Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Anti-Kasha's rule for semiconductor photocatalytic reactions: The wavelength dependence of quantum efficiency

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Materials and Methods

Zinc oxide (~15 nm) was obtained from Alfa Aesar. Cadmium sulfide (99.99%, ~40 nm) and Indium sesquioxide (99.99%, ~42 nm) were purchased from Aladdin. Before use, the solid powders were calcined at 300 °C for 3 hours to gain a clean surface. Rhodamine B (A.R.) was obtained from Aladdin. Methanol (HPLC), isopropanol (HPLC) were purchased from J.T. Baker. For isotopic experiments, methanol-d_4 (99.8%), isopropanol-d_8 (99.0%) were purchased from Acros. The toluene-d_8 used in NMR experiments was from Innochem. 2, 4, 6-tri-tert-butylphenol (97%) was purchased from Acros. The corresponding phenoxyl radical ^{t}Bu$_3$ArO$^{\bullet}$ was prepared according to the reference[1]. Pentachlorobenzene used in MAS-^{1}H NMR was purchased from J&K. Tris (2,2'-bipyridyl) dichlororuthenium (II) hexahydrate (98%)

was purchased from Acros, and N,N-Diisopropylethylamine (99%) was purchased from Innochem.

Experimental Details

The concentration of Rhodamine B (RhB) acetonitrile solution employed in this report was 10^{-3} M. All the target reactions and measurements were carried out under anaerobic conditions.

Online EPR measurements

In a typical procedure, 20 mg catalyst powder was dispersed in 8 mL methanol for the direct excitation case (365, 420 nm irradiation) or 7.2 mL methanol + 0.8 ml dye for the dye-sensitization indirect excitation case (520 nm irradiation). Then the suspension was purged by Argon for 10 min and transferred to the Ar glovebox. After that, 0.5 mL $^{t}\mathrm{Bu_3ArO}^{\bullet}$ in acetonitrile of 25 mmol/L was added to it. Finally, the resulting suspension was sealed into a special tube for online EPR measurement under the irradiation of a certain wavelength. In other reactions, methanol could be replaced with isopropanol.

NMR analysis of reaction products

After the reaction of $^{t}\mathrm{Bu_3ArO}^{\bullet}$ with alcohol suspension under the irradiation of a certain wavelength, the solvent was removed by purging with Ar. Then the residue was transferred to the Ar glovebox and dissolved in toluene-d_8 for H-NMR measurement.

MAS-^{1}H NMR measurements

For the four samples in Figure 3a or 3b, the preparation processes were as follows: For each sample, 200 mg of catalyst powder was dispersed in 3 mL methanol (for the direct excitation case) or 2.7 mL methanol + 0.3 ml dye (for the dye-sensitization indirect excitation case). Then all the four samples were purged with Ar for 10 minutes. After that, the four samples were placed under darkness, the irradiation of 365 nm, 420 nm, and 520 nm for 3 hours, respectively. Afterwards, all the four samples were transferred to a glovebox, filtered, washed with methanol for several times, and dried. For the MAS-^{1}H NMR measurement, the amounts of each sample and the internal standard (pentachlorobenzene) were 50 mg and 10 mg, respectively.

H/D KIEs experiments

In a typical procedure, 20 mg catalyst was dispersed in 8 mL methanol-d_0 for the direct excitation case (365, 420 nm irradiation) or 7.2 mL methanol-d_0 + 0.8 ml dye for the dye-sensitization indirect excitation case (520 nm irradiation). Then the suspension was purged by Argon for 10 min and transferred to the Ar glovebox. After that, 0.5 mL $^{t}\mathrm{Bu_3ArO}^{\bullet}$ in acetonitrile of 25 mmol/L for the direct excitation case or 0.3 mL $^{t}\mathrm{Bu_3ArO}^{\bullet}$ in acetonitrile of 25 mmol/L for the dye-sensitization indirect excitation case was added to it. Finally, the resulting suspension was sealed into a special tube for Online EPR experiment under the irradiation of a certain wavelength. Deuterated methanol-d_4 was used to repeat the experiment above under otherwise identical conditions to obtain the KIE value. Besides, methanol-d_0/d_4 was replaced with isopropanol-d_0/d_8 in other reactions to investigate the effects of the sacrificial agent on H/D KIEs.

