Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

SUPPORTING INFORMATION

Synthesis of *brookite* TiO_2 nanorods with isolated Co(II) surface sites and photocatalytic degradation of 5,8-dihydroxy-1,4-naphthoquinone dye

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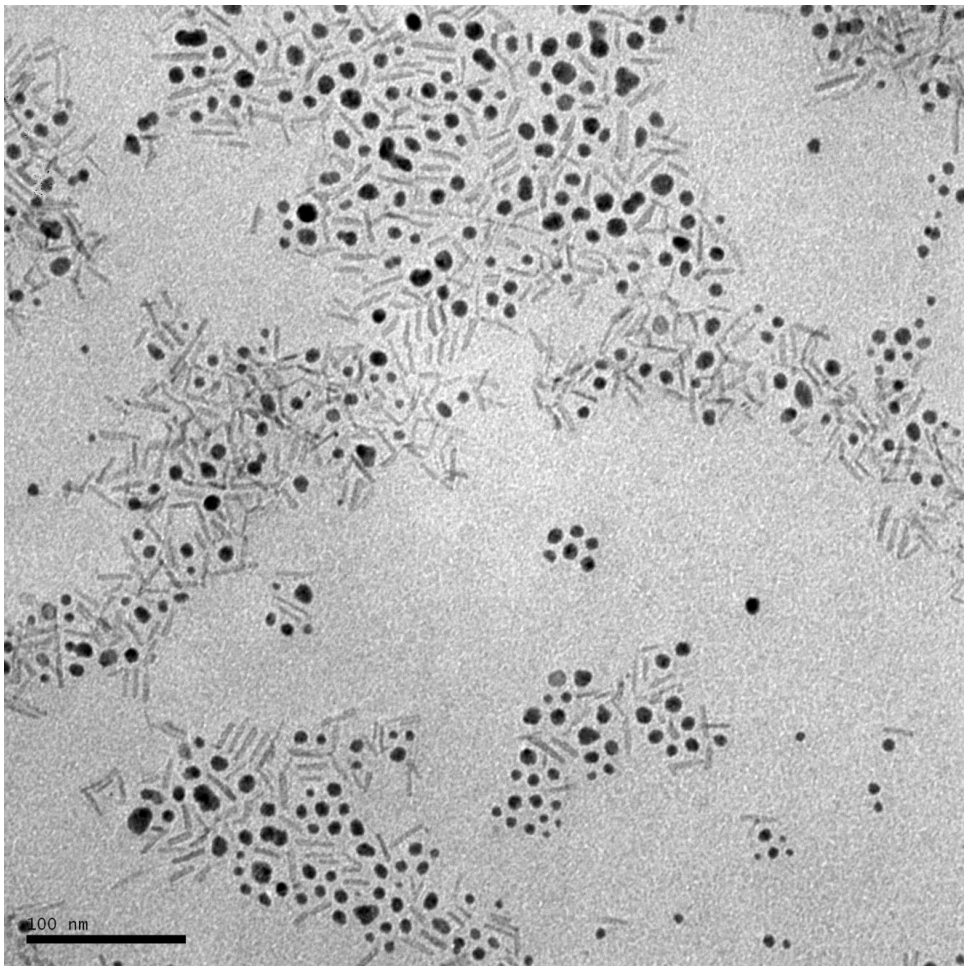

Figure S1. TEM image of dispersion of TiO_2 NR and Co NPs typically formed via decomposition of $Co_2(CO)_8$ in the presence of TiO_2 NR under the reaction conditions reported by Casavola et al.[1].

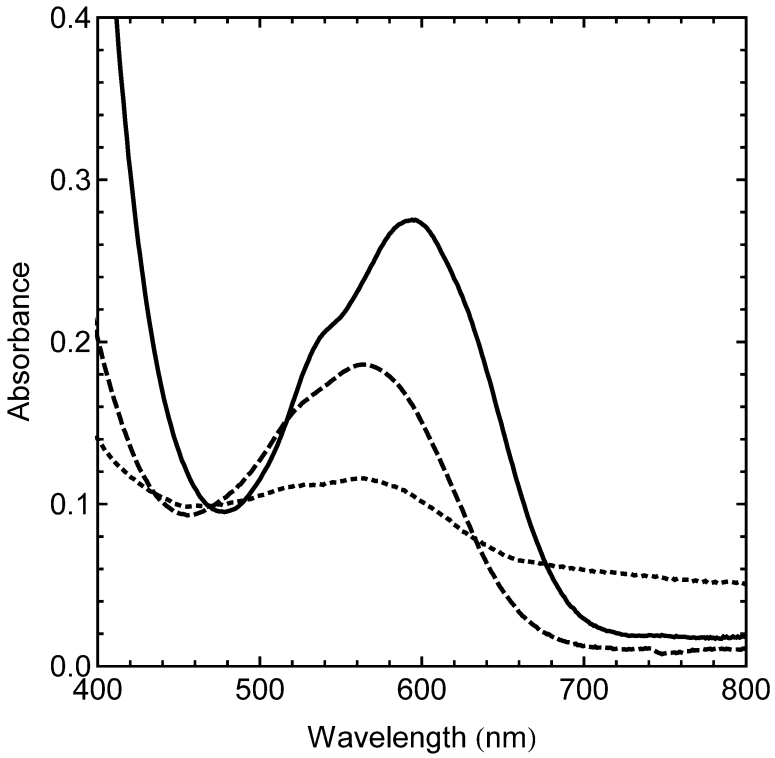

Figure S2. UV-visible spectrum of pink supernatant upon decomposition of $Co_2(CO)_8$ in the absence of TiO_2 NR (---), pink supernatant separated from the dispersion of Co(II)-TiO_2 NR (——), and blue Co(II)-TiO_2 dispersion (—).

