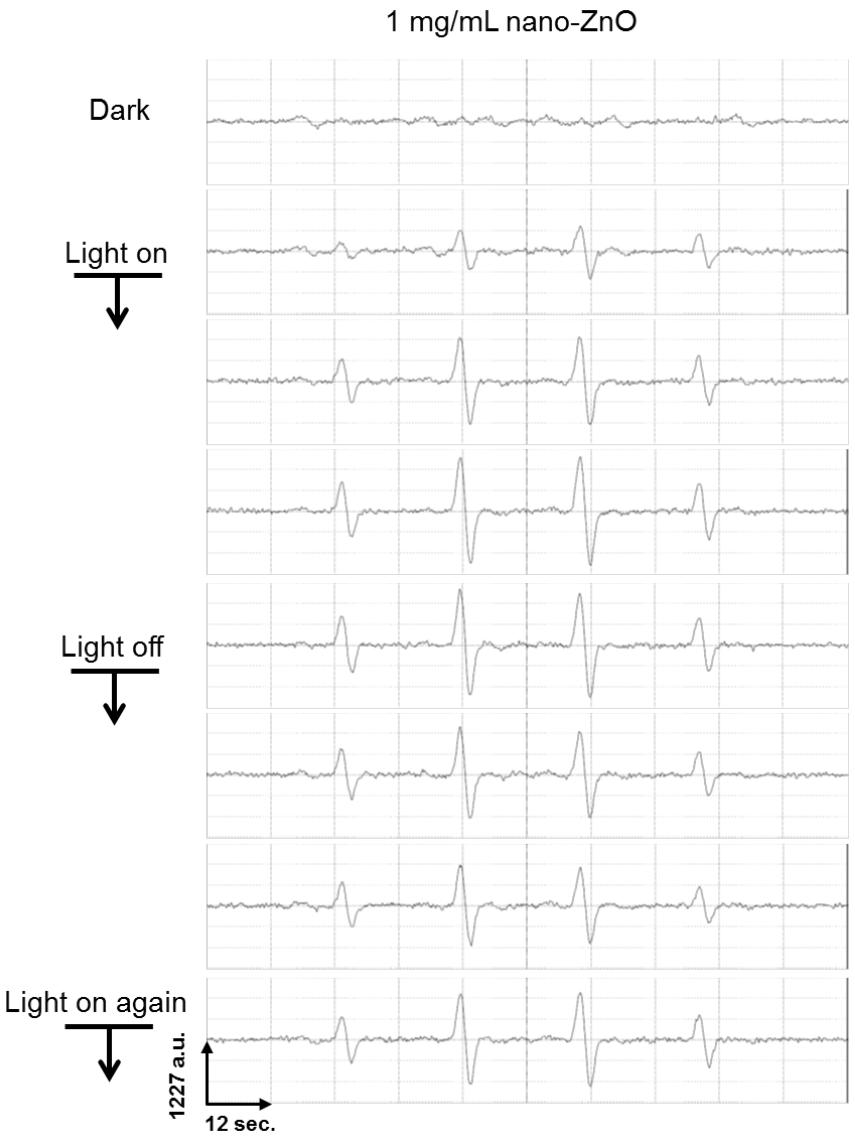
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Figure S1-d

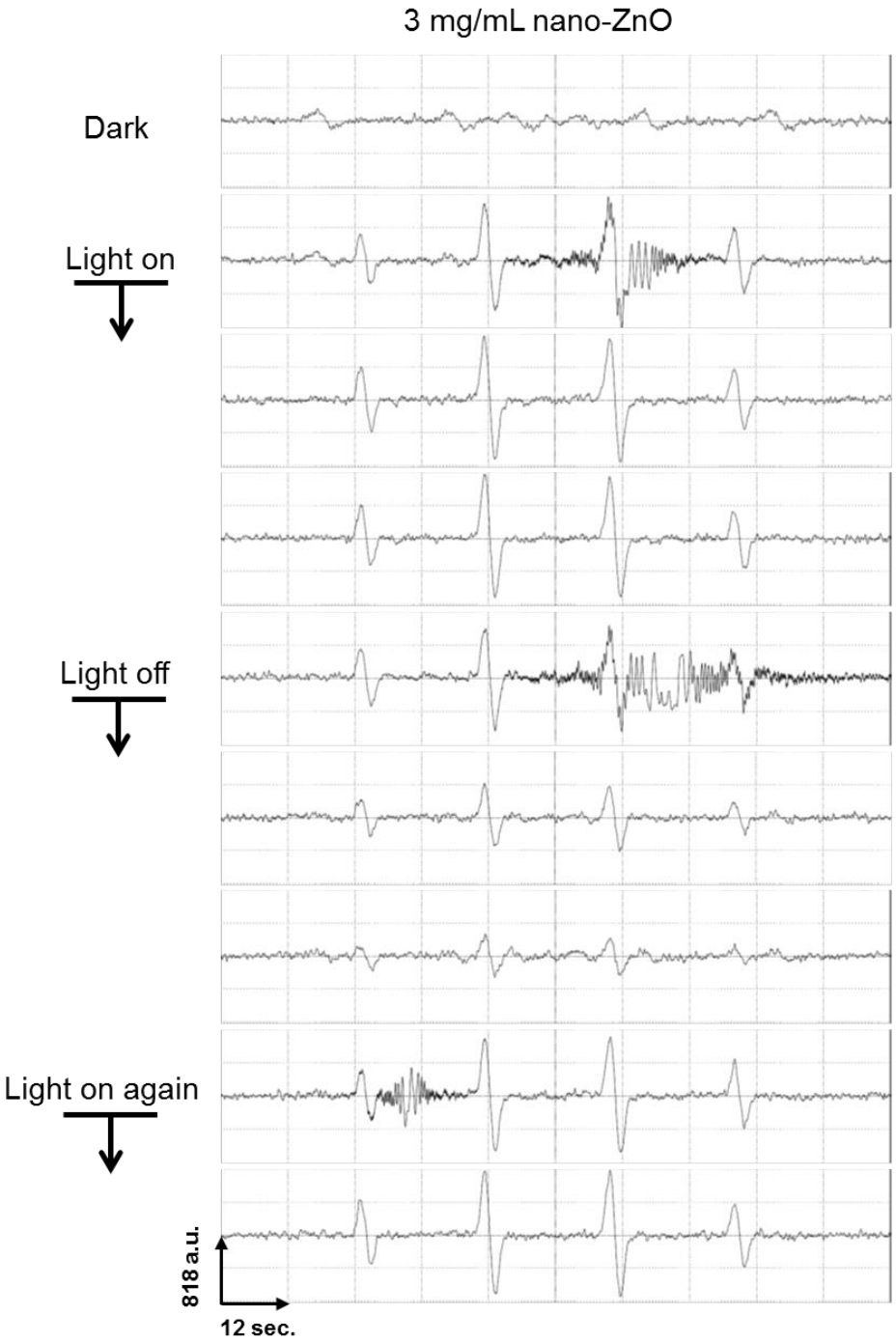
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Figure S1-e