Experimental Apparatus

XRD measurements

The crystalline structures of ZnO, CdS, and In_2O_3 were studied by X-ray diffractometer (XRD, Bruker D8 Advance) over the 2θ range from 20° to 90° at the scan rate of 2° min^{-1}. And the average particle sizes were determined by the Scherrer formula.

UV-vis Diffusive Reflectance Spectra and UV-Vis Absorption Spectra

The UV-vis diffusive reflectance spectra (UV-vis DRS) and UV-Vis absorption spectra were measured on a Hitachi U3900 spectrometer. And the forbidden band widths (E_g) were obtained according to the Tauc Plot method.

Mott-Schottky measurements

Mott-Schottky measurements for used semiconductors were carried out on an electrochemical workstation (CHI600E) with the reference electrode of Ag/AgCl.

Online EPR measurements

In-situ EPR was applied to observe the change of $^{t}Bu_3ArO^{\bullet}$ signal in the reaction system with irradiation time. The EPR spectra were obtained on a Bruker E500 X-band spectrometer. The setting for the EPR spectrometer were as follows: center field, 3517 G; sweep width, 100 G; microwave frequency, ≈9.8 GHz; sweep cycle, 10 times.

H-NMR analysis

The H-NMR spectra were recorded on a Bruker Avance III 400 HD NMR spectrometer.

MAS-^{1}H NMR measurement

The solid-state magic angle spinning ^{1}H nuclear magnetic resonance (MAS-^{1}H NMR) measurements were performed on a Bruker AVI 400 MHz NMR spectrometer.

Supplementary Figures

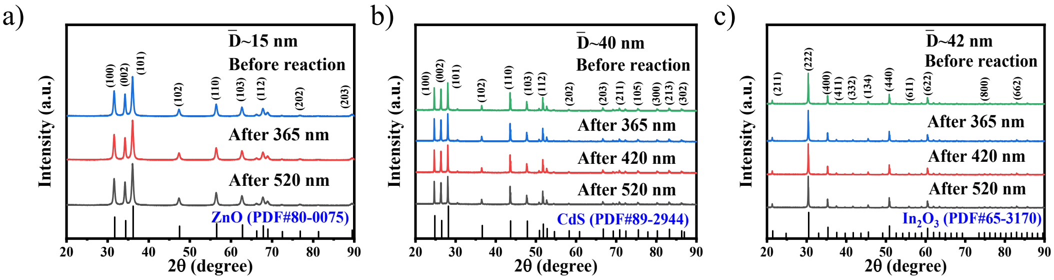

Figure S1. XRD patterns of ZnO (a), CdS (b), and In_2O_3 (c) nanoparticles before and after reactions under different wavelengths of irradiation. The particle sizes calculated by the Scherrer formula were also labeled respectively.