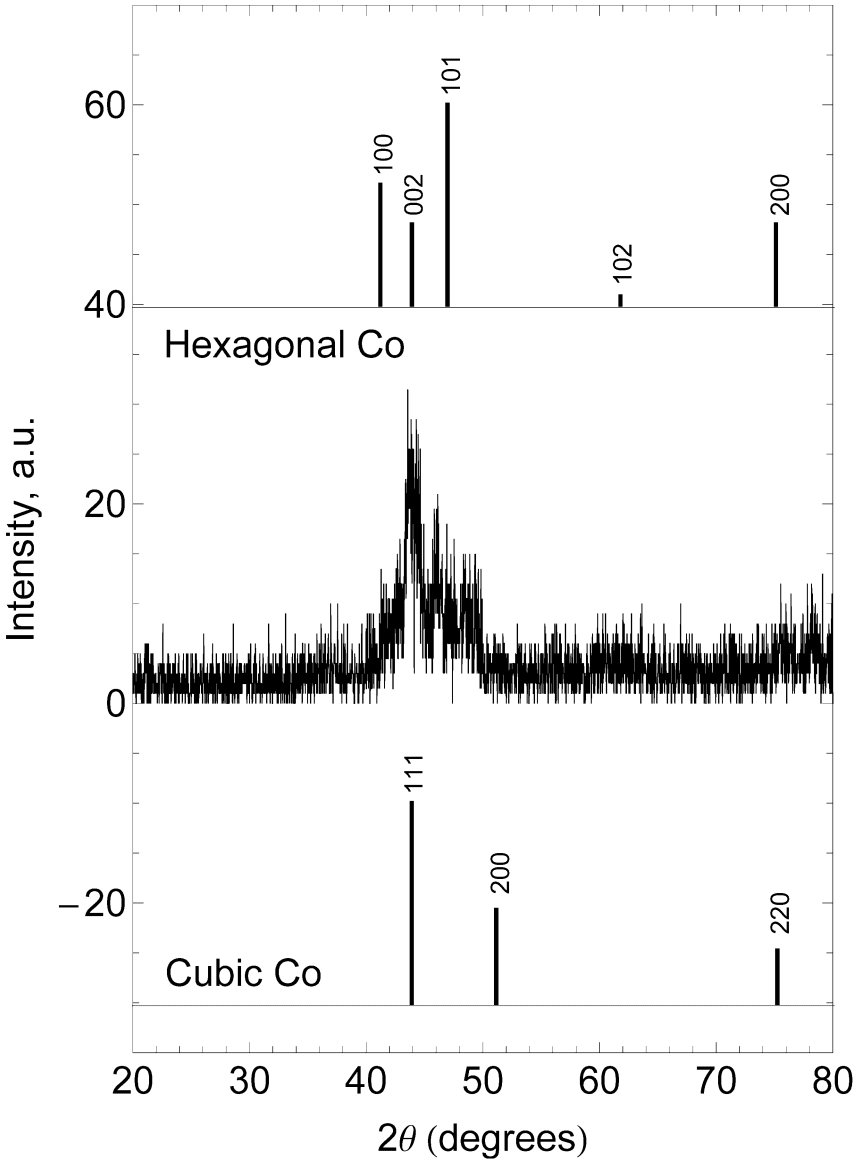

Figure S3. Powder XRD data of the highly amorphous cobalt precipitate formed during synthesis of Co(II)-TiO_2 NRs.

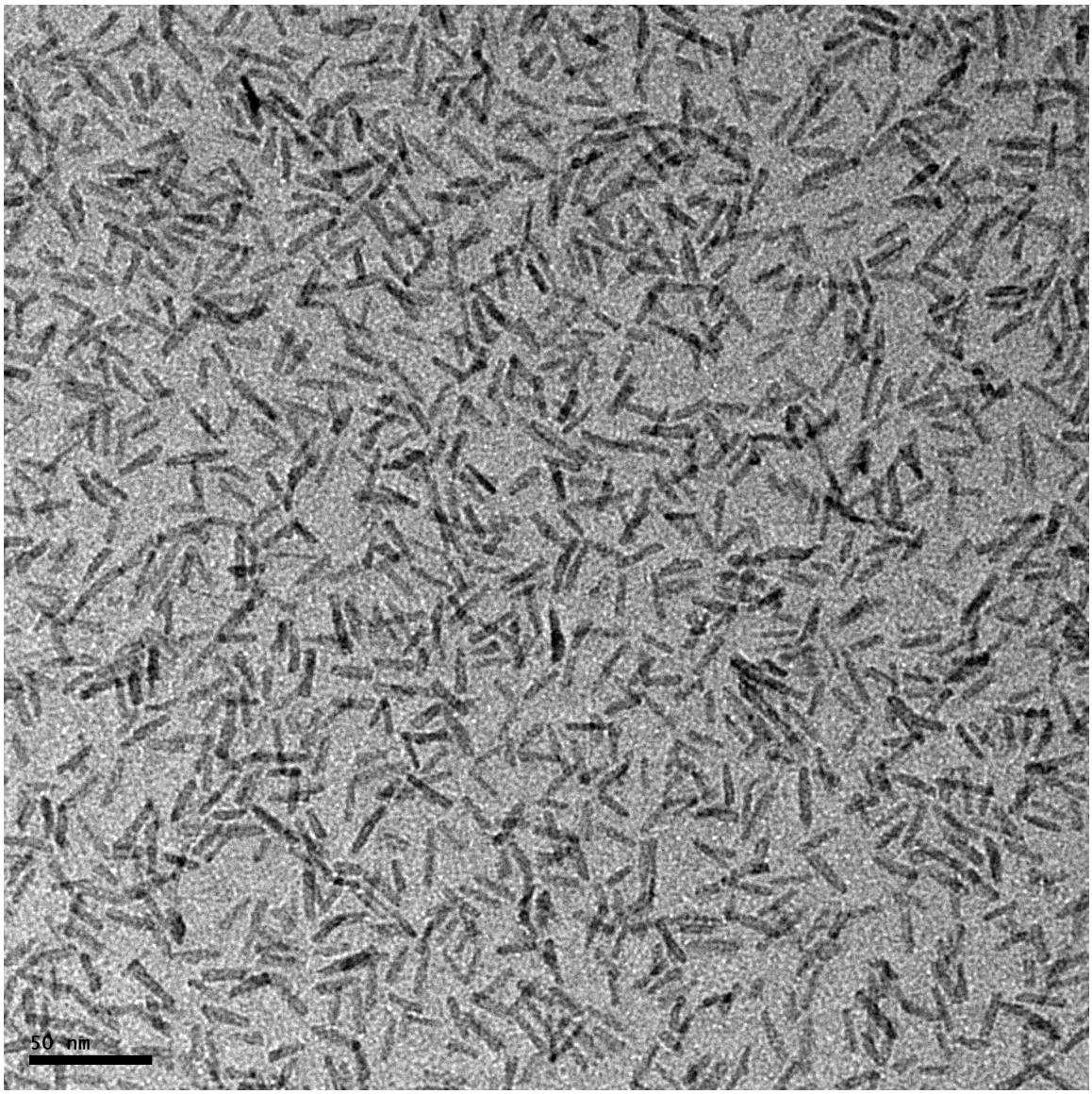

Figure S4. TEM image of Co(II)-TiO_2 NR.