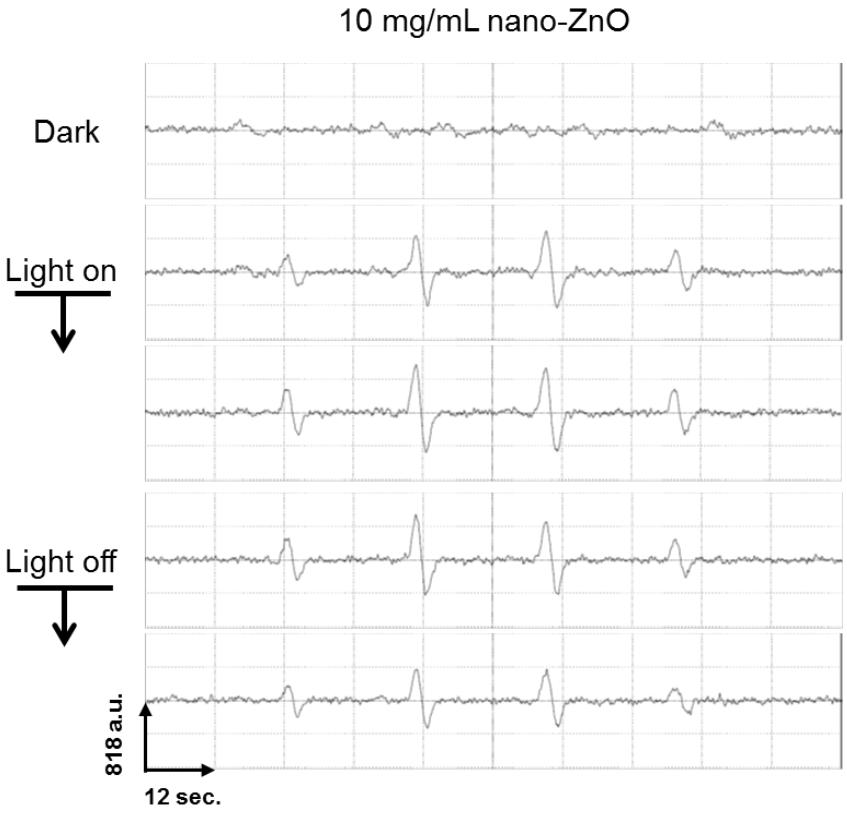


Figure S1-f

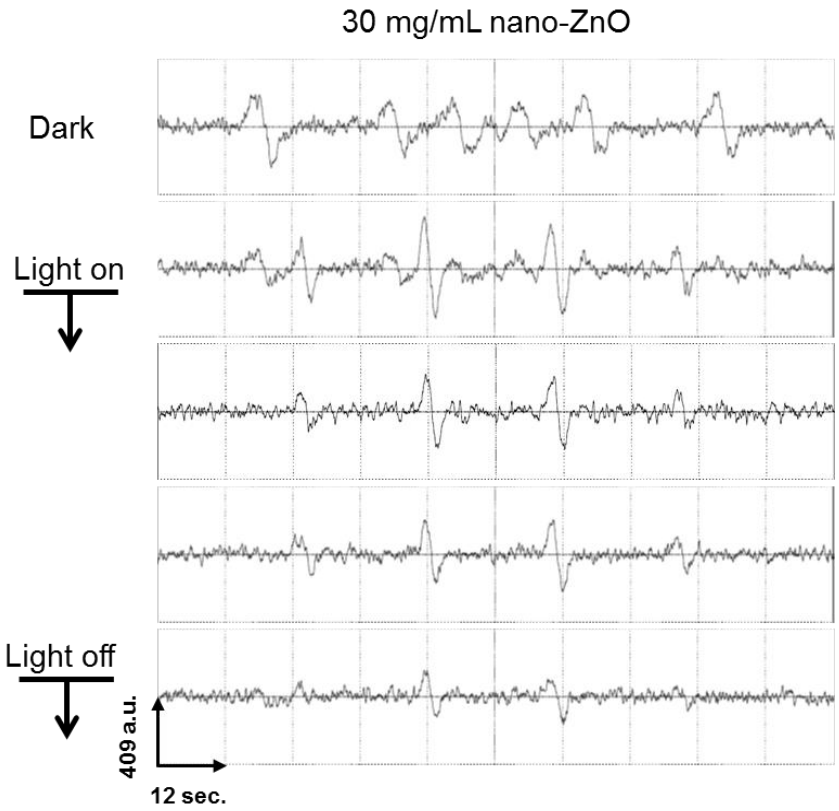


Figure S1 Electron spin resonance analysis of free hydroxyl radicals production under irradiation by 50-70 nm ZnO nanoparticles in aqueous suspension with different dosages of 0.1, 0.5, 1, 3, 10 and 30 mg/mL as a function of time.