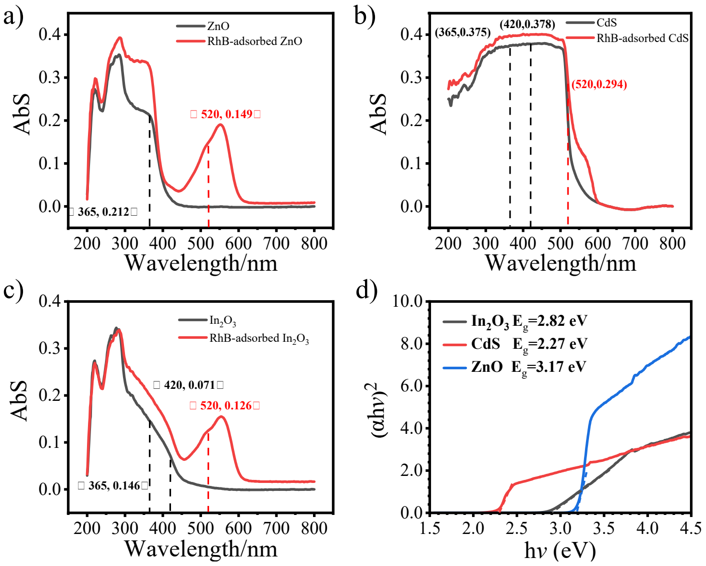

Figure S2. UV-vis DRS of different (a) ZnO samples, (b) CdS samples, and (c) In_2O_3 samples. (d) Plots of $(\alpha h\nu)^2$ versus energy ($h\nu$) of ZnO, CdS, and In_2O_3 samples.

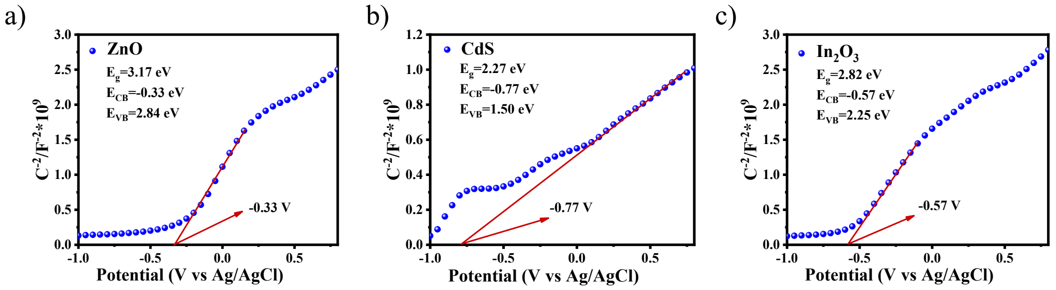

Figure S3. Mott-Schottky curves of (a) ZnO, (b) CdS, and (c) In_2O_3 samples.

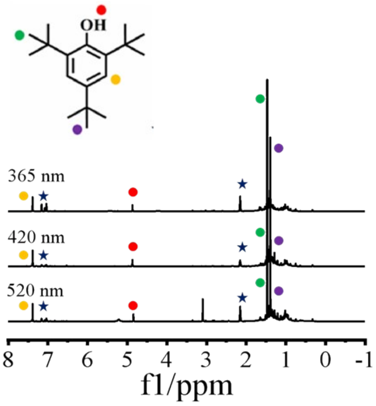

Figure S4. H-NMR spectra of the reaction product $^{t}Bu_3ArOH$ under the irradiation of different wavelengths.

