

**SUPPLEMENTARY INFORMATION**

**Light-triggered and cysteine-mediated nitric oxide release  
from a biodegradable starch-based film**

*Antonio Carlos Roveda Jr.<sup>†</sup>, Helena de Fazio Aguiar<sup>#</sup>, Katrina M. Miranda<sup>‡</sup>,*

*Carmen Cecília Tadini<sup>#</sup>, Douglas Wagner Franco<sup>†\*</sup>.*

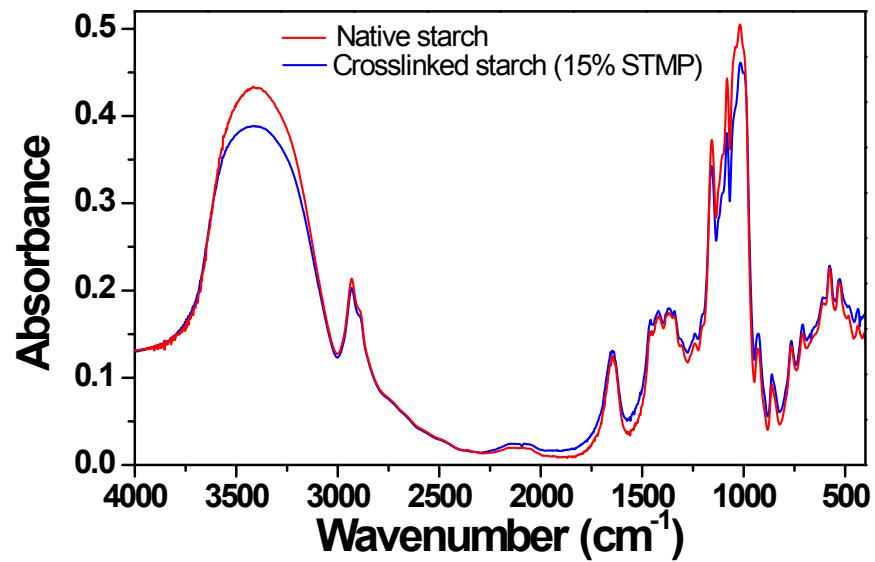
<sup>†</sup>Instituto de Química de São Carlos, Universidade de São Paulo – USP, P.O.Box 780, CEP 13566-590, São Carlos, SP, Brazil

<sup>#</sup>Department of Chemical Engineering, Escola Politécnica, University of São Paulo, Av. Prof. Luciano Gualberto, Travessa 3, nº 380, São Paulo, SP, Brazil

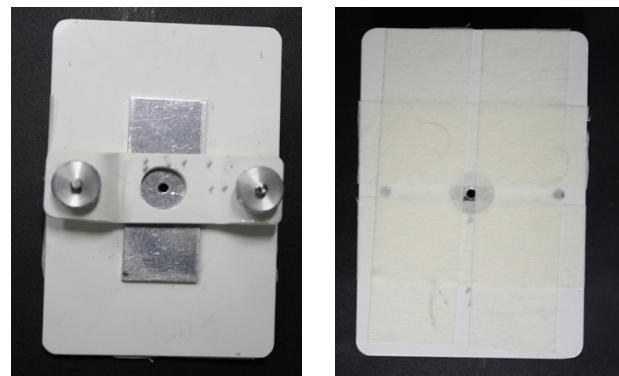
<sup>‡</sup>Department of Chemistry and Biochemistry, University of Arizona, Tucson, Arizona 85721, United States