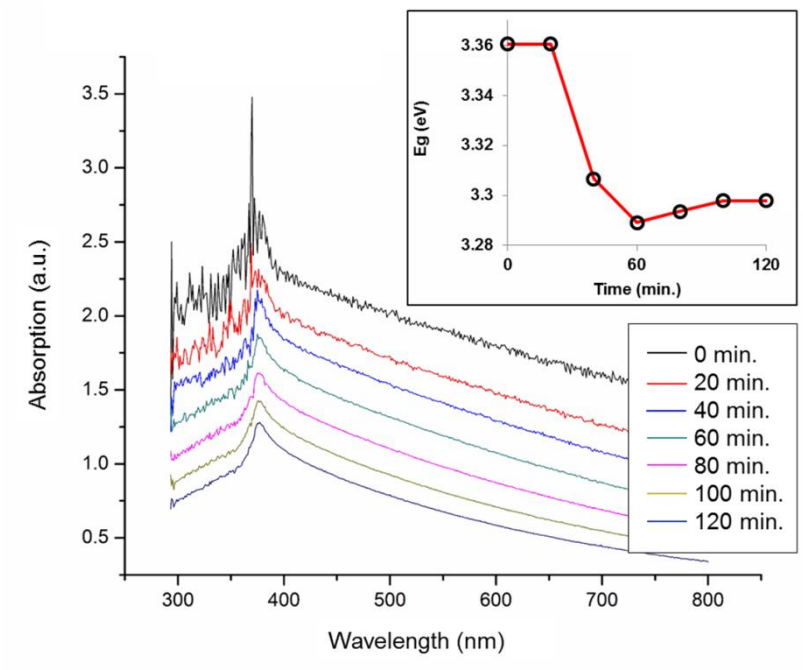
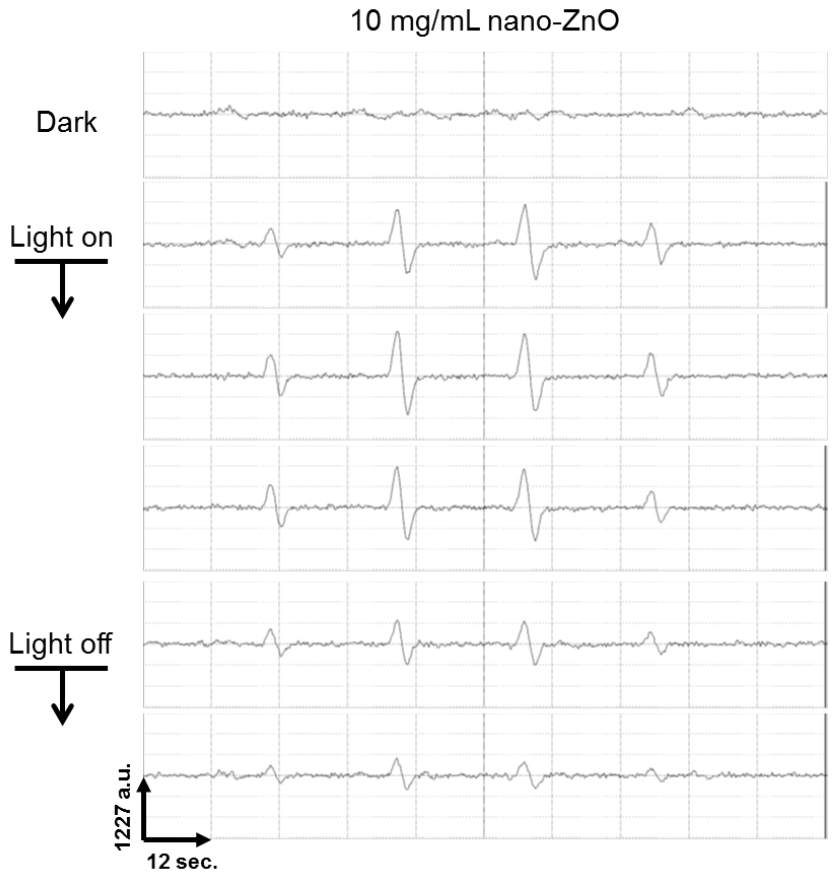


Figure S2 UV/Vis absorption measurement and calculated band gap energy (E_g) plotting (inset) of 1 mg/mL 50-70 nm ZnO aqueous suspension for two hours under irradiation.

Figure S3-a



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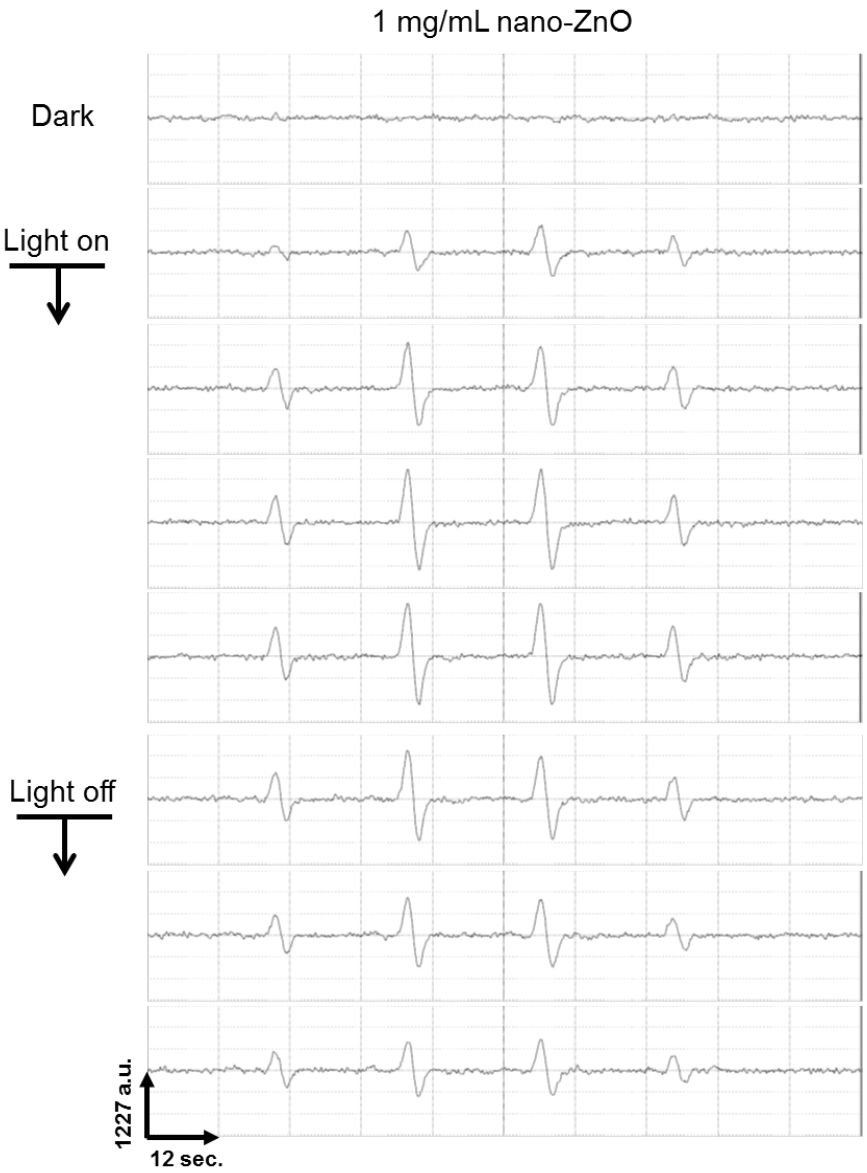