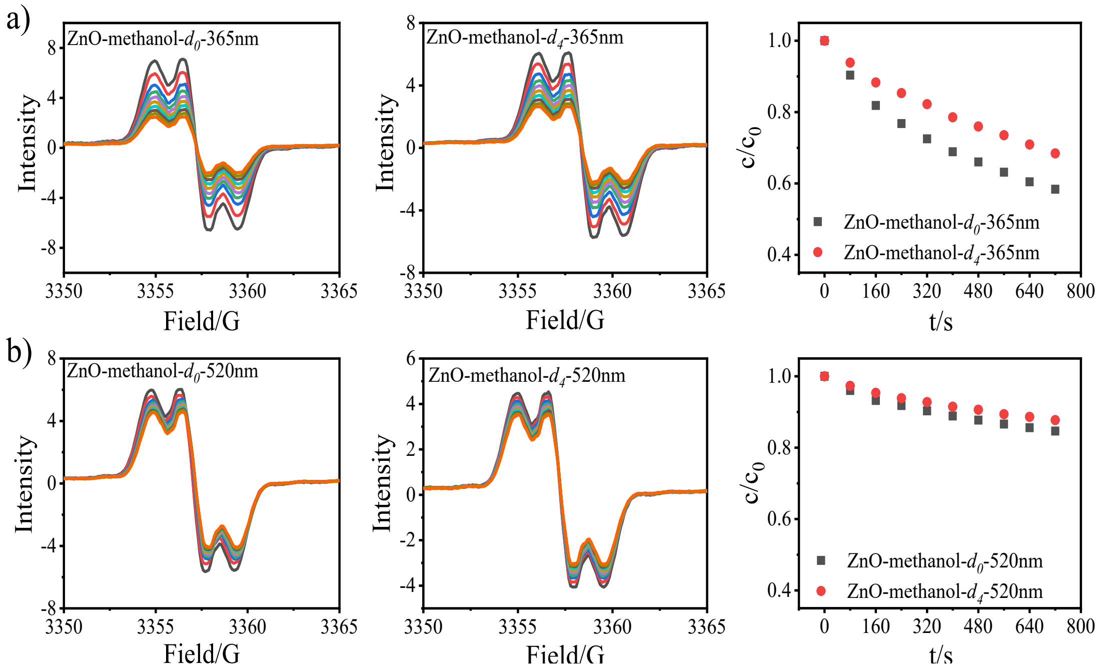

Figure S5. Online EPR spectra showing the changes in concentration of ${}^{t}Bu_3ArO^{\bullet}$ in ZnO methanol-d_0/d_4 suspension samples with the irradiation time and the corresponding kinetic curves. (a) 365 nm irradiation. (b) RhB-sensitization 520 nm irradiation.

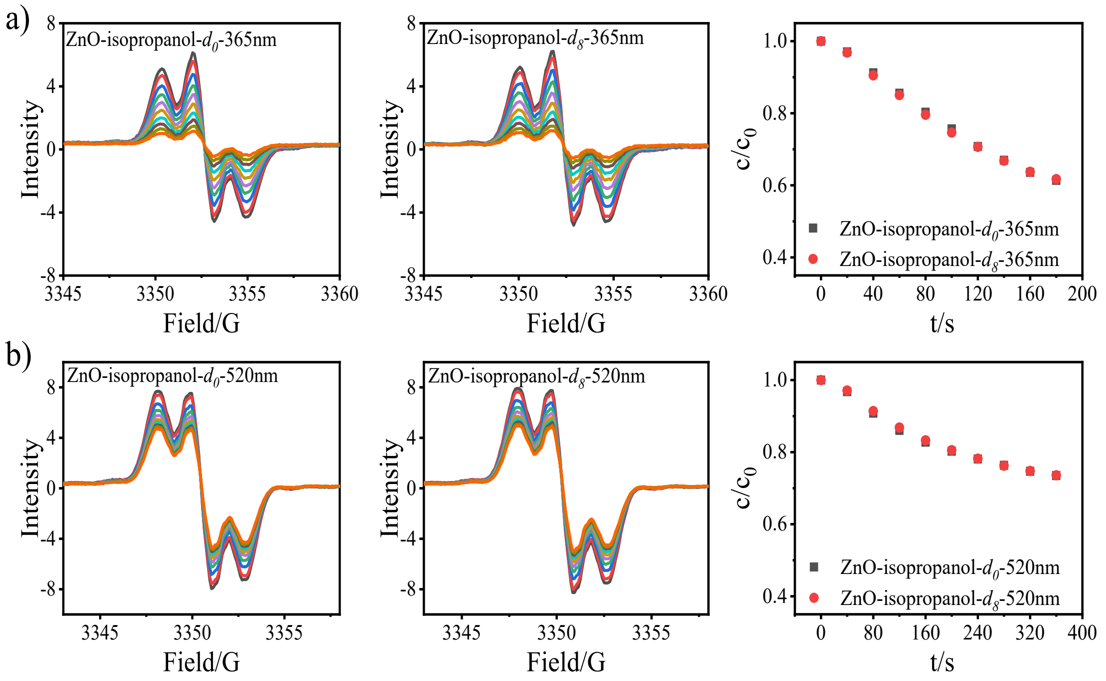

Figure S6. Online EPR spectra showing the changes in concentration of ${}^{t}Bu_3ArO^{\bullet}$ in ZnO isopropanol-d_0/d_8 suspension samples with the irradiation time and the corresponding kinetic curves. (a) 365 nm irradiation. (b) RhB-sensitization 520 nm irradiation.

