

Supporting Information

Plasmonic Ru/Hydrogen Molybdenum Bronze with Tunable Oxygen Vacancies for Light-Driven Reduction of *p*-Nitrophenol

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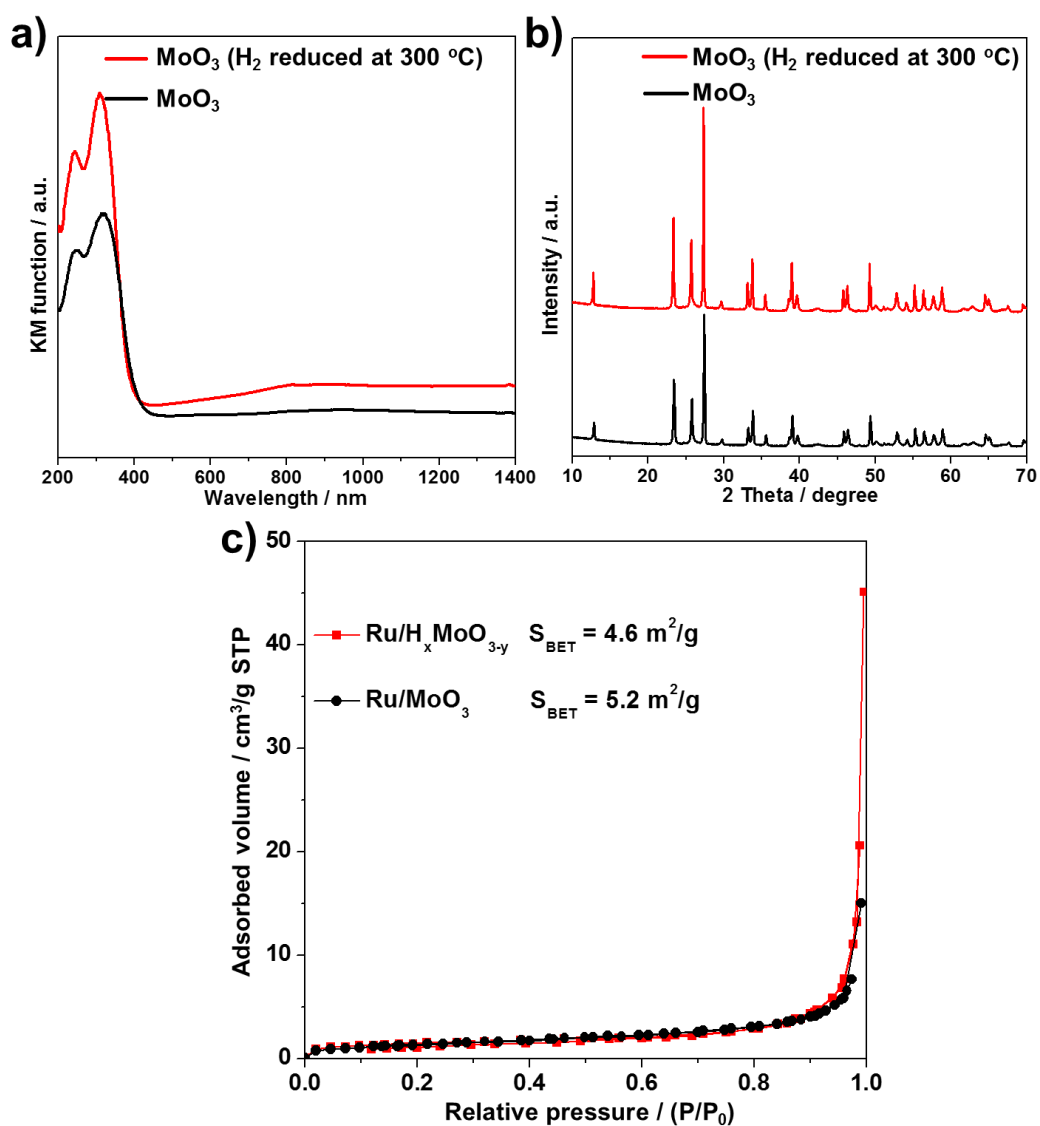


Figure S1. a) UV-vis-NIR diffuse reflectance spectra and b) XRD patterns of the MoO_3 before and after H_2 reduction at 300 °C. c) N_2 adsorption-desorption isotherms of Ru/MoO_3 and $\text{Ru}/\text{H}_x\text{MoO}_{3-y}$ hybrid.