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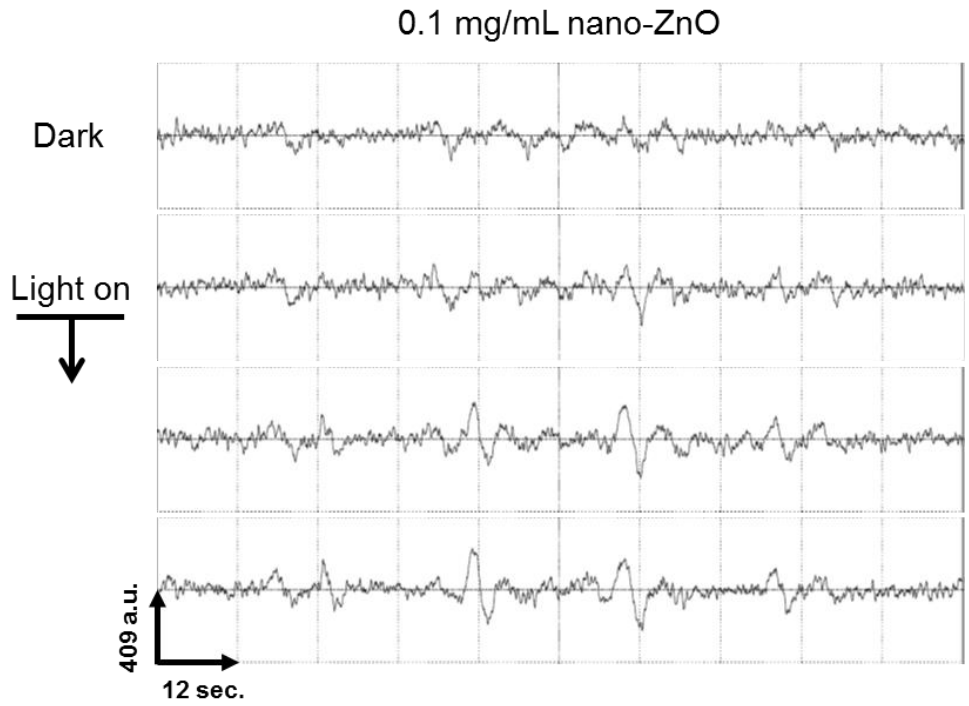

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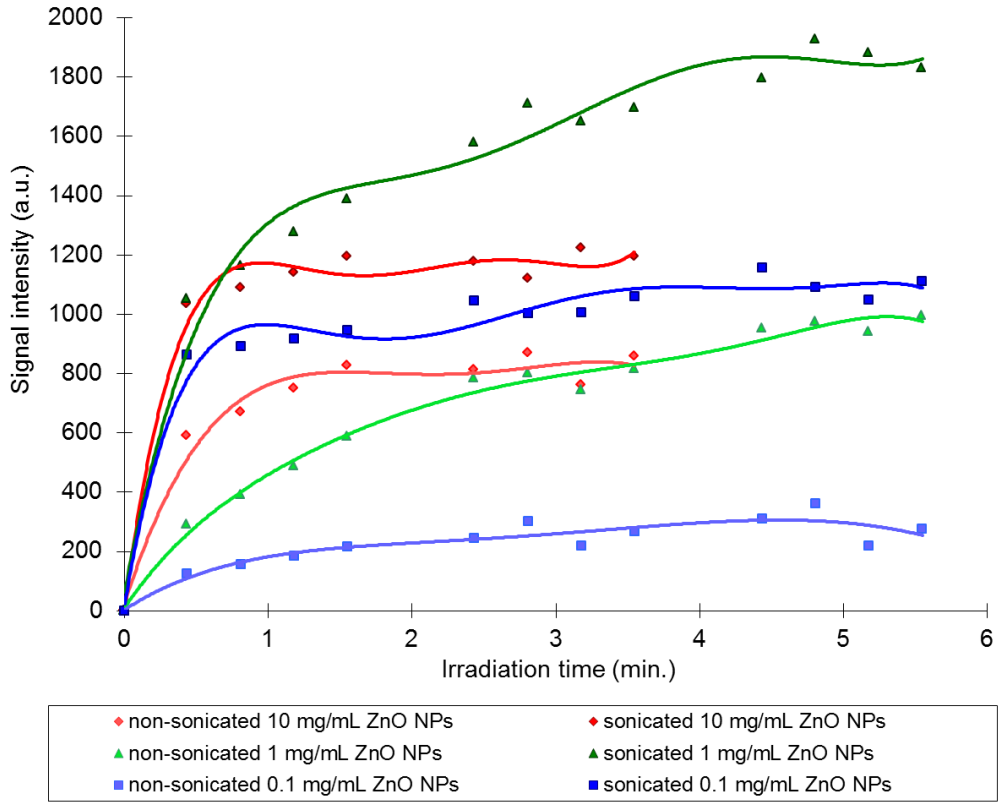


Figure S3 Effect of ultrasonication on ESR signal intensity of 10, 1 and 0.1 mg/mL 50-70 nm ZnO NPs.