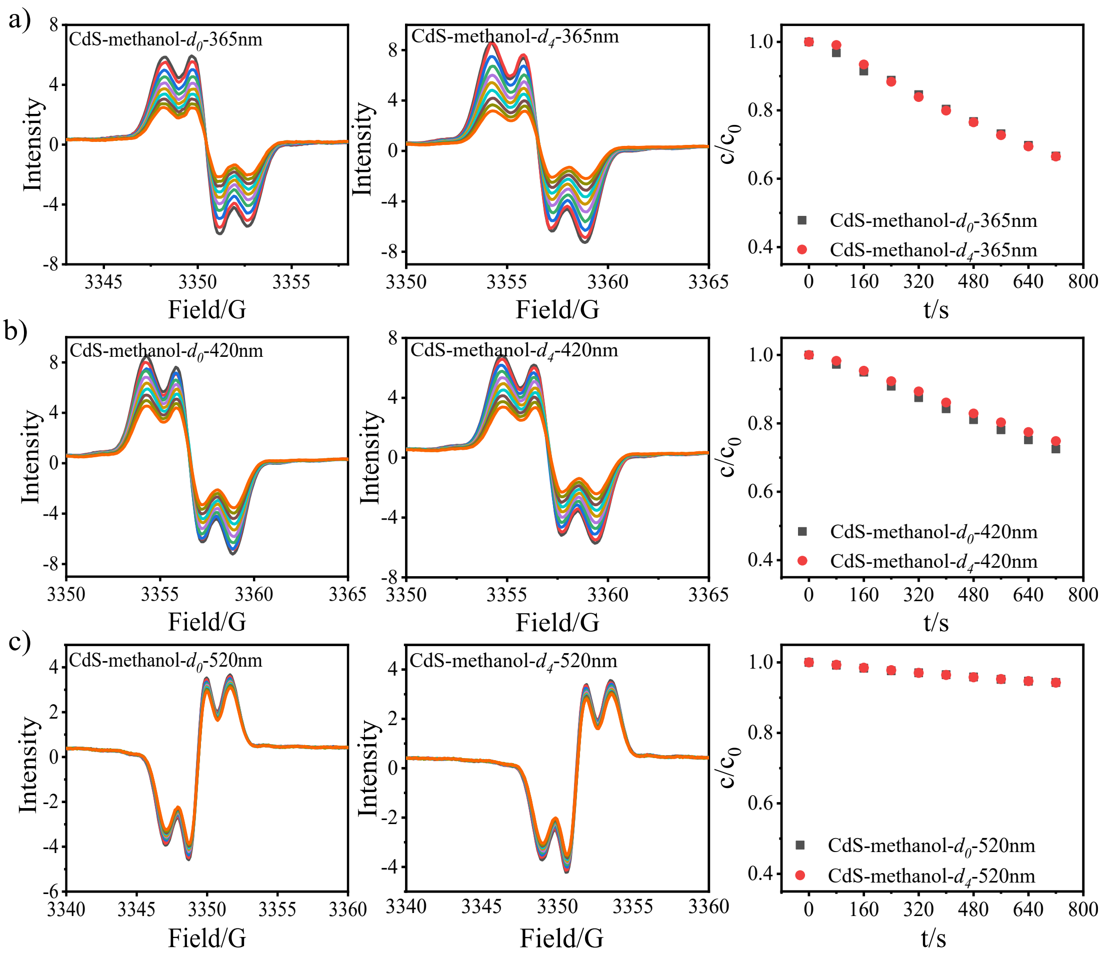

Figure S7. Online EPR spectra showing the changes in concentration of $^{t}\mathrm{Bu}_3\mathrm{ArO}^{\bullet}$ in CdS methanol-d_0/d_4 suspension samples with the irradiation time and the corresponding kinetic curves. (a) 365 nm irradiation. (b) 420 nm irradiation. (c) RhB-sensitization 520 nm irradiation.

