

UV and Visible Light-Driven Production of Hydroxyl Radicals by Reduced Forms of N, F, and P Codoped Titanium Dioxide

A. M. Abdullah ¹, Miguel Á Gracia-Pinilla ², Suresh C. Pillai ³ and Kevin O'Shea ^{1,*}

¹ Department of Chemistry & Biochemistry, Florida International University, Miami, FL 33199, USA; am.abdullah@fiu.edu (A.M.A.); osheak@fiu.edu (K.O)

² Facultad de Ciencias Físico Matemáticas, Universidad Autónoma de Nuevo León, Av. Universidad s/n, Cd. Universitaria, San Nicolás de los Garza, Nuevo León 66455, México; miguel.graciapl@uanl.edu.mx

³ Nanotechnology and Bio-engineering Research Group, Department of Environmental Science, Institute of Technology, Sligo, Ireland; pillai.suresh@itsligo.ie

* Correspondence: osheak@fiu.edu; Tel +1-305-348-3968

HRTEM analysis

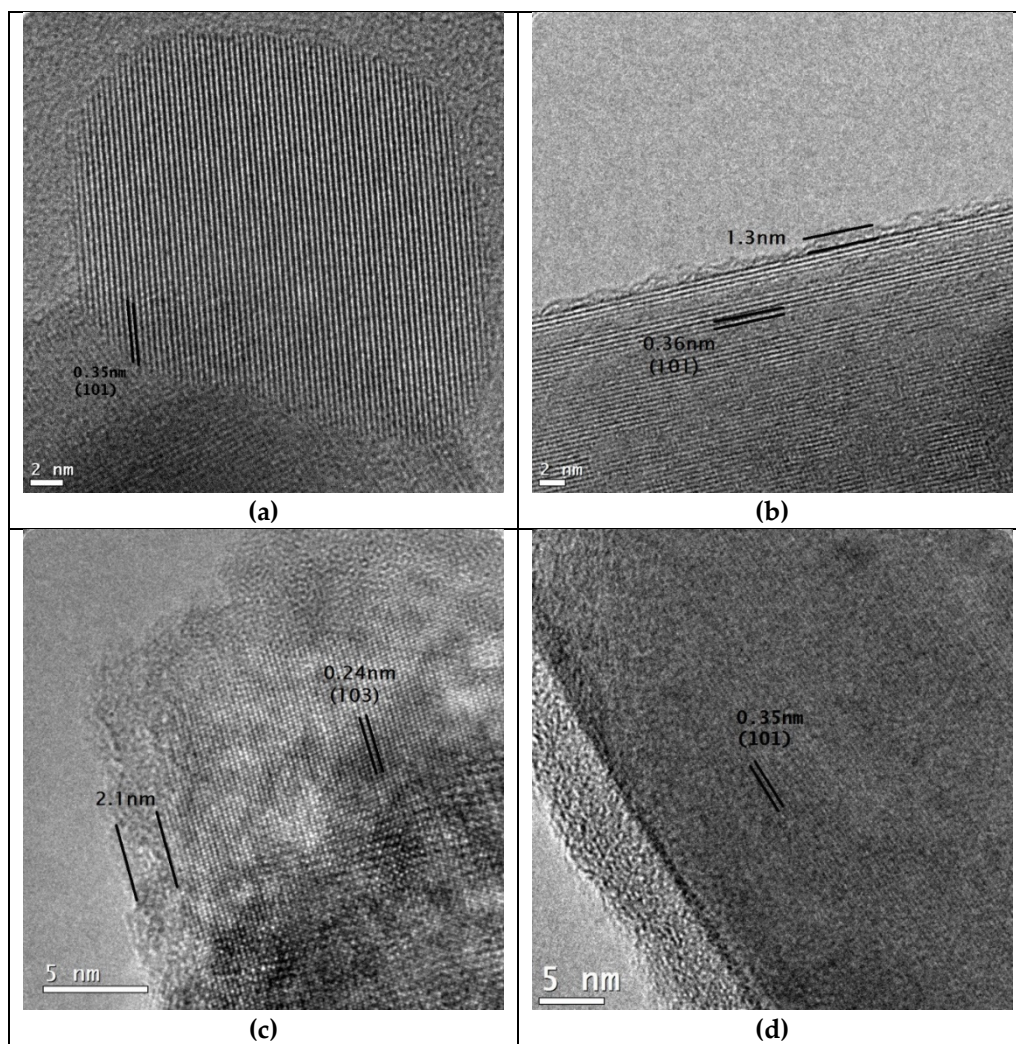


Figure S1a. HRTEM images of N, and F codoped TiO₂ nanocrystals (a) NF-TiO₂ before reduction, (b) NF-TiO₂^{red 30} (1.3 nm of the amorphous layer), (c) NF-TiO₂^{red 50} (2.1 nm of the amorphous layer) and (d) NF-TiO₂^{red 70} (6.0 nm of the amorphous layer)