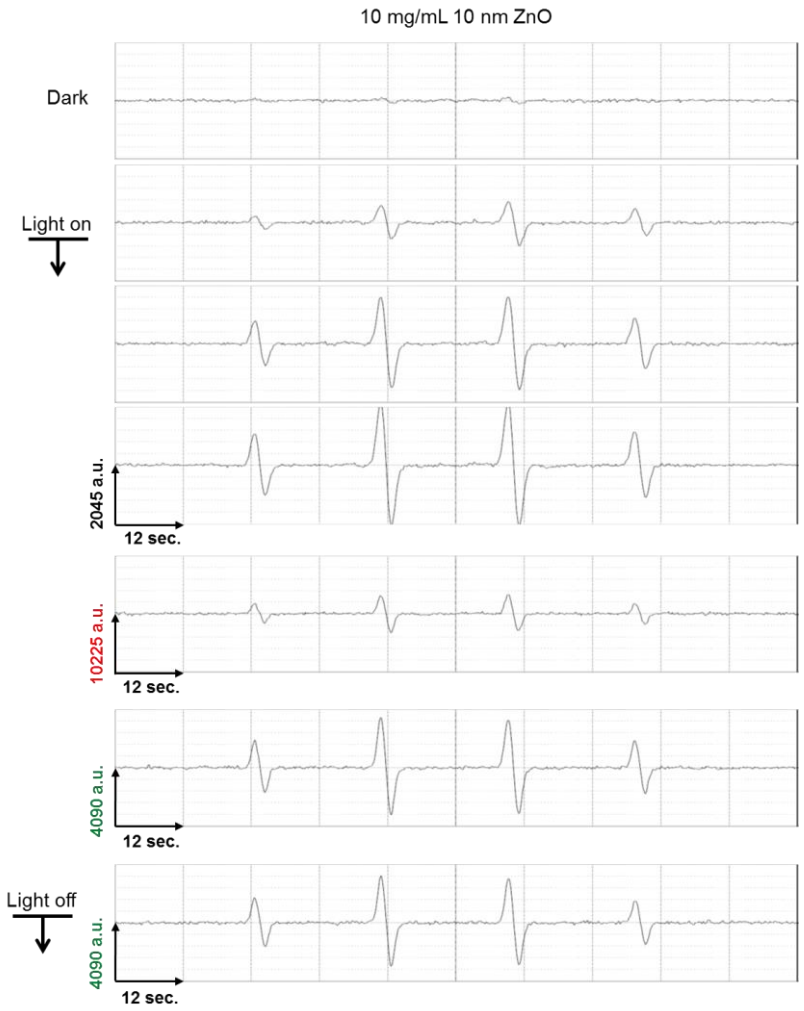


Figure S4 ESR signals of irradiating 10 mg/mL ZnO NPs (10 nm) in aqueous suspension for 10 minutes.