**Corresponding Author**

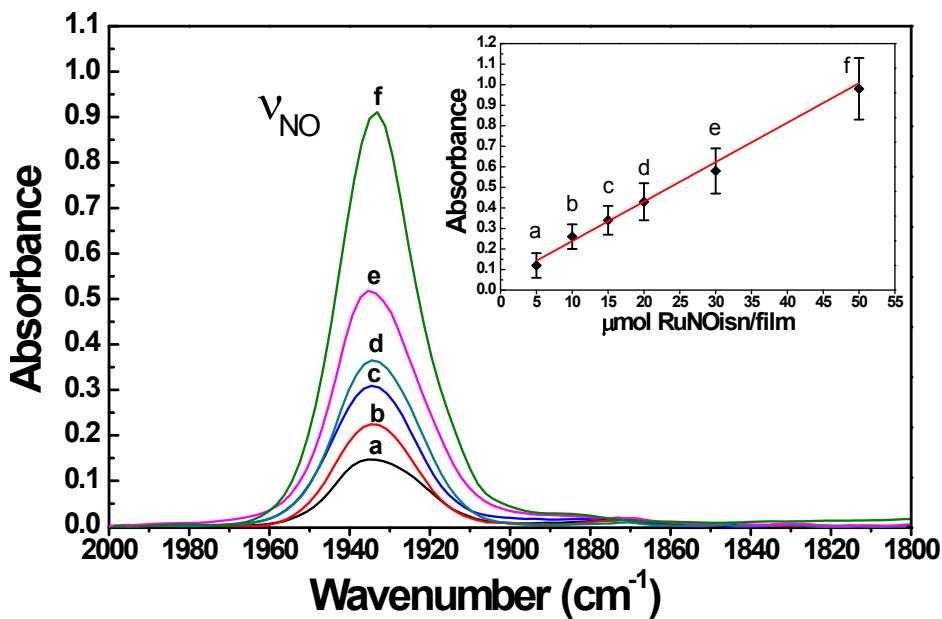
\*E-mail: douglas@iqsc.usp.br



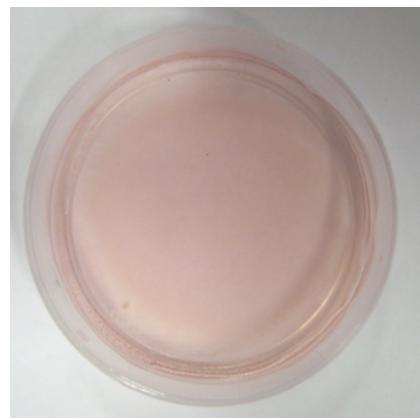
**Figure S1.** FT-IR spectra of native and modified (crosslinked with 15% STMP) starch.



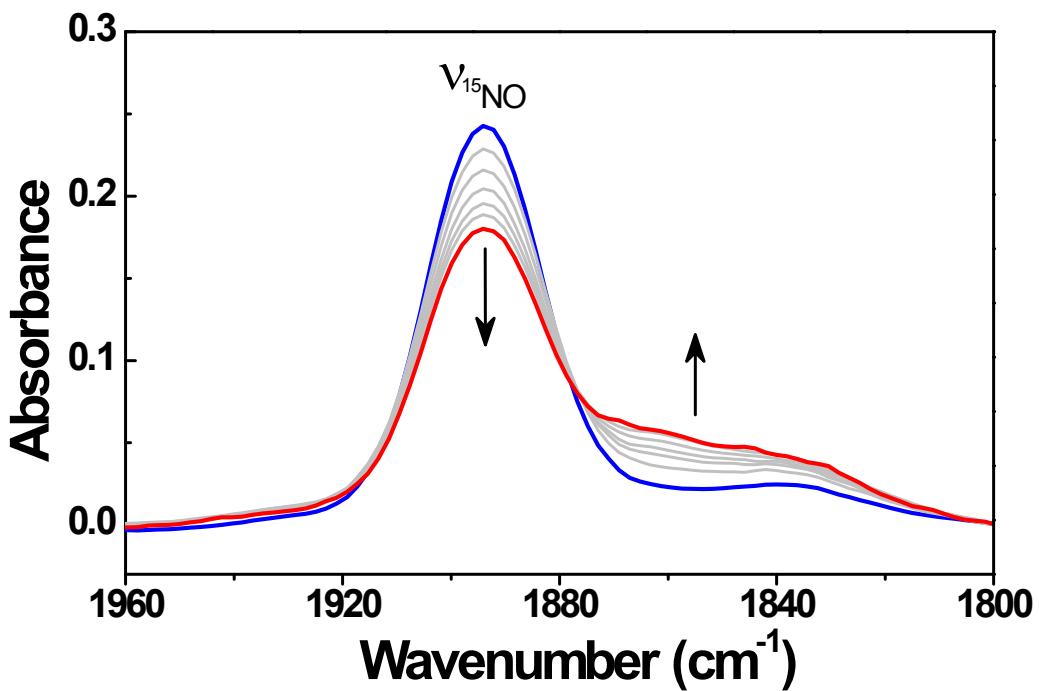
**Fig. S2.** FT-IR cell holder used for photolysis of CS films.



**Fig. S3.** FT-IR of  $\text{CS}_x\text{-RuNOisn}$  with different **RuNOisn** contents/film (in  $\mu\text{mol}$  of **RuNOisn**/film). Concentrations of 5, 10, 15, 20, 30, 50  $\mu\text{mol}$  **RuNOisn**/film are represented respectively by the spectra with labels “a” to “f”. Inset: plot of **RuNOisn** content/film vs. NO stretch absorbance,  $R^2 = 0.9905$ .