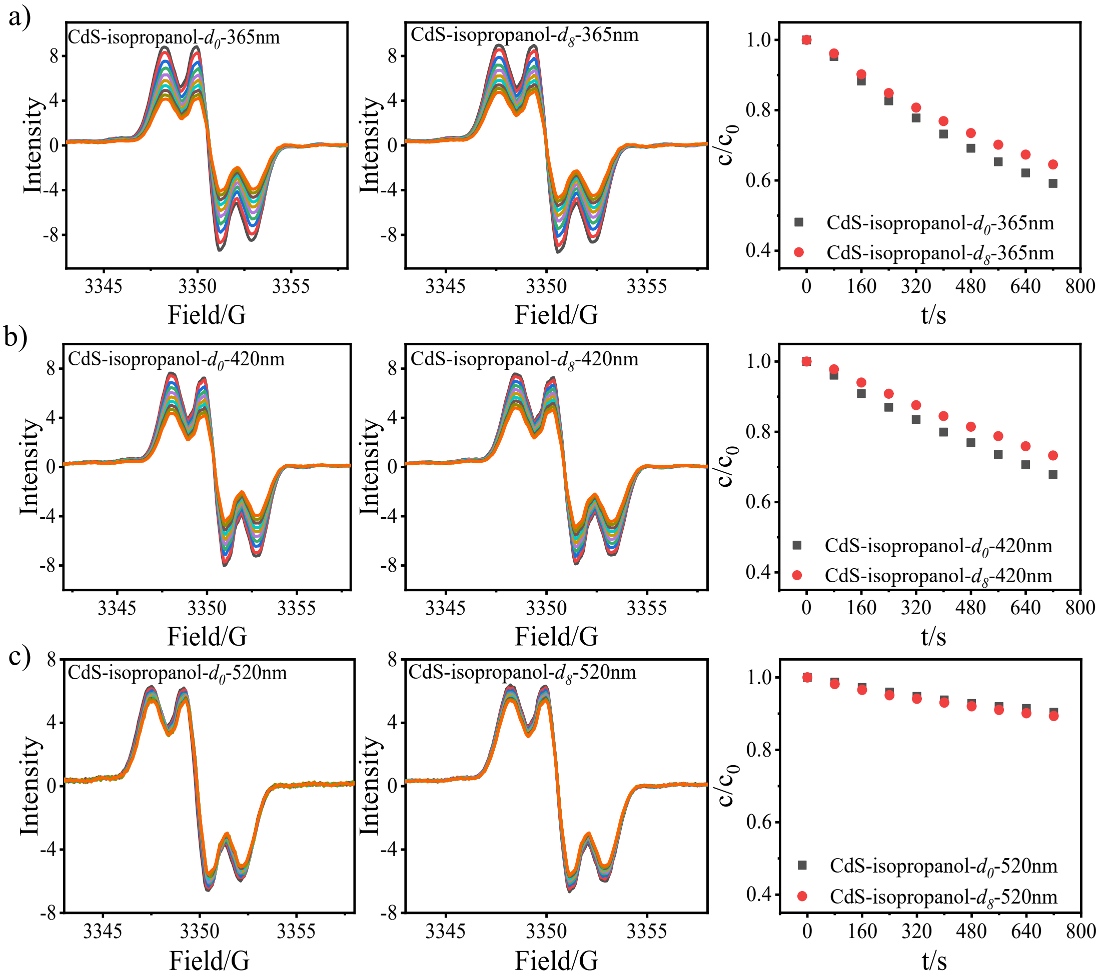

Figure S8. Online EPR spectra showing the changes in concentration of ${}^{t}\mathrm{Bu}_3\mathrm{ArO}^{\bullet}$ in CdS isopropanol-d_0/d_8 suspension samples with the irradiation time and the corresponding kinetic curves. (a) 365 nm irradiation. (b) 420 nm irradiation. (c) RhB-sensitization 520 nm irradiation.