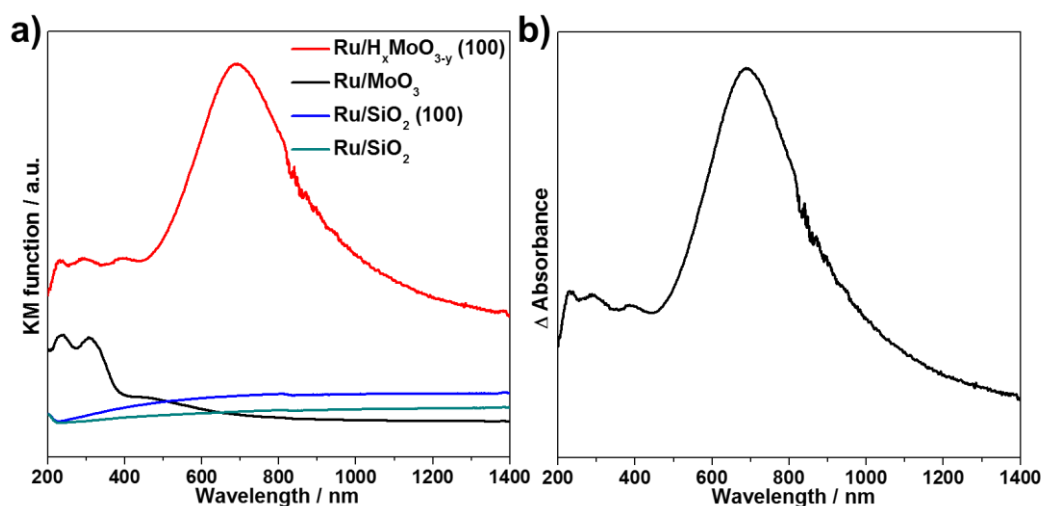


Figure S2. a) UV-vis-NIR diffuse reflectance spectra of the Ru/MoO₃ and Ru/SiO₂ hybrids before and after H₂ reduction at 100 °C. b) The absorbance different between the Ru/MoO₃ and Ru/SiO₂ hybrids after H₂ reduction at 100 °C through subtraction of their corresponding UV-vis-NIR diffuse reflectance spectra in a).

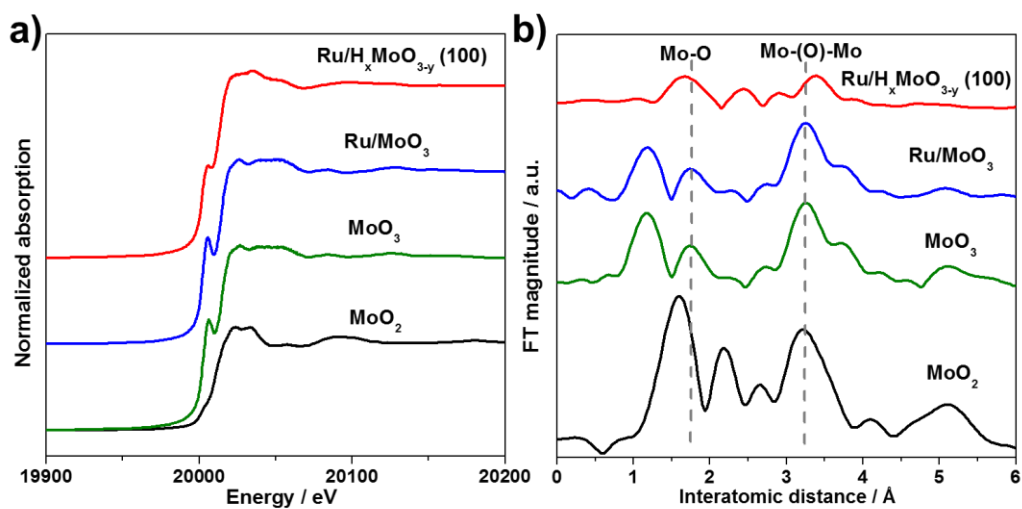


Figure S3. a) Mo *K*-edge XANES and b) FT-EXAFS spectra for the Ru/MoO₃ samples before and after H₂ reduction and reference materials (MoO₃ and MoO₂).