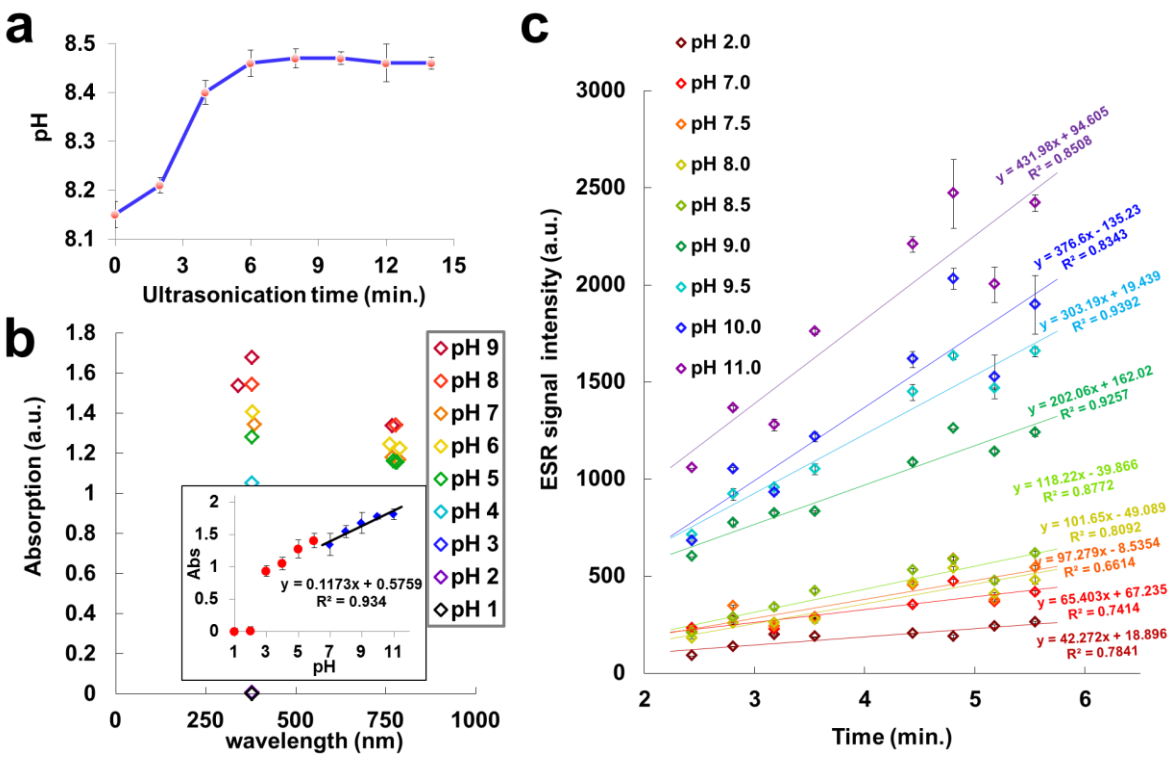
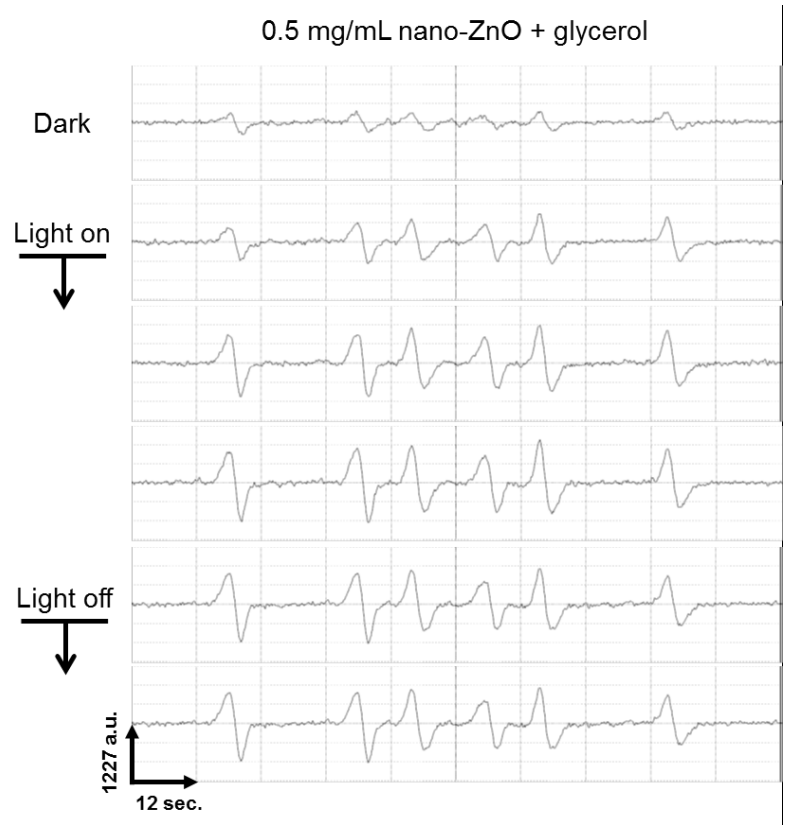


Figure S5 a) Influence of ultrasonication on the pH of freshly made ZnO NPs suspension. Again, 1 mg/mL 50-70 nm ZnO NPs was used combined with the PBS solution. The PBS buffer pH had been adjusted to 7.4 before mixing with NPs. **b**) UV/Vis absorption behavior of ZnO NP suspension under varied pH conditions. Inset: Linear correlation plot of ZnO NP suspension absorption vs. basic pH conditions. Acidic condition (> pH 3) also support a linear Abs./pH correlation, but it is apparently different from basic side. **c**) The initial •OH generation rate plotted based on ESR signal intensity vs. the first four-minute's irradiation time. Triplicated data was acquired for statistical analysis.


0.5 mg/mL nano-ZnO + glycerol
Dark
Light on
Light off
1227 a.u.
12 sec.

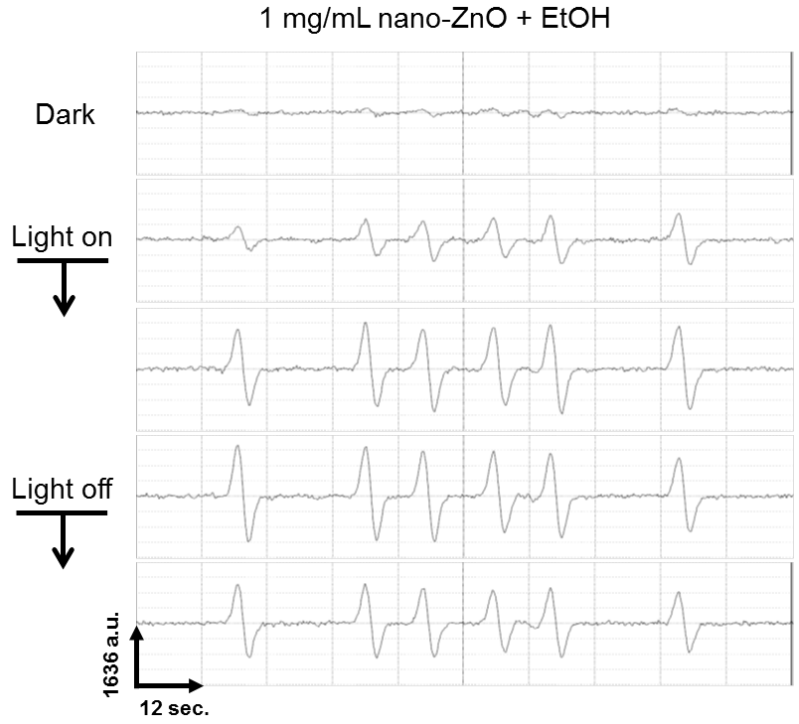

1 mg/mL nano-ZnO + EtOH
Dark
Light on
Light off
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Figure S6 ESR spectra of the DMPO-trapped radicals obtained through irradiation of 50-70 nm ZnO in glycerol or ethanol (EtOH).