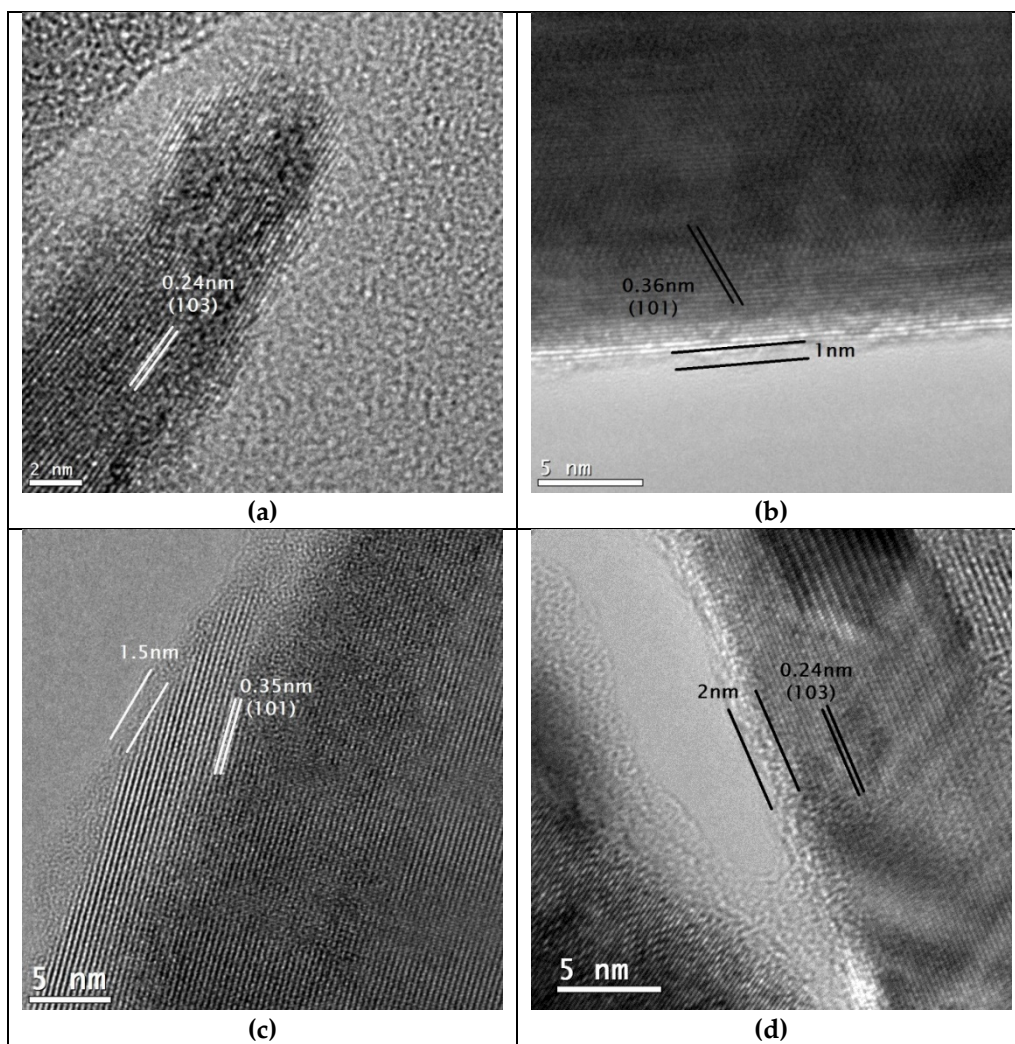


Figure S1b. HRTEM images of N, F, and P codoped TiO_2 nanocrystals (a) NFP- TiO_2 before reduction, (b) NFP- $\text{TiO}_2^{\text{red } 30}$ (1.0 nm of the amorphous layer), (c) NFP- $\text{TiO}_2^{\text{red } 50}$ (1.5 nm of the amorphous layer) and (d) NFP- $\text{TiO}_2^{\text{red } 70}$ (2.0 nm of the amorphous layer)