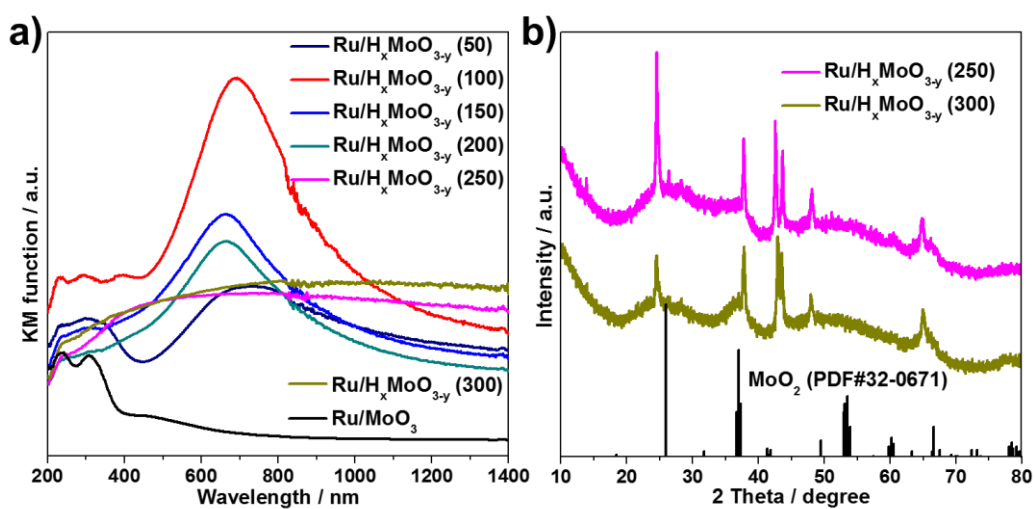


Figure S4. a) UV-vis-NIR diffuse reflectance spectra of Ru/MoO₃ samples after H₂ reduction at different temperatures. b) XRD patterns of the Ru/H_xMoO_{3-y} (250 and 300).

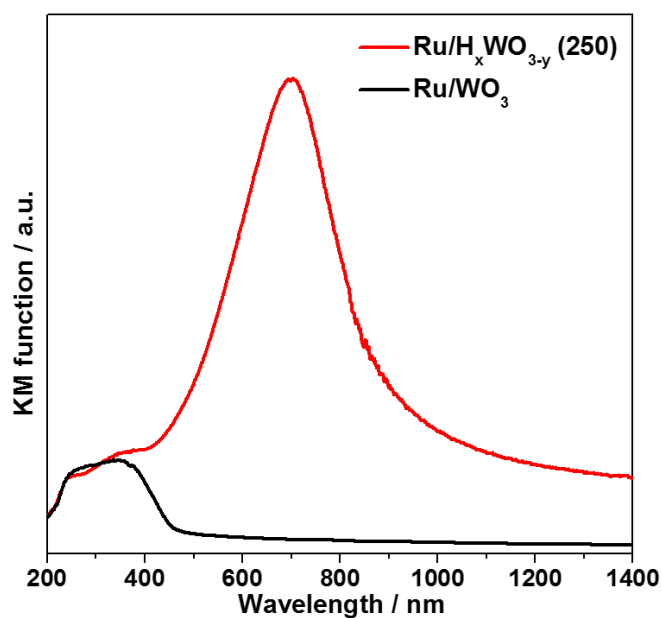


Figure S5. UV-vis-NIR diffuse reflectance spectra of Ru/WO₃ before and after H₂ reduction at 250 °C, respectively.