Figure S7-a

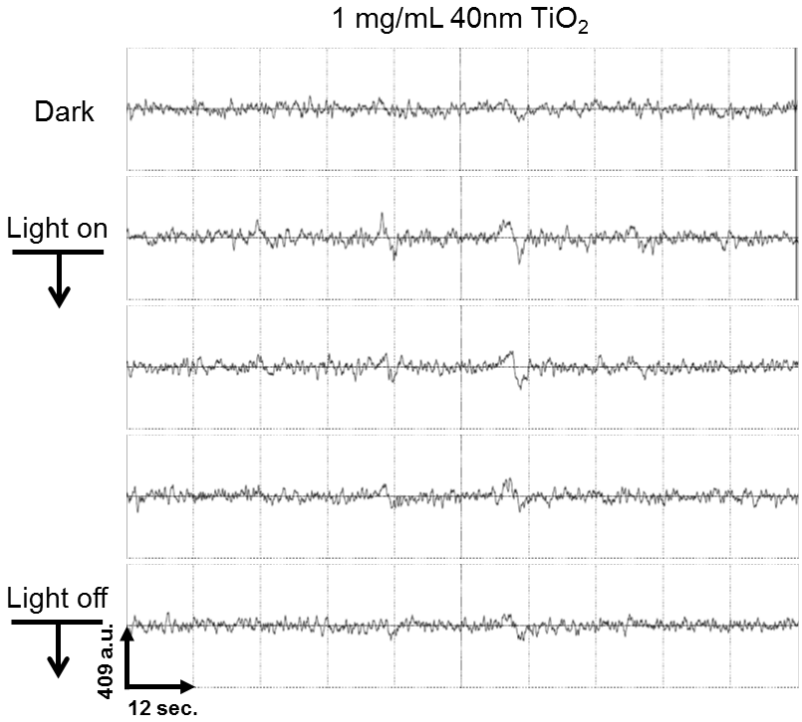

Figure S7-b

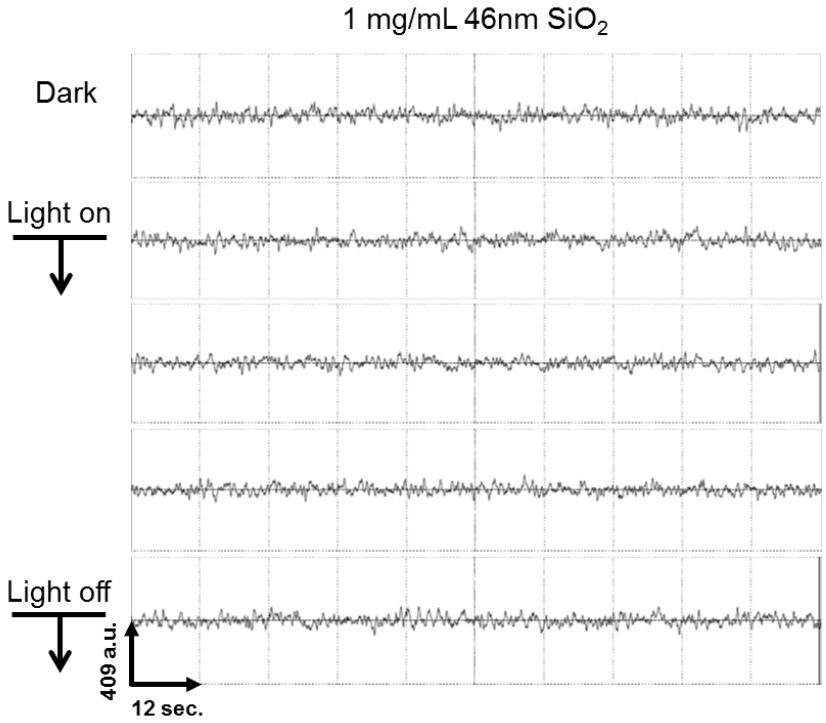

Figure S7-c

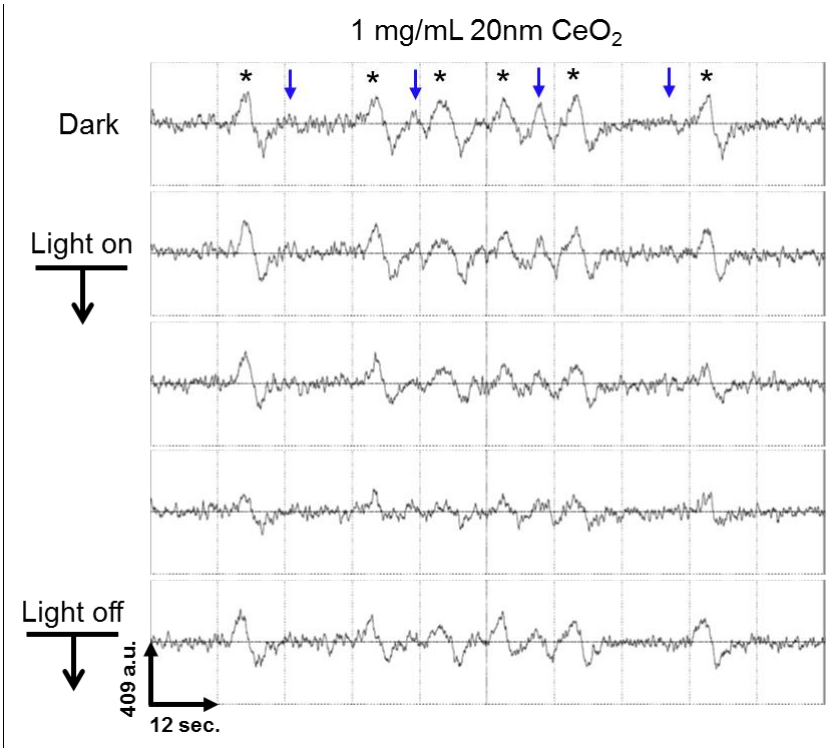

Figure S7 ESR spectrum of DMPO-trapped-radicals generated by irradiation on 1 mg/mL of TiO_2, SiO_2 or CeO_2 NPs with similar fabricated sizes. Labelled positions denote hydroxyl (blue arrow) and carbon-based (dark asterisk) free radicals.[1]