EDXRF Analysis

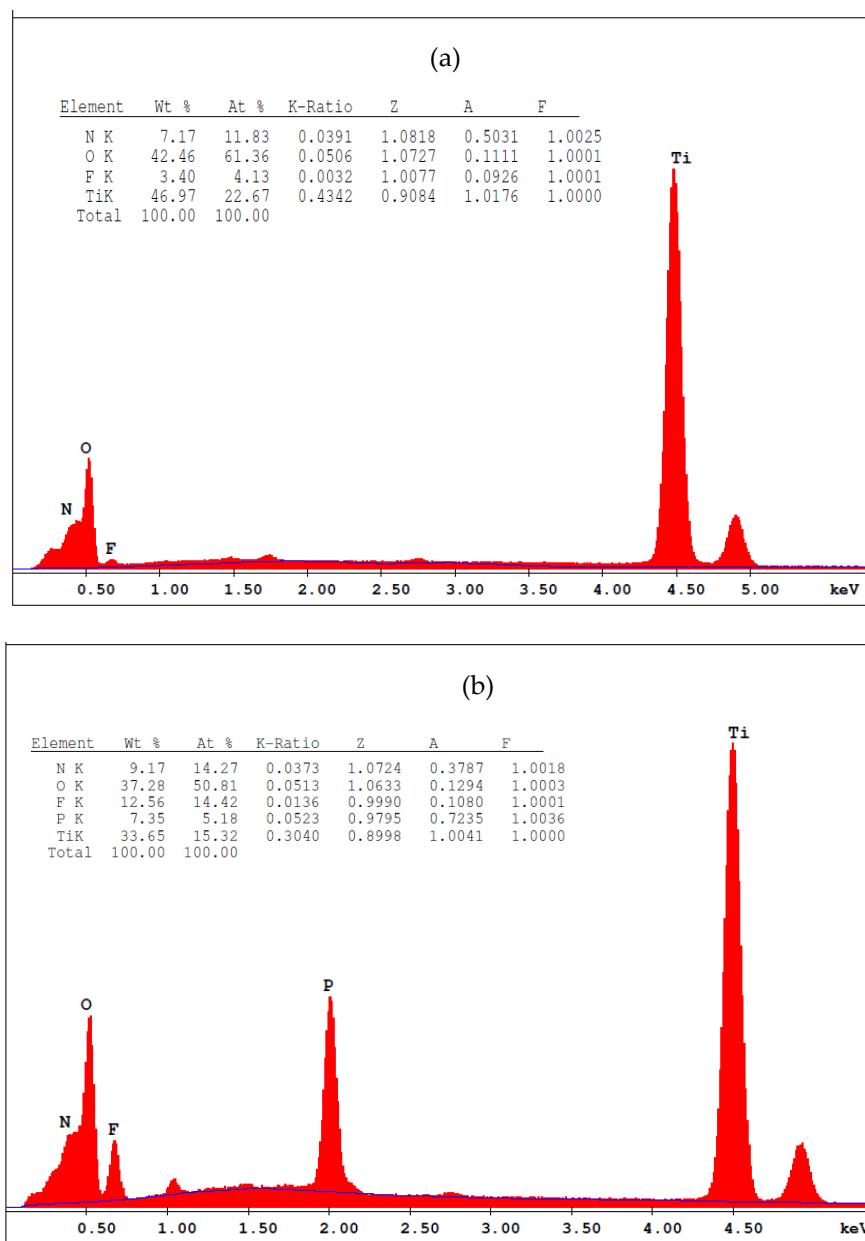


Figure S2. EDXRF spectrum of (a) N, and F codoped TiO_2 (NF- TiO_2) and (b) N, F, and P codoped TiO_2 (NFP- TiO_2)