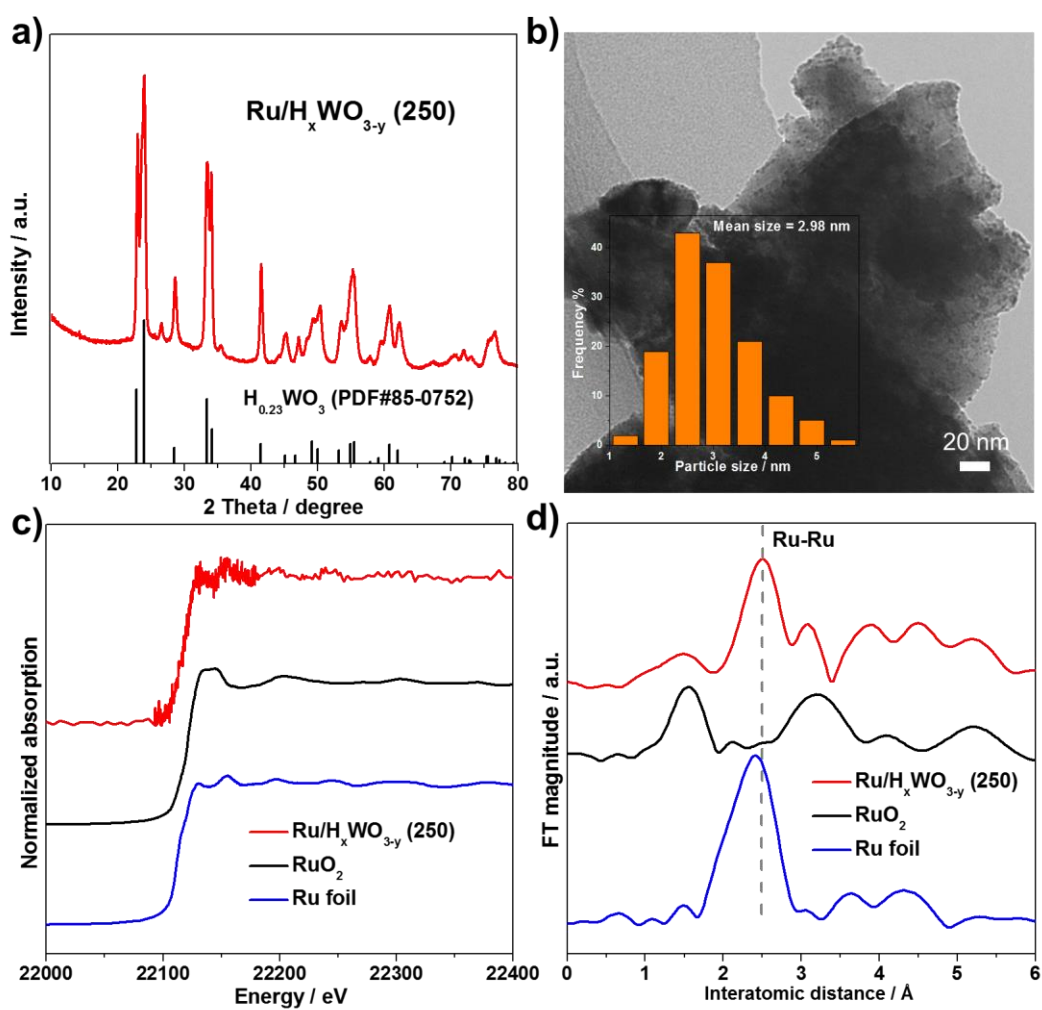


Figure S6. a) XRD patterns of the Ru/H_xWO_{3-3-y} (250). b) TEM image of the Ru/WO₃ after H₂ reduction at 250 °C and (inset) the corresponding particle size distribution of Ru NPs. c) Ru K-edge XANES and d) FT-EXAFS spectra for the Ru/WO₃ after H₂ reduction at 250 °C and reference materials (Ru foil and RuO₂)

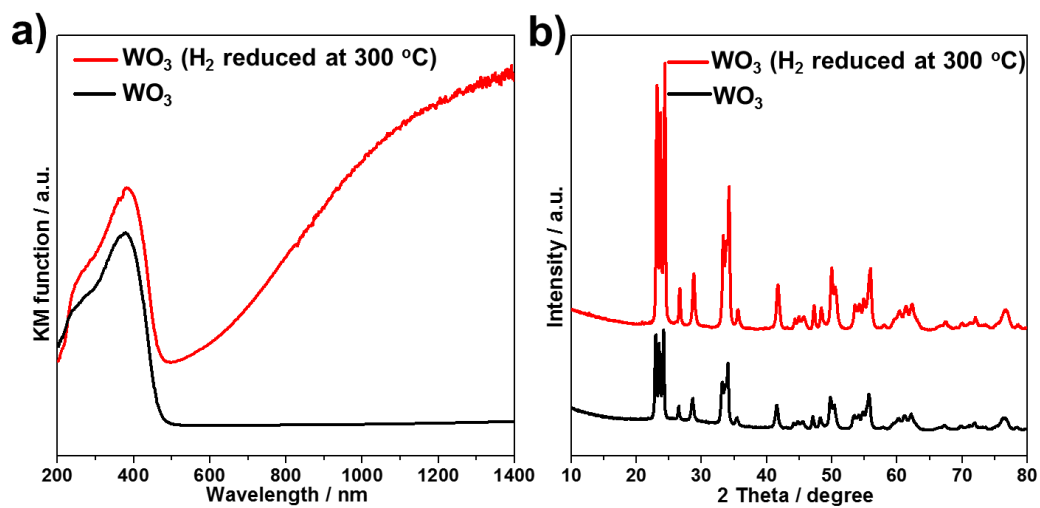


Figure S7. a) UV-vis-NIR diffuse reflectance spectra and b) XRD patterns of the WO₃ before and after H₂ reduction at 300 °C.

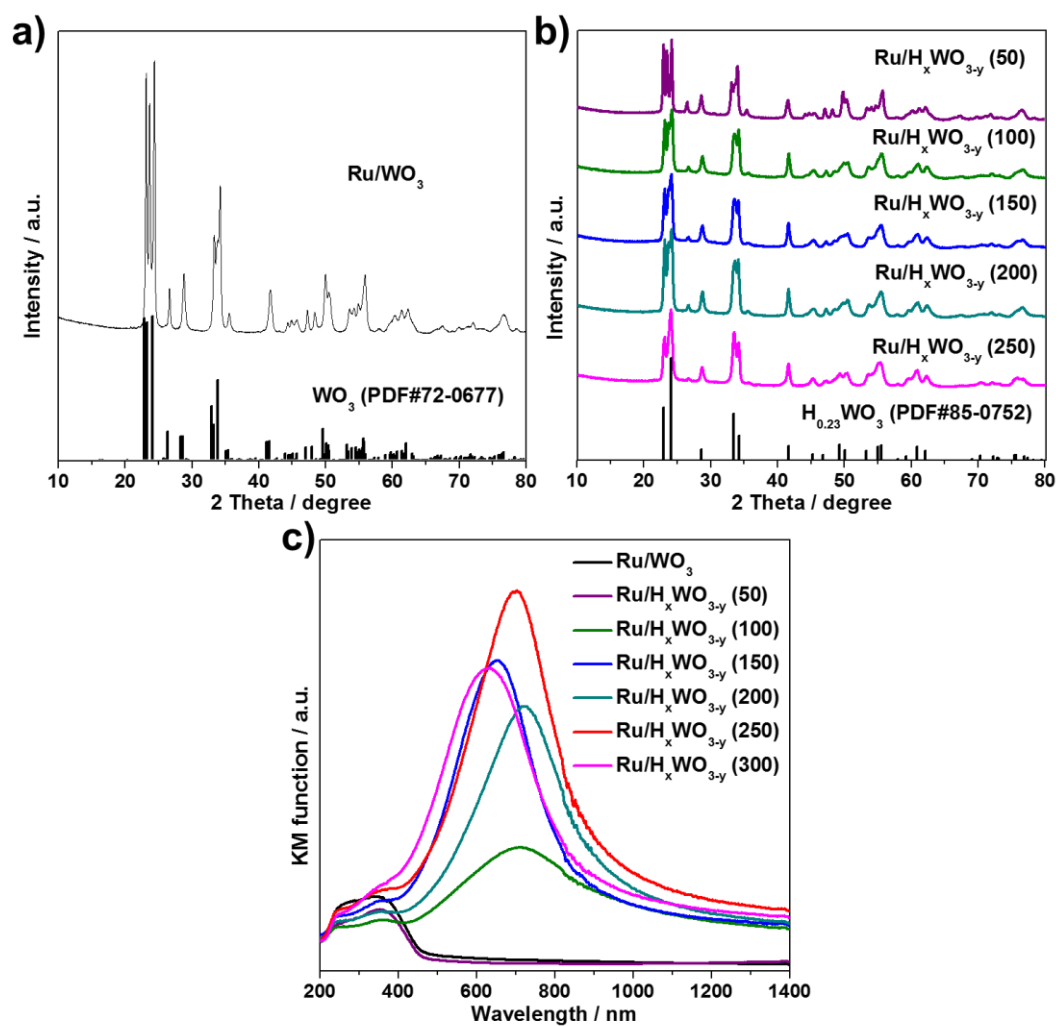


Figure S8. XRD patterns of a) the Ru/WO₃ and b) Ru/WO₃ samples after H₂ reduction at different temperatures. c) UV-vis-NIR diffuse reflectance spectra of Ru/WO₃ samples before and after H₂ reduction at different temperatures.

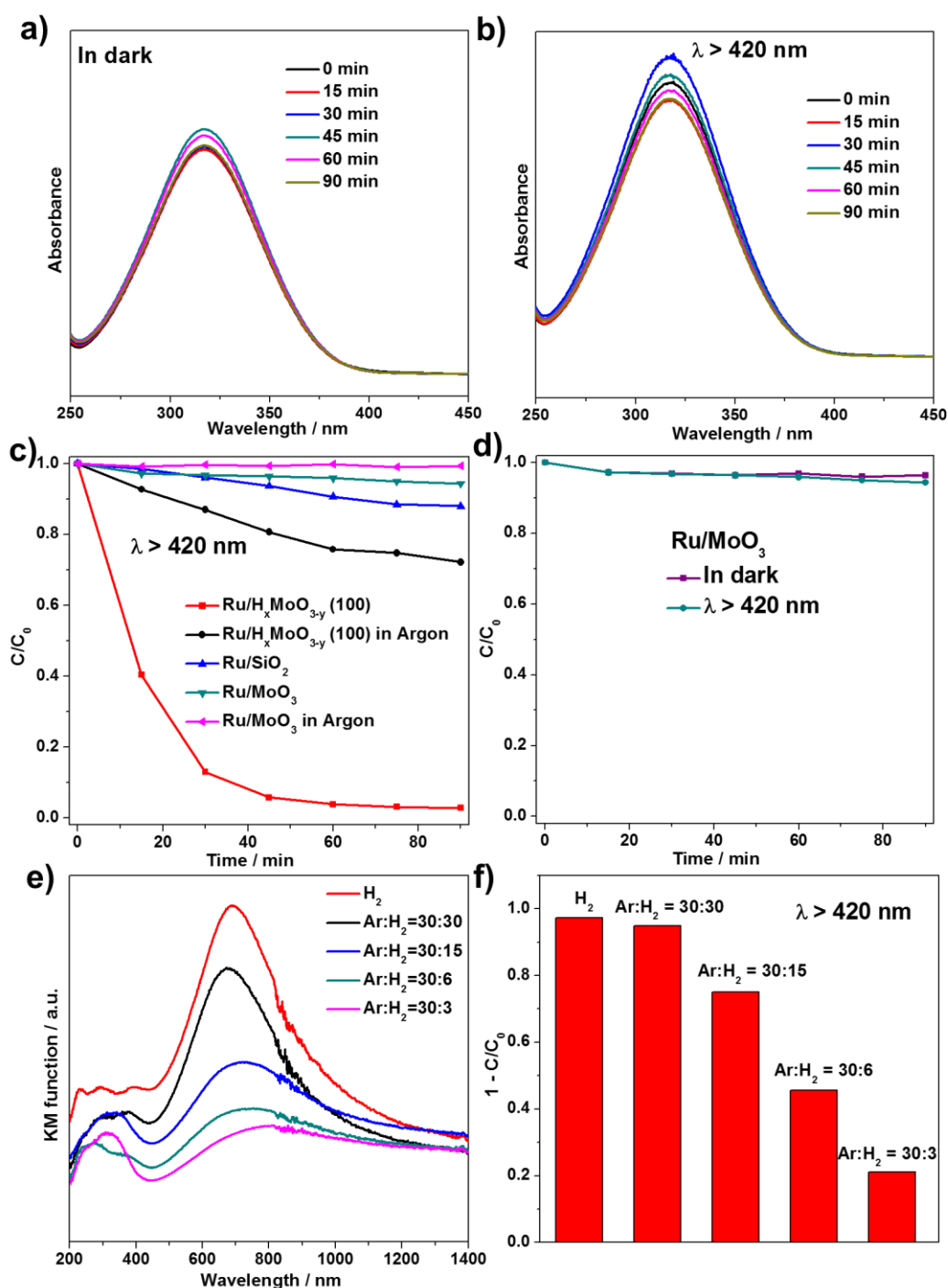


Figure S9. Time-dependent evolution of UV-vis absorption spectra of reaction solutions without catalyst a) in the dark and b) under visible irradiation ($\lambda > 420$ nm). c) Plots of relative concentration of *p*-nitrophenol over Ru/H_xMoO_{3-y} (100) catalyst and reference samples as a function of time. d) Plots of relative concentration of Ru/MoO₃ against the initial point at 317 nm peak for PNP as a function of time. e) UV-vis-NIR diffuse reflectance spectra and f) comparison of catalytic activity in the hydrogenation of *p*-nitrophenol over Ru/MoO₃ samples under different ratios reducing atmosphere of Ar (mL/min) : H₂ (mL/min).

Table S1 Summary of PNP reduction by using the reported catalysts.

Catalysts	Reaction condition	Hydrogen source	TOF/h ⁻¹ (mol of PAP/mol of catalyst*h)	Ref.
Ru/H _x MoO _{3-y}	H ₂ O, 298.15 K λ > 420 nm	H ₂	2.8	This study
Ru/H _x MoO _{3-y}	H ₂ O, 298.15 K λ > 420 nm	H ₂	0.14	This study
Pd/MoO ₃ H ₂ -RT	H ₂ O, 298.15 K λ > 420 nm	NH ₃ BH ₃	6.50	J. Am. Chem. Soc. 2016, 138, 9316-9324.
Cu-Ag-Au alloy	H ₂ O, 300 K	NaBH ₄	18.60	Environ. Sci. Technol. 2016, 50, 11263-11273.
Reduced Co ₃ O ₄	H ₂ O, 303.15 K	NaBH ₄	0.50	Appl. Catal., B 2017, 209, 648-656.
Cu ₂ O@h-BN (boron nitride)	H ₂ O	NaBH ₄	~ 0.50	ACS Appl. Mater. Interfaces 2014, 6, 14469-14476.
Au/HCNM	H ₂ O, 295.15 K	NaBH ₄	64	ACS Sustainable Chem. Eng. 2013, 1, 746-752.
NM/MoS ₂ NSs	H ₂ O	NaBH ₄	0.20	Cryst. Growth Des. 2017, 17, 3538-3547.
AuNPs-SPEG	H ₂ O	NaBH ₄	1.14	ACS Catal. 2016, 6, 5553-5560.
pf- Au@SiO ₂ NPs	H ₂ O, room temperature	NaBH ₄	~ 20	ACS Catal. 2017, 7, 5391-5398.
Co-colloid	THF, 373 K	THF	51.84	Chem. Commun., 2005, 0, 2026-2028
NiPd-colloid	THF, 373 K	THF	~ 70.77	Chem. Commun., 2005, 0, 2026-2028

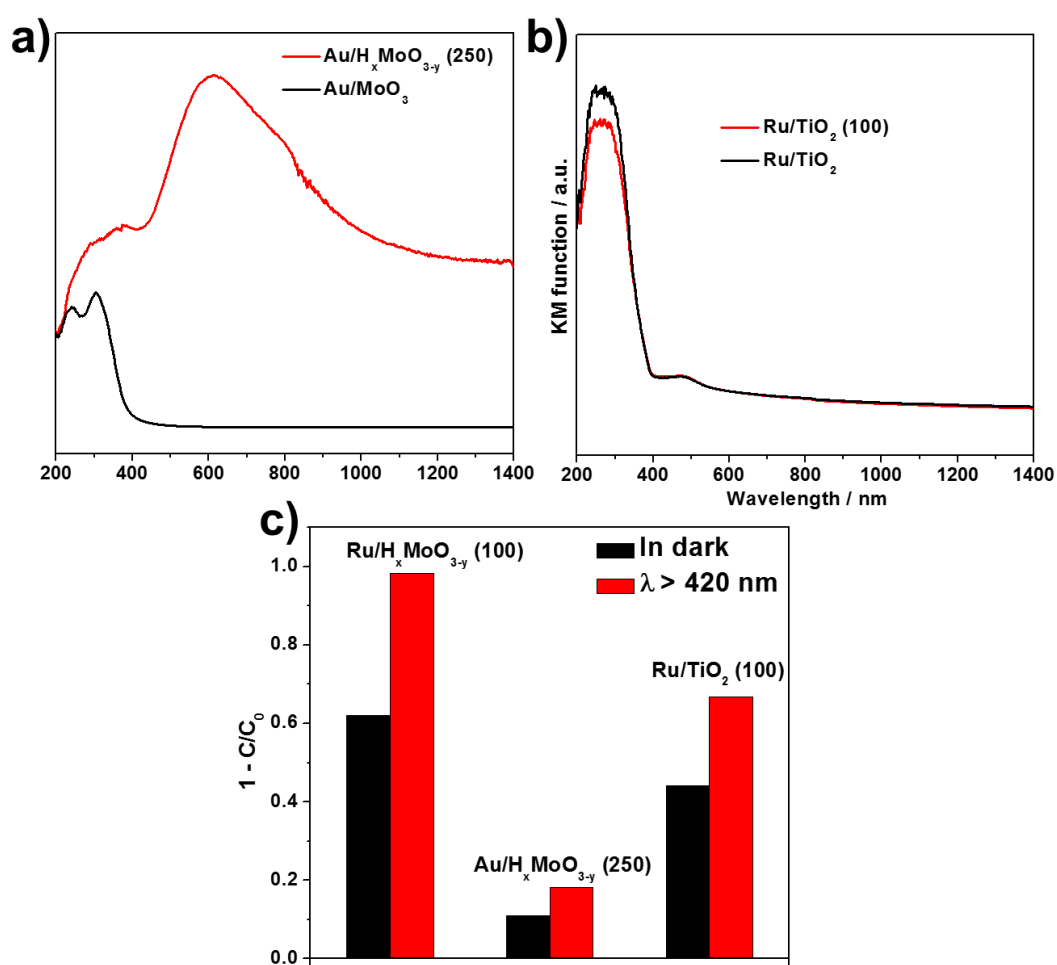
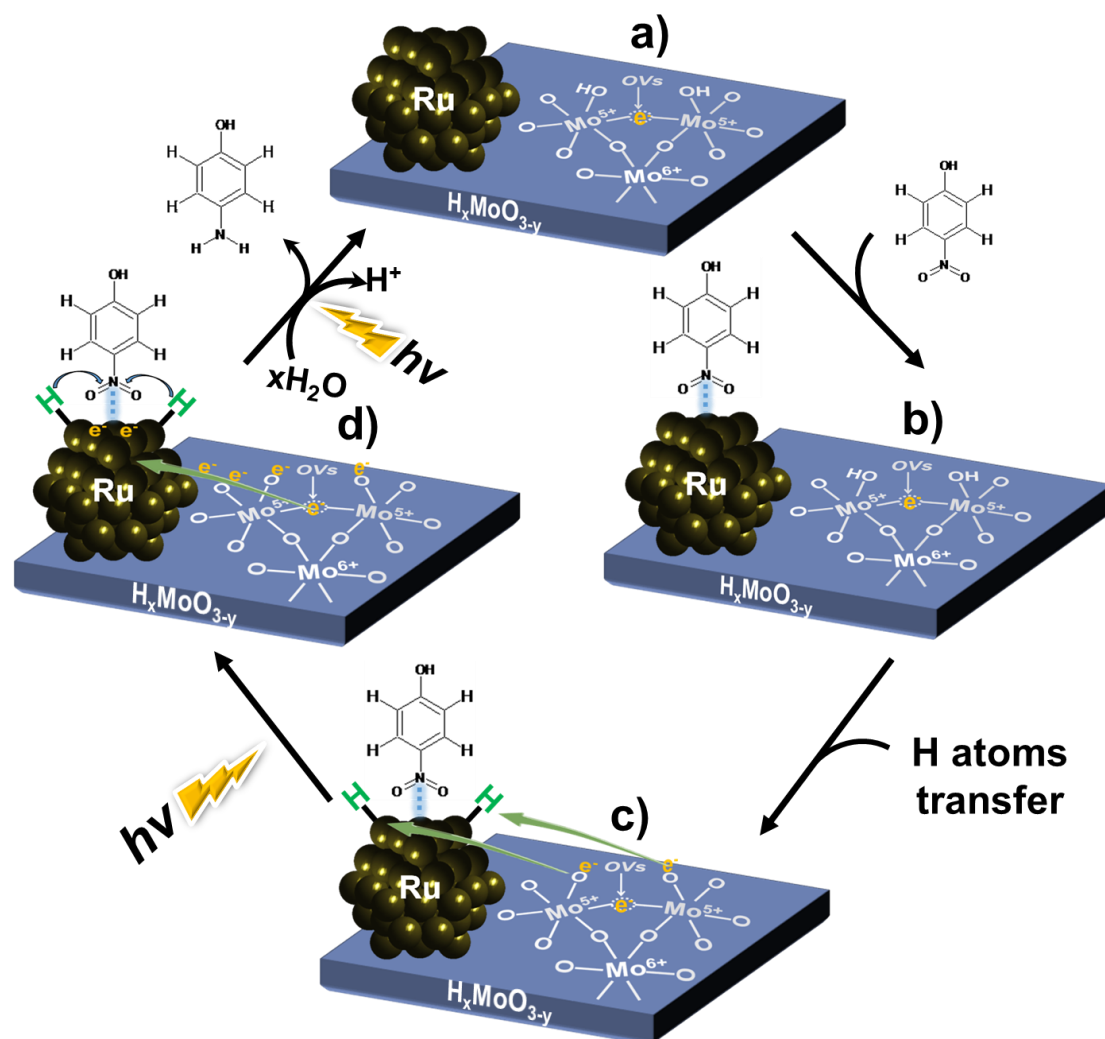


Figure S10. UV-vis-NIR diffuse reflectance spectra of a) Au/MoO_3 and b) Ru/TiO_2 samples before and after H_2 reduction at different temperatures. c) Comparison of catalytic activity in the hydrogenation of *p*-nitrophenol over $\text{Au}/\text{H}_x\text{MoO}_{3-y}$ (250) and Ru/TiO_2 (100) after 90 min of reaction.



Scheme S1. Proposed mechanism of PNP hydrogenation on Ru/H_xMoO_{3-y} (T) without H₂ gas atmosphere.