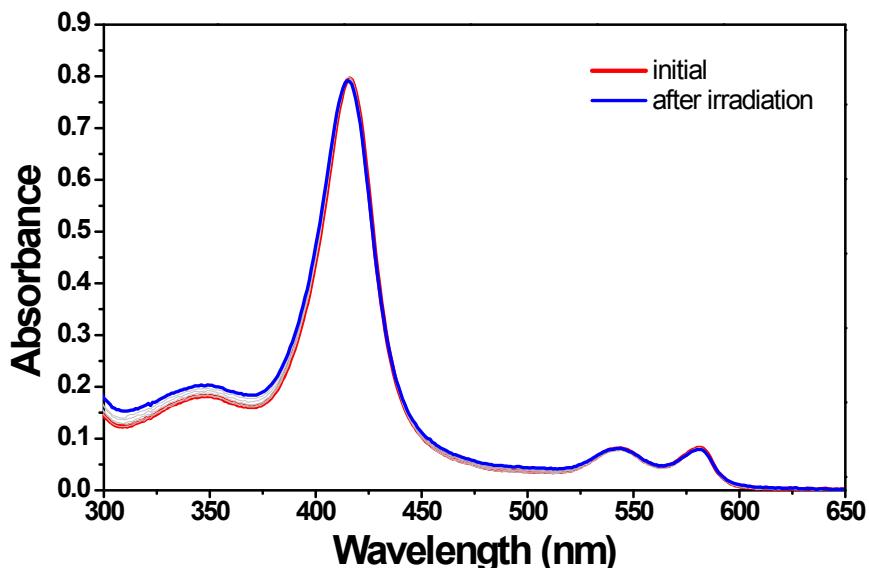


**Fig. S4.** Photograph of a cassava starch film containing  $\text{trans-}[\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{isn})(\text{NO}^+)](\text{BF}_4)_3$ .

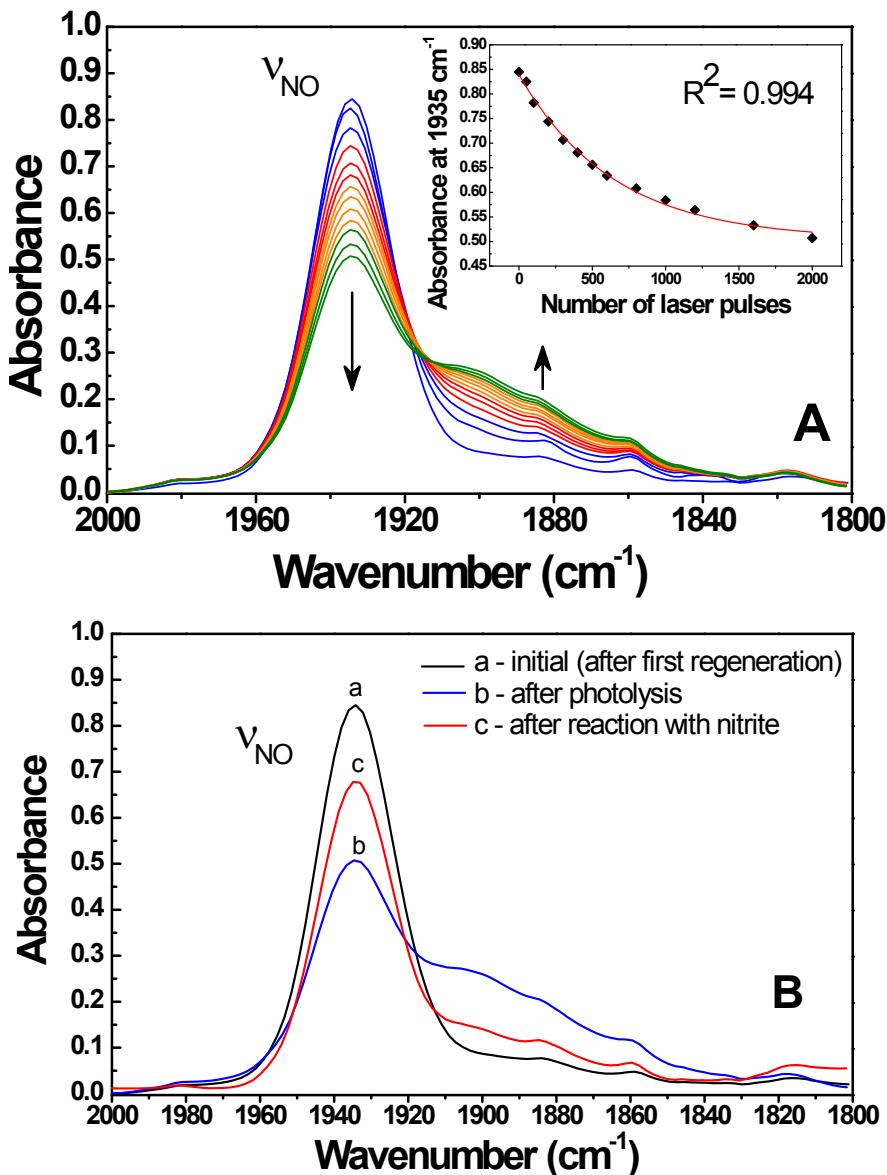


**Fig. S5.** Spectral changes during photolysis of CS film containing *trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>(isn)(<sup>15</sup>NO<sup>+</sup>)].