UV-Visible spectroscopy

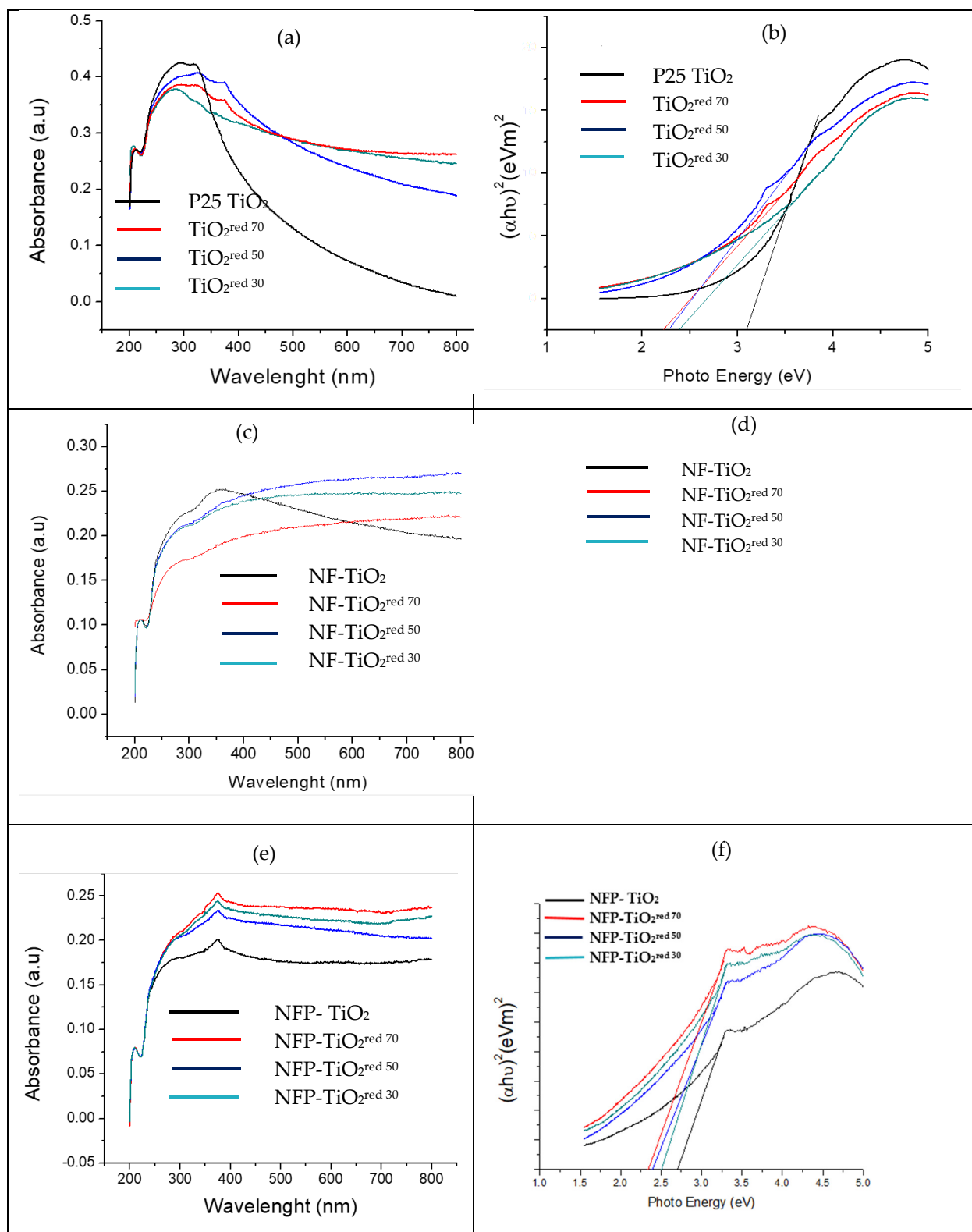


Figure 3. UV-Visible diffuse reflectance spectra of (a) P25 TiO₂ series, (c) NF-TiO₂ series, and (e) NFP-TiO₂ series. The Kubelka-Munk plot for band energy calculation for (b) P25 TiO₂ series, (d) NF-TiO₂ series, and (f) NFP-TiO₂ series.