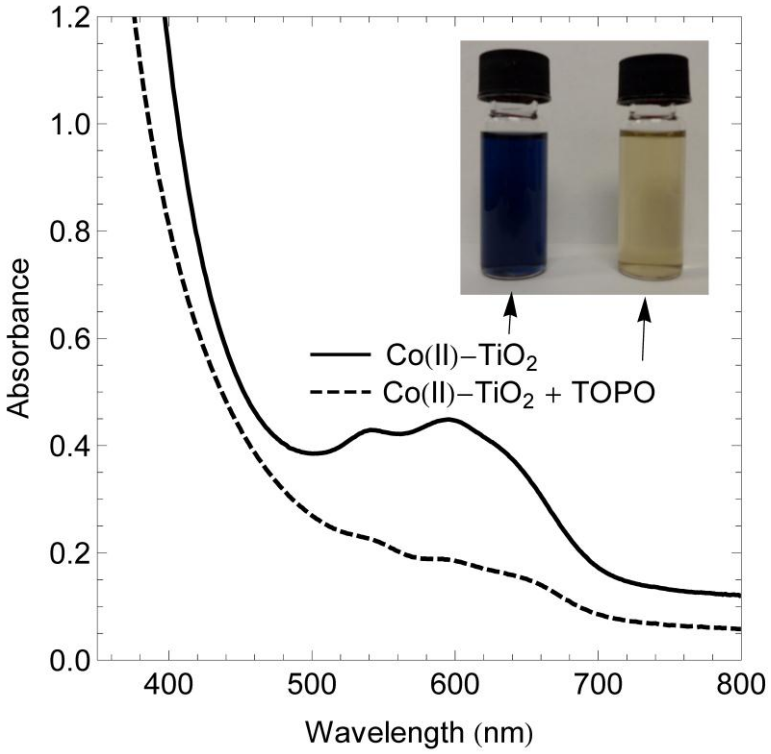

Figure S5. Photographs and UV-visible spectra of Co(II)-TiO_2 NRs before and after treatment with trioctylphosphine oxide. The Co(II)-TiO_2 NR dispersion is blue and shows prominent absorbance feature at 600 nm. After treatment with trioctylphosphine oxide at 250°C for 14 hours, much of the cobalt was removed from the nanorods and into the supernatant. Precipitation of the nanorods allowed separation of the supernatant. The nanorods (Co(II)-TiO_2 + TOPO) redispersed in hexanes and were pale yellow, having lost ~70% of the cobalt content. The UV-visible spectrum shows greatly reduced absorbance features from cobalt(II).

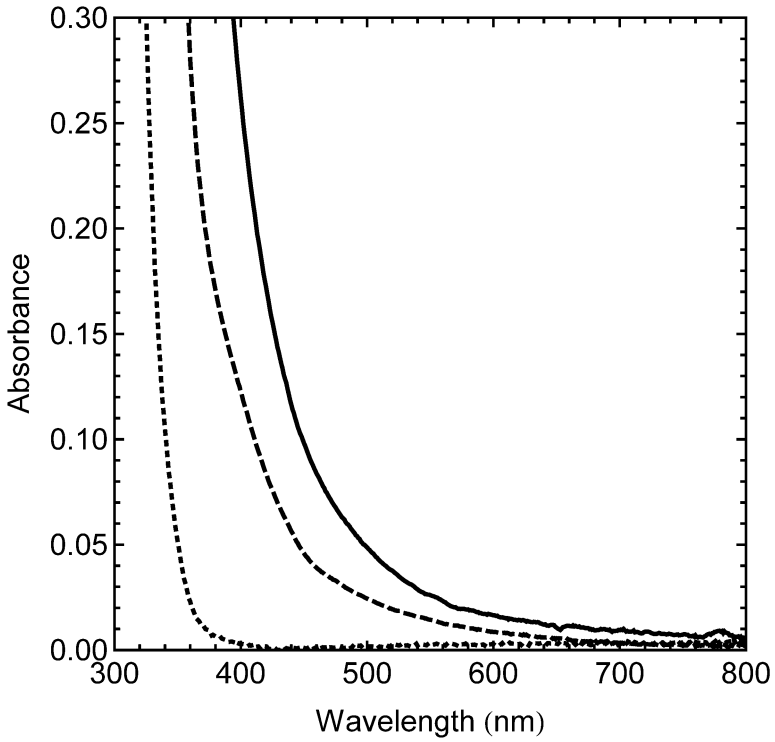

Figure S6. UV-visible spectra of TiO_2 NR (---), Co(II)-TiO_2 treated with DMG (——), and TiO_2 treated with DMG (—).

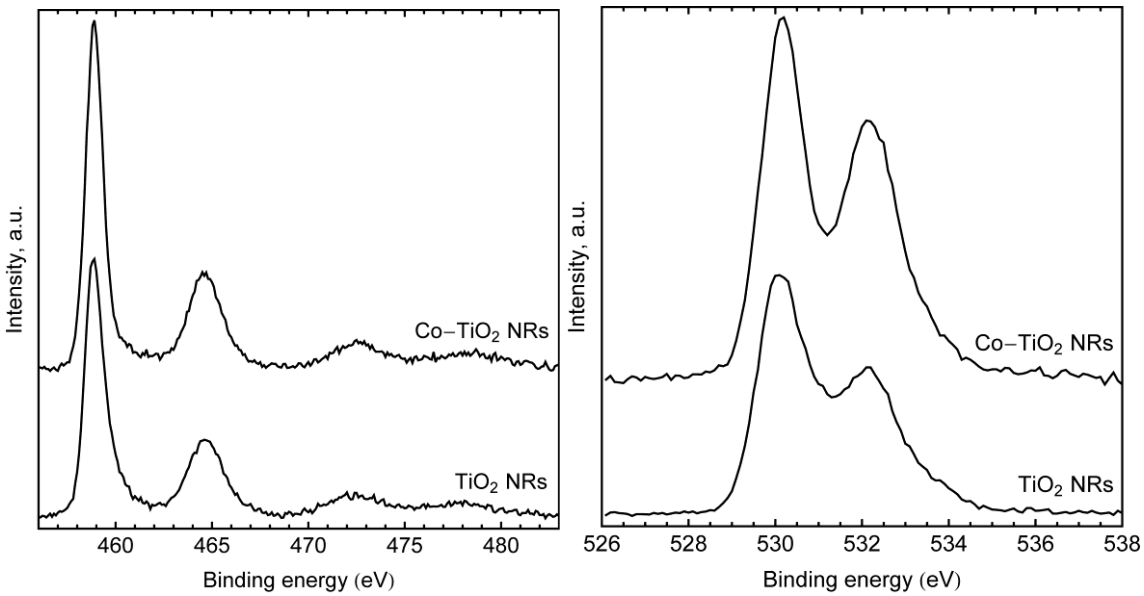

Figure S7. Ti 2p (left) and O 1s (right) XPS data of TiO_2 NR and Co(II)-TiO_2 NR.

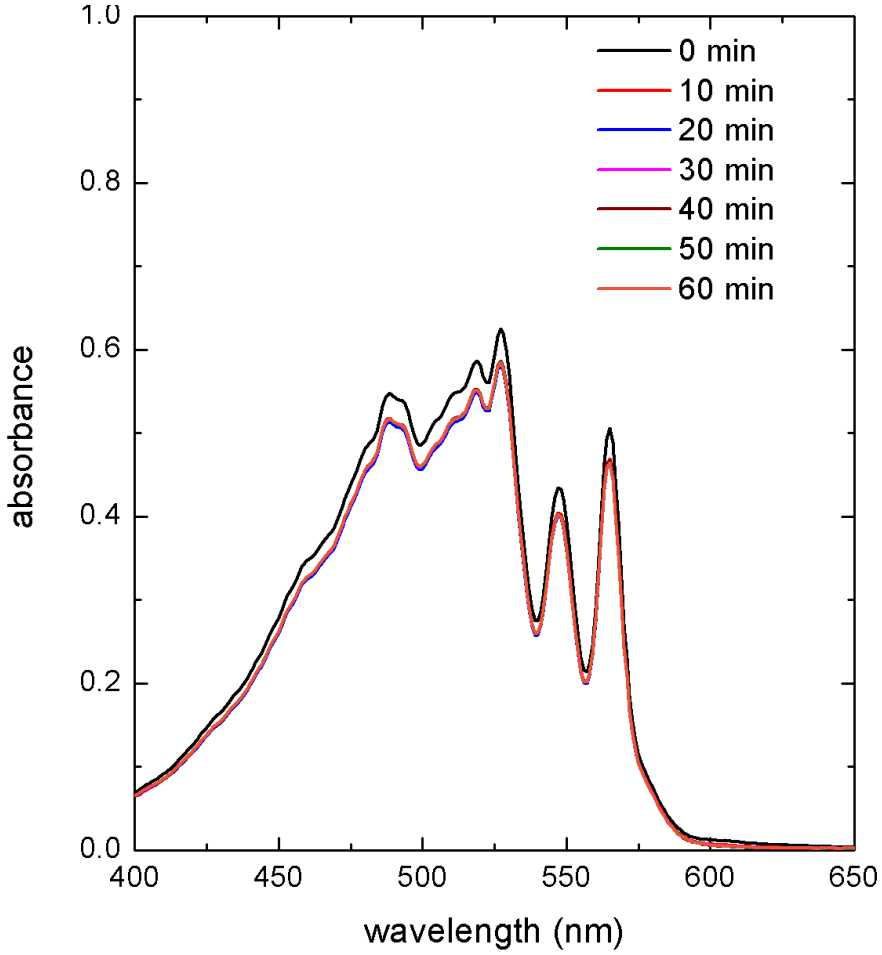

Figure S8. UV-visible spectra of DHNQ under visible light irradiation at room temperature in hexane. Spectra were recorded in 10-minute intervals. The dye concentration at 0 min was 99.9 ± 5.3 μM. The extinction coefficient, $\varepsilon = 7.0\times10^3 \pm 0.4\times10^3$ $M^{-1}cm^{-1}$ at λ_{max} = 527nm.

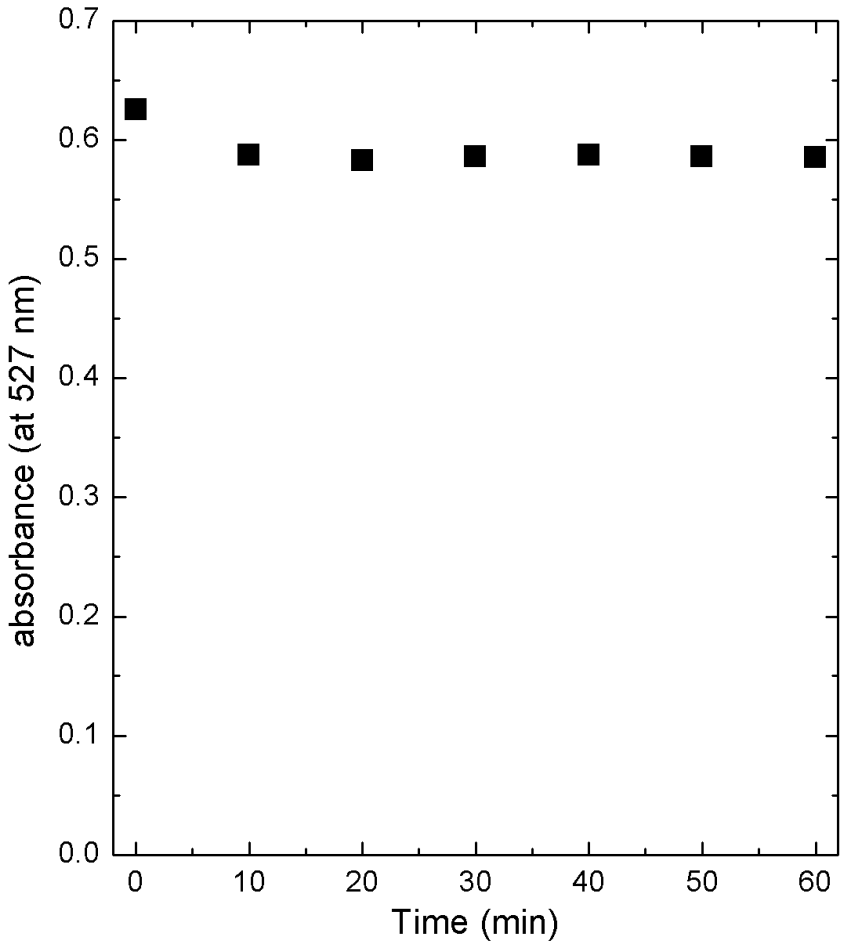

Figure S9. Time-dependent absorption of DHNQ dye at λ=527nm in hexane at room temperature. The dye concentration at 0 min was 99.9 ± 5.3 *μ*M. Absorbance data from Figure S2.

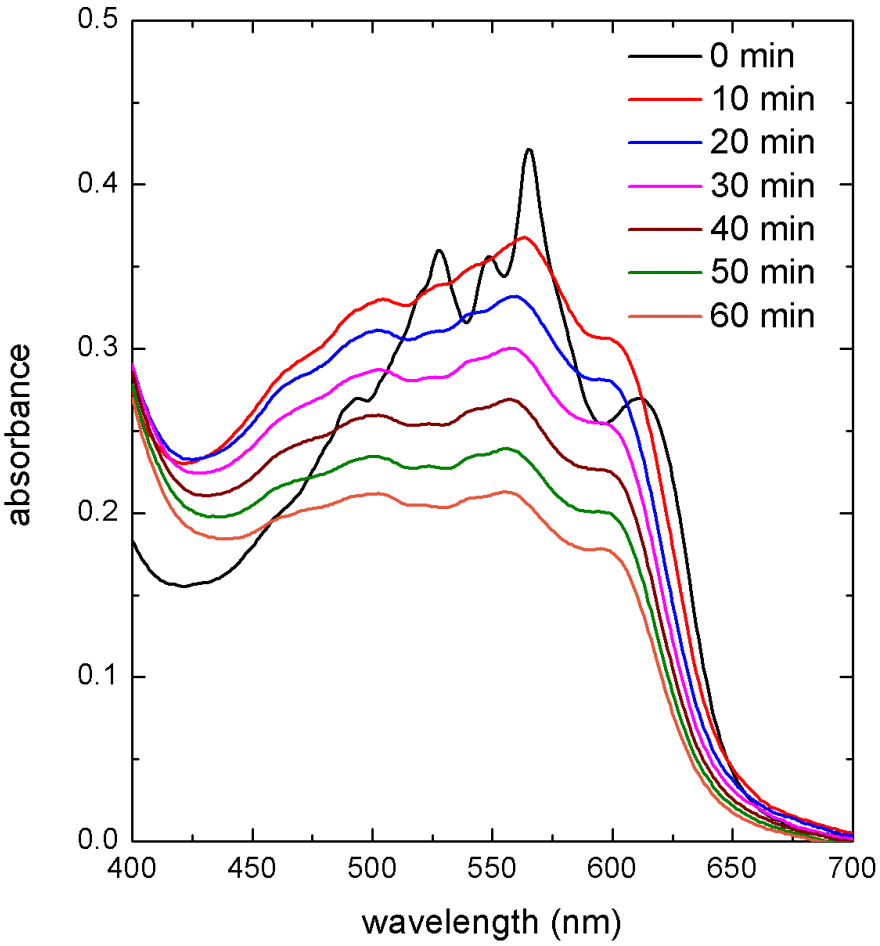

Figure S10. UV-visible spectra of DHNQ + TiO_2 NR under visible light irradiation at room temperature in hexane. Spectra were recorded in 10-minute intervals. At zero minutes, the spectrum resembles the spectrum of free DHNQ. The spectra afterward are presumed to be the adsorbed molecule on TiO_2 NR. The local absorbance maximum, λ = 502 nm has a measured extinction coefficient, $\varepsilon = 4.0 \times 10^3 \pm 0.2 \times 10^3$ $M^{-1}cm^{-1}$.

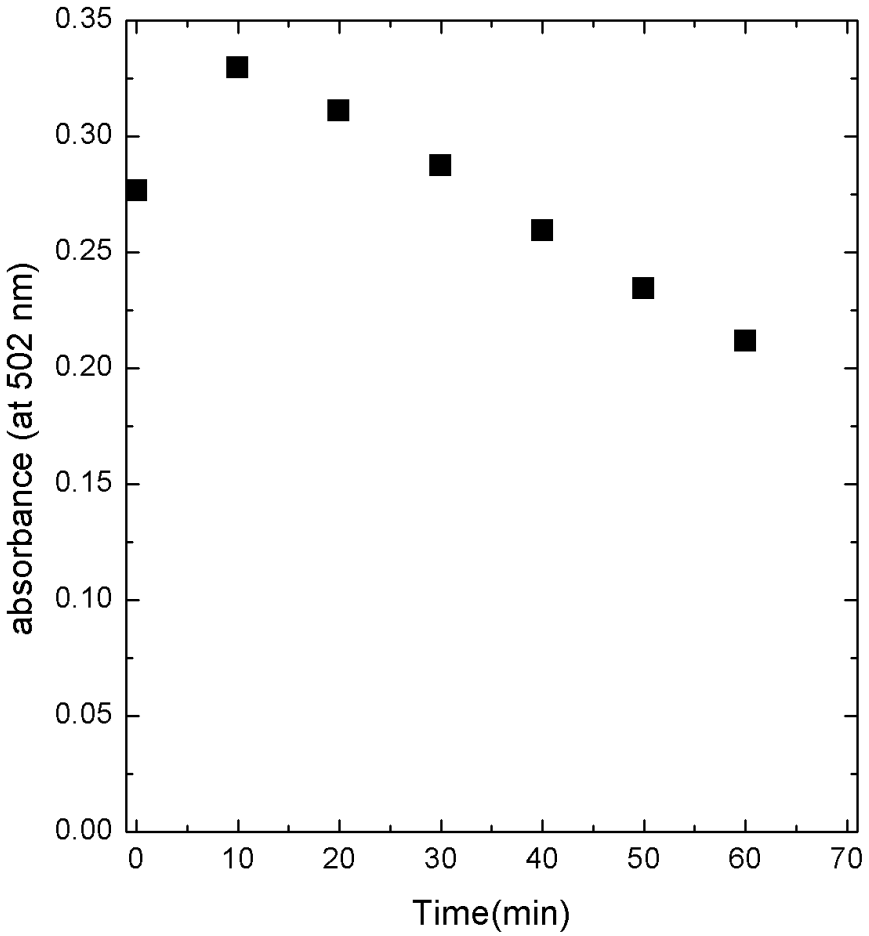

Figure S11. Time-dependent absorbance of DHNQ in the presence of TiO_2 NRs at λ = 502 nm in hexane at room temperature. The absorbance was determined by subtracting the spectrum of the TiO_2 NRs from each spectra in Figure S4. The slope of the absorbance data from t = 10-60 minutes was used to determine the absorbance at t = 0. From a linear regression analysis, the equation, $absorbance = -2.4\times10^{-3}(t) + 0.357$ fit the data with a correlation coefficient, R^2 of 0.997.

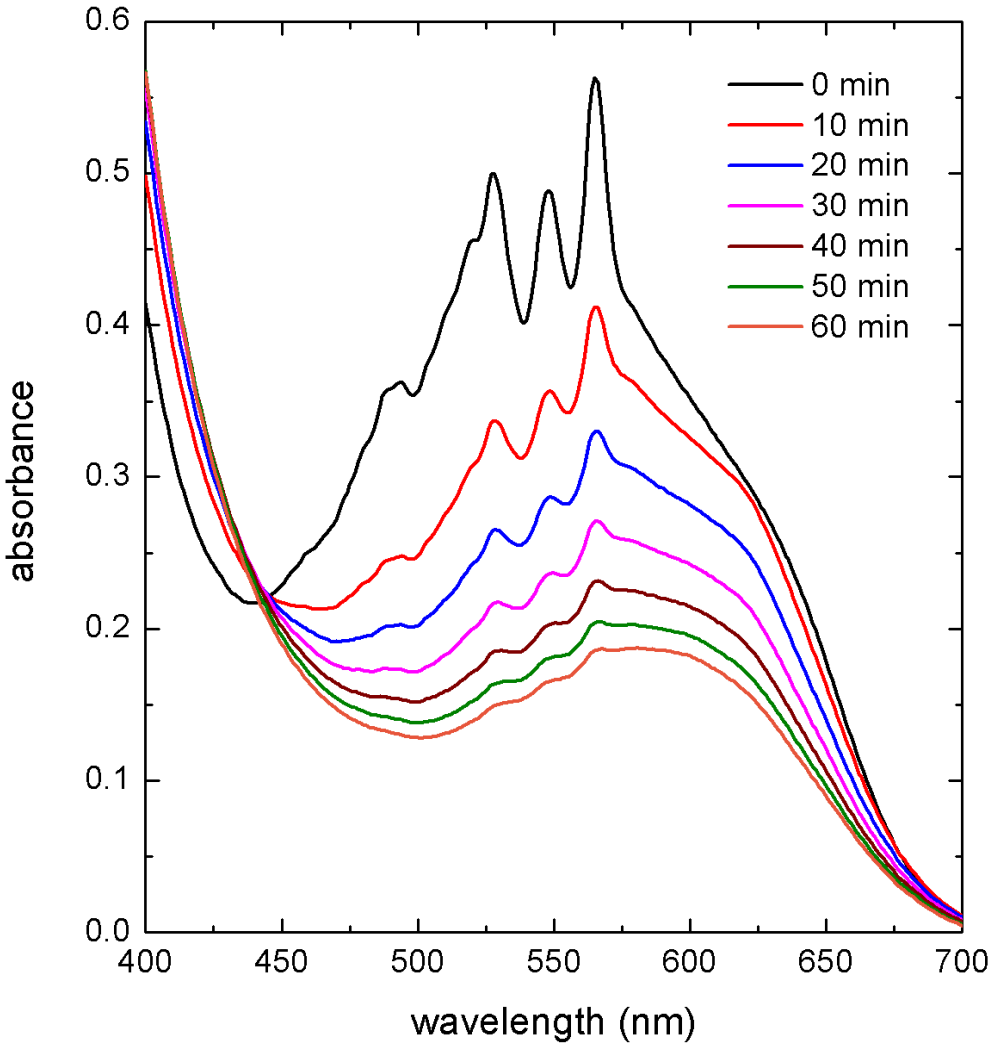

Figure S12. UV-visible spectra of DHNQ + Co(II)-TiO_2 NR under visible light irradiation at room temperature in hexane. Spectra were recorded in 10-minute intervals. The transition (λ_{max} = 565 nm) is superimposed with the Co(II) d-d transitions from the Co(II)-TiO_2 NRs. Subtraction of the Co(II)-TiO_2 NR spectrum yields an extinction coefficient, $\varepsilon \approx 4.3 \times 10^3 \pm 0.2 \times 10^3$ $M^{-1}cm^{-1}$.

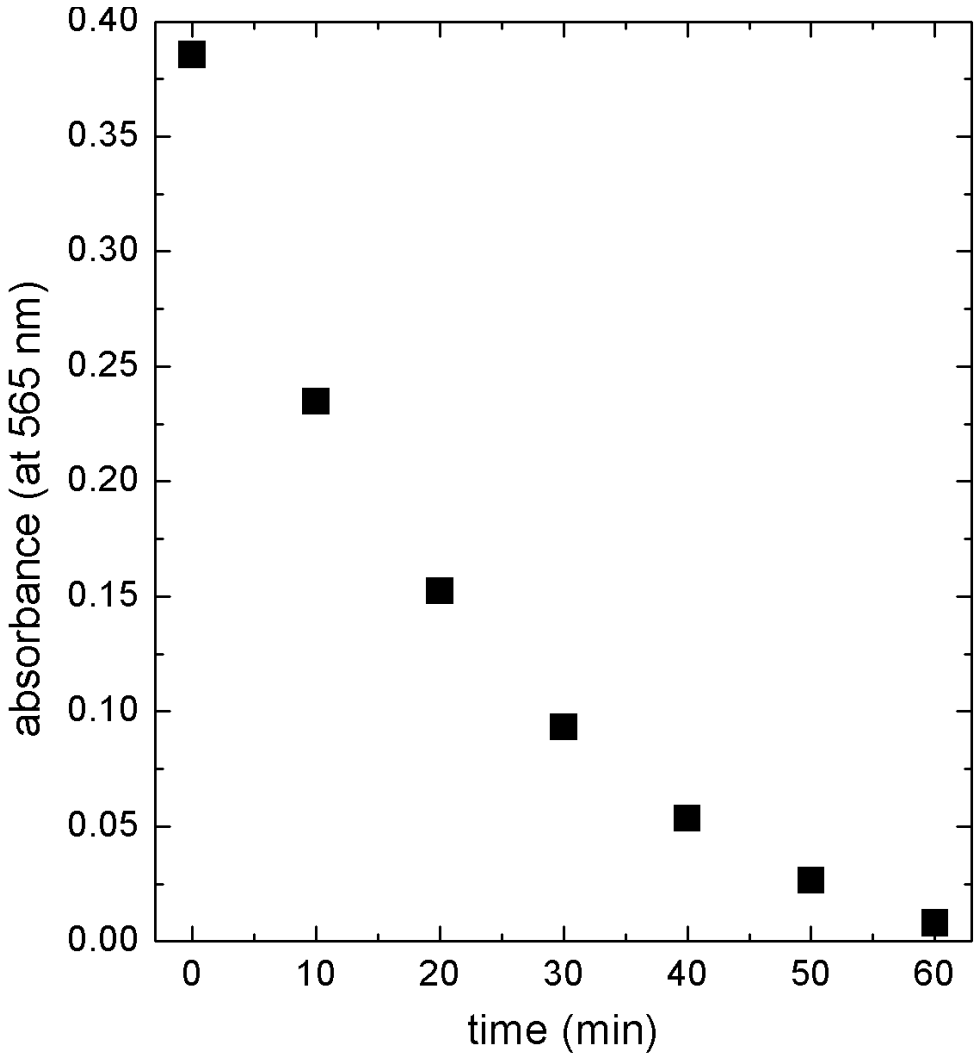

Figure S13. Time-dependent absorbance of DHNQ in the presence of Co(II)-TiO_2 NRs at λ = 565 nm in hexane at room temperature. The absorbance was determined by subtracting the spectrum of the Co(II)-TiO_2 NRs from each spectra in Figure S6.

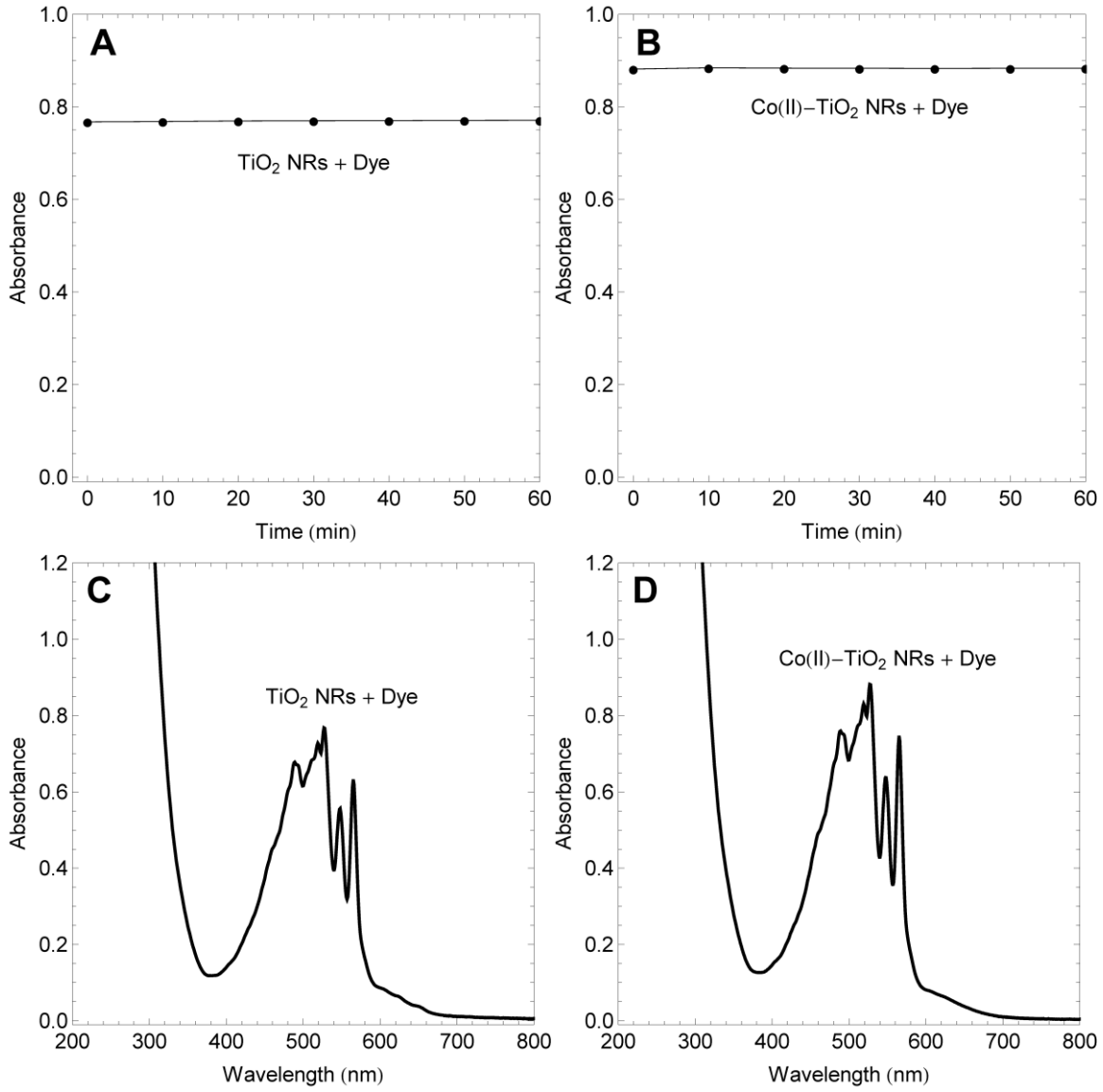

Figure S14. Top left: Absorbance versus time for TiO_2 + DHNQ in the dark. Bottom left: UV-visible spectra of TiO_2 + DHNQ in the dark. Top right: Absorbance versus time for Co(II)-TiO_2 + DHNQ in the dark. Bottom left: UV-visible spectra of Co(II)-TiO_2 + DHNQ in the dark.

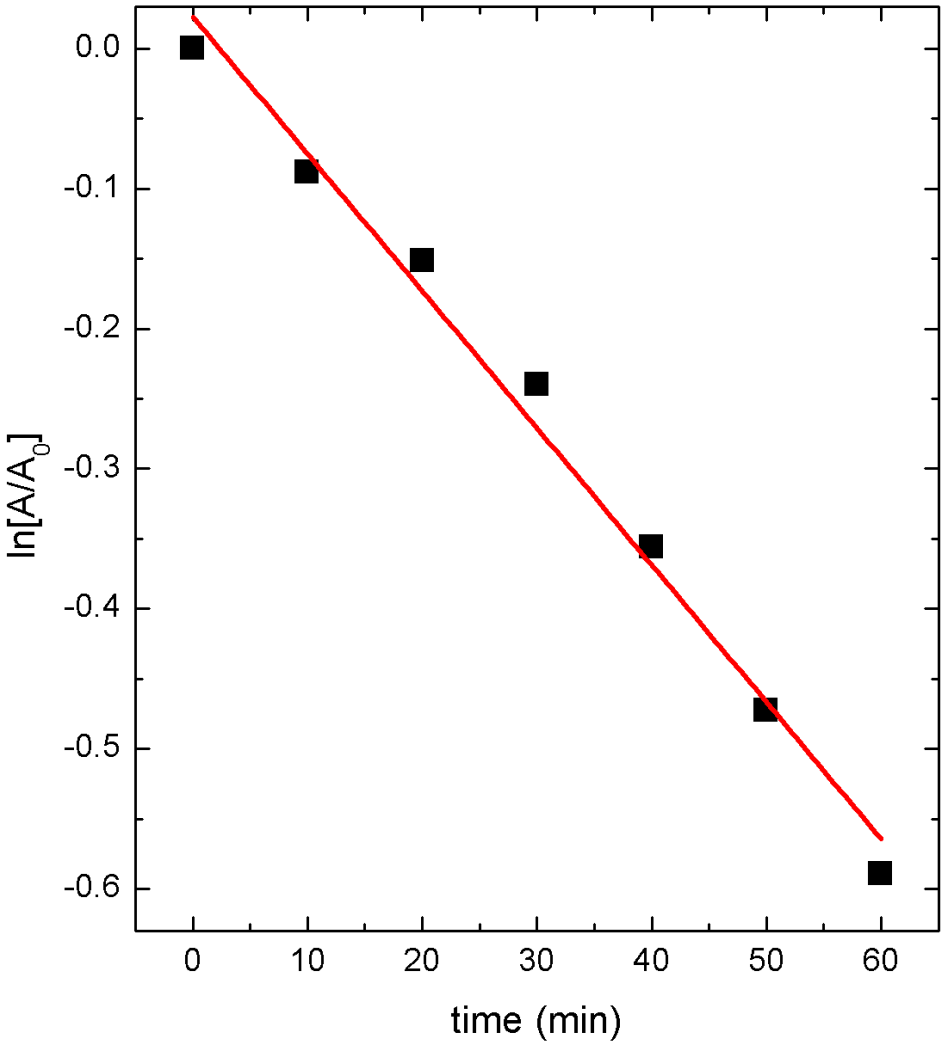

Figure S15. Linear plot of normalized absorbance versus time for DHNQ + TiO_2 at room temperature in hexane. From a linear regression analysis, the equation, $\ln[A/A_0] = -0.0098(t) + 0.0227$ fit the data with a correlation coefficient, R^2 of 0.98917.

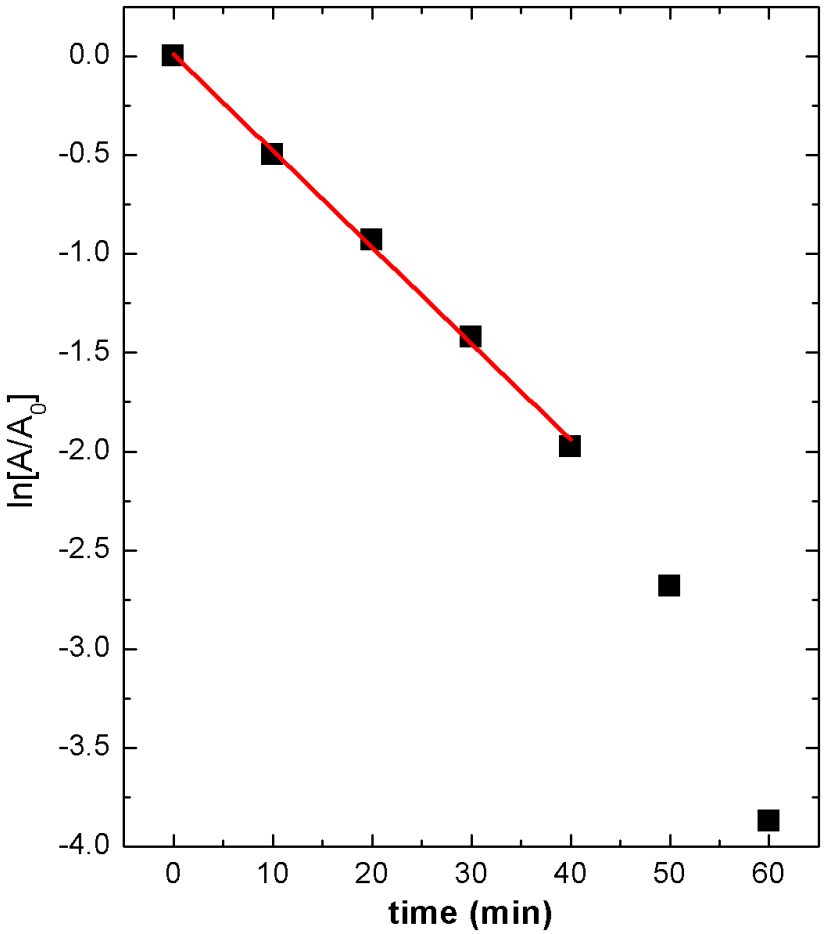

Figure S16. Linear plot of normalized absorbance versus time for DHNQ + Co(II)-TiO_2. From the linear regression analysis, the equation, $\ln[A/A_0] = -0.0488(t) + 0.0112$ fit the data with a correlation coefficient, R^2 of 0.99825 over the time interval 0-40 minutes. The last two data points were discarded because the data was obtained by subtracting the absorbance of Co(II)-TiO_2 NR from the spectrum of DHNQ + Co(II)-TiO_2 NR, and at t > 40 minutes most of the DHNQ was decomposed.

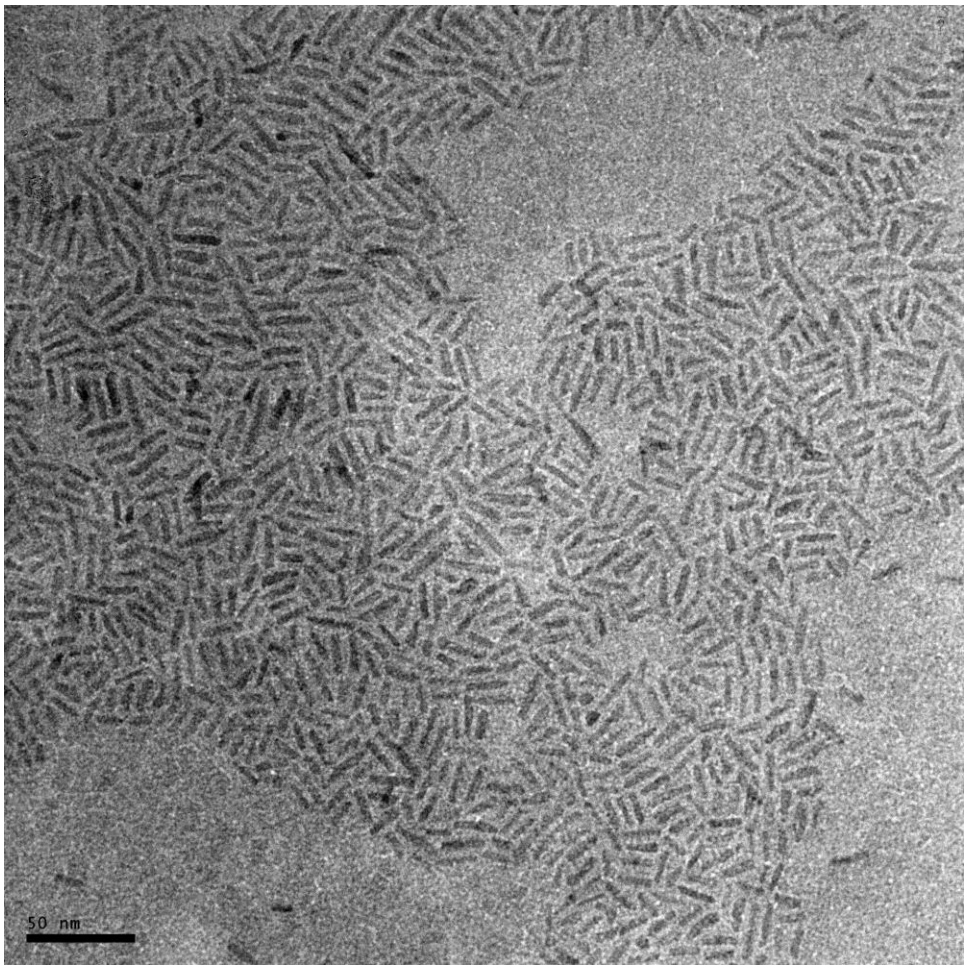

Figure S17. TEM data of Co(II)-TiO_2 NR sample recovered from the photocatalysis experiment.

Calculation of dispersion of brookite TiO_2 NR.

We base our calculations on the findings reported by Gong and Selloni [2]. The nanorod geometry was assumed to be a cylinder with a diameter of 4.2 nm and a height of 20.9 nm. Therefore the volume of the cylinder is $V = \pi r^2 h = 289.6$ nm^3.

The unit cell parameters of brookite are a = 5.456 Å, b = 9.182 Å, c = 5.143 Å, α = 90°, V = 0.2576 nm^3 and Z = 8. Therefore, there are 1124 brookite unit cells per nanorod and 8991 TiO_2 formula units per nanorod.

The brookite nanocrystal consists of the (210) facet, which has an area of 0.49 nm^2 per unit cell. The area of the (210) plane per unit cell is

$$c\left(\left(\frac{a}{2}\right)^2 + b^2\right)^{1/2} \qquad (1)$$

The surface area of the nanorod is $2\pi rh + 2\pi r^2$. The surface area of a single nanorod with a diameter of 4.2 nm and a height of 20.9 nm is 303.5 nm^2.

There are 616 (210) 'unit planes' per nanorod, and each (210) 'unit plane' contains 4 Ti atoms. We estimate there are 2464 surface Ti atoms per nanorod.

The dispersion, D or the ratio of the number of surface Ti atoms to the total number of Ti atoms is 2464/8991 = 0.274.

References

1. Casavola, M.; Grillo, V.; Carlino, E.; Giannini, C.; Gozzo, F.; Pinel, E.F.; Garcia, M.A.; Manna, L.; Cingolani, R.; Cozzoli, P.D., *Nano Lett.*, **2007**, *7*, 1386-1395.
2. Gong, X.-G.; Selloni, A., *Phys. Rev. B*, **2007**, *76*, 235307.