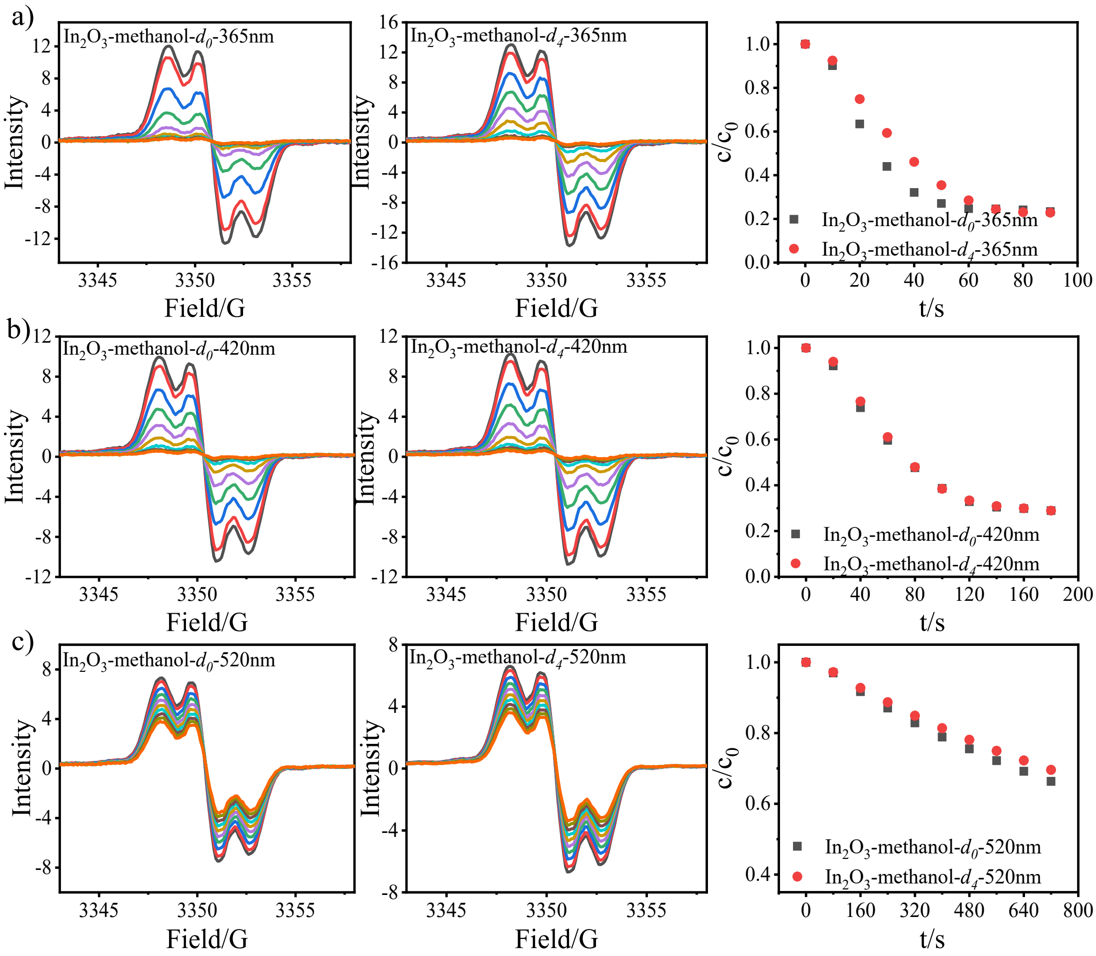

Figure S9. Online EPR spectra showing the changes in concentration of ^{t}Bu$_3$ArO$^\bullet$ in In$_2$O$_3$ methanol-d_0/d_4 suspension samples with the irradiation time and the corresponding kinetic curves. (a) 365 nm irradiation. (b) 420 nm irradiation. (c) RhB-sensitization 520 nm irradiation.