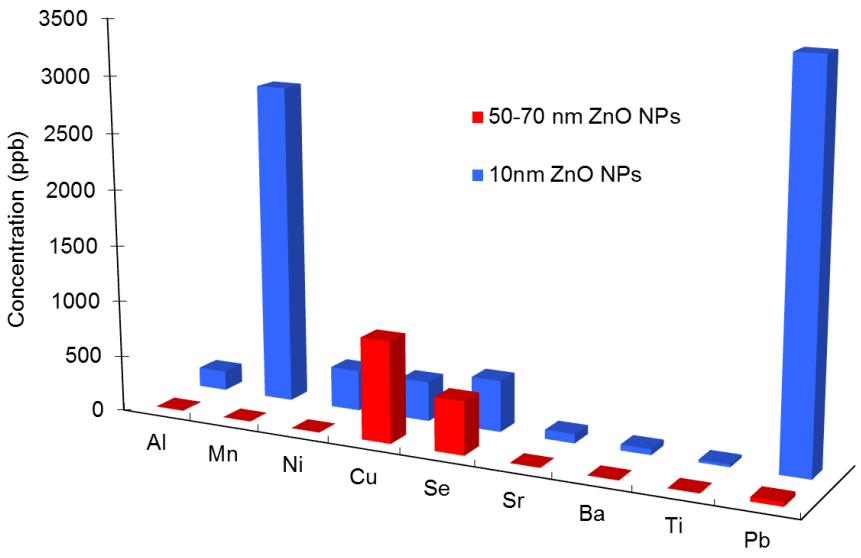

Figure S8 ICP-MS analysis of the trace amount of impurity elements within 1mg/mL 10 nm or 50-70 nm sized ZnO particles that were used in this study. Particle suspensions were freshly prepared and ultrasonicated, followed by 1 hour of microwave digestion using 3 M nitric acid. ICP-MS analysis was conducted thereafter with properly dilution of dissolved samples.

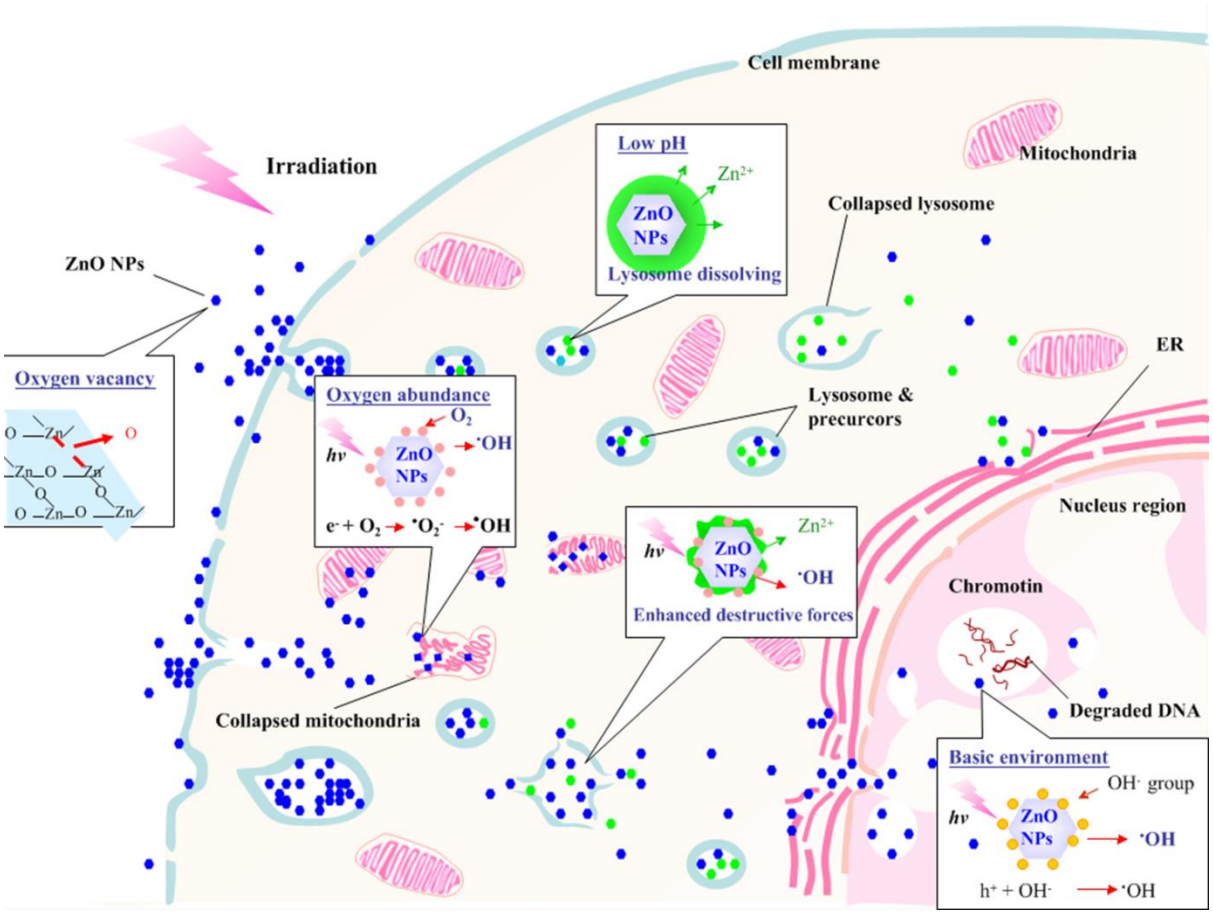

Figure S9 Proposed cytotoxic intracellular pathway by ZnO NPs. Compared to a relatively slow zinc ion releasing process, a much quicker way of hydroxyl radicals production and toxicating process would be expected with the assistance of: oxygen abundance, basic local pH environment as well as irradiation.

References

1. Mazumdar, A.; Adak, S.; Chatterjee, R.; Banerjee, R. Mechanism-based inactivation of lacrimal-gland peroxidase by phenylhydrazine: a suicidal substrate to probe the active site. *Biochem. J* **1997,** *324*, 713-719.