Raman Spectroscopy

Table S1a. Raman band position of P25 TiO₂ and reduced P25 TiO₂ (TiO₂^{red})

P25 TiO ₂ (cm ⁻¹)	TiO ₂ ^{red} 70 (cm ⁻¹)	TiO ₂ ^{red} 50 (cm ⁻¹)	TiO ₂ ^{red} 30 (cm ⁻¹)	Band
143	146	143	145	Eg ₁
396	394	395	397	Bg ₁
516	511	511	521	Ag ₁
637	634	634	636	Eg ₃

Table S1b. Raman band position of NF-TiO₂ and reduced NF-TiO₂^{red}

NF-TiO ₂ (cm ⁻¹)	NF-TiO ₂ ^{red} 70 (cm ⁻¹)	NF-TiO ₂ ^{red} 50 (cm ⁻¹)	NF-TiO ₂ ^{red} 30 (cm ⁻¹)	Band
142	144	145	144	Eg ₁
393	393	392	393	Bg ₁
512	511	512	511	Ag ₁
635	634	633	633	Eg ₃

Table S1c. Raman band position of NFP- TiO₂ and reduced NFP-TiO₂^{red}

NFP-TiO ₂ (cm ⁻¹)	NFP-TiO ₂ ^{red} 70 (cm ⁻¹)	NFP-TiO ₂ ^{red} 50 (cm ⁻¹)	NFP-TiO ₂ ^{red} 30 (cm ⁻¹)	Band
143	148	147	149	Eg ₁
393	390	390	391	Bg ₁
511	506	509	507	Ag ₁
636	630	634	633	Eg ₃

Production of hydroxyl radicals by reduced doped TiO₂

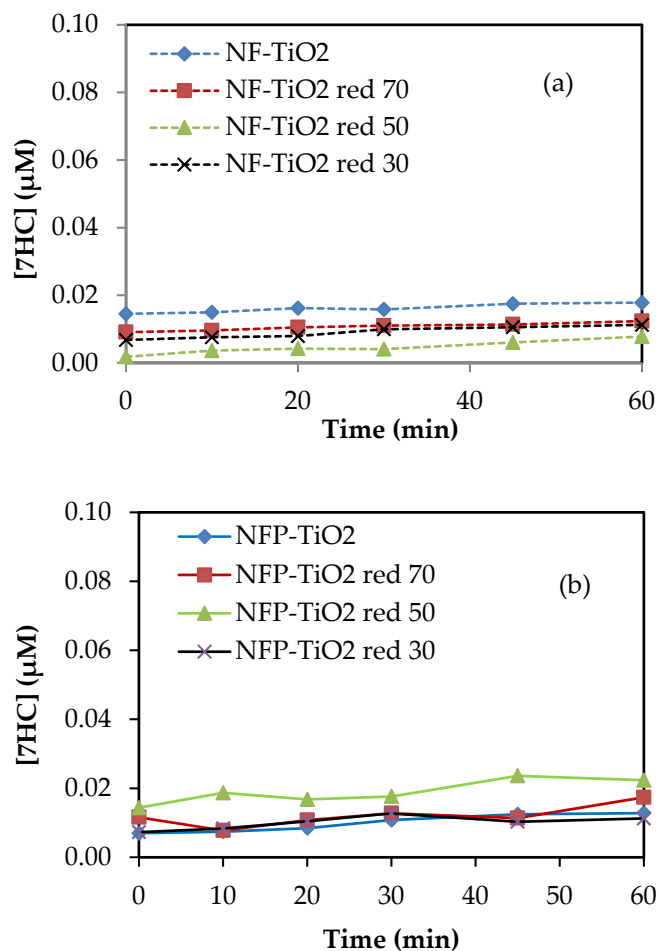


Figure S4. The production of 7HC at 350 nm by (a) reduced NF-TiO₂ and (b) NFP-TiO₂ photocatalyst

Calibration curve for the measurement of 7-Hydroxycoumarin

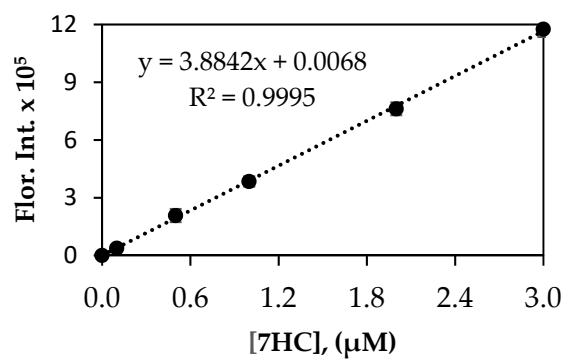


Figure S5. Spectrofluorometric calibration curve for measuring of 7HC. The data is reproducible within 5% standard deviation based on triplicate runs.