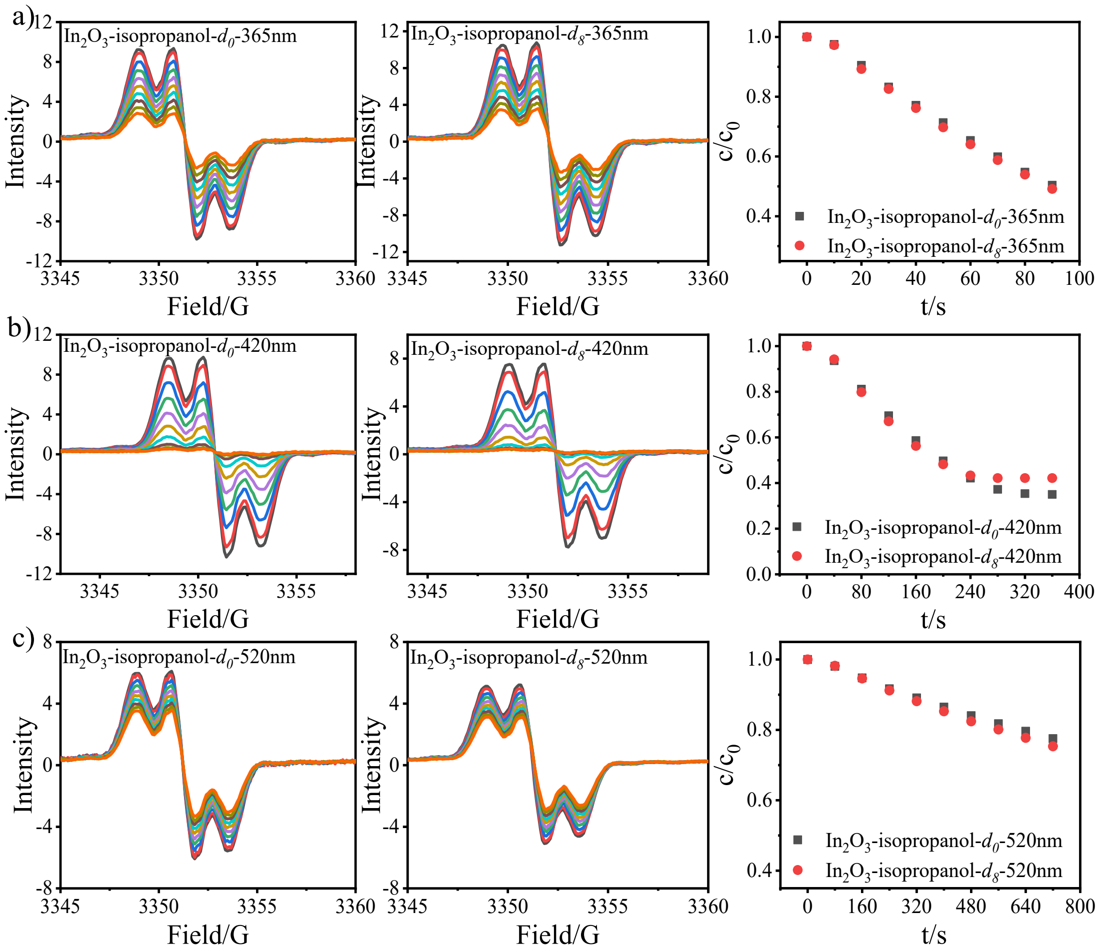

Figure S10. Online EPR spectra showing the changes in concentration of ${}^{t}Bu_3ArO^{\bullet}$ in In_2O_3 isopropanol-d_0/d_8 suspension samples with the irradiation time and the corresponding kinetic curves. (a) 365 nm irradiation. (b) 420 nm irradiation. (c) RhB-sensitization 520 nm irradiation.

References

(1) Manner, V. W.; Markle, T. F.; Freudenthal, J. H.; Roth, J. P.; Mayer, J. M. The First Crystal Structure of a Monomeric Phenoxyl Radical: 2,4,6-Tritert-Butylphenoxyl Radical. *Chem. Commun.* **2008**, 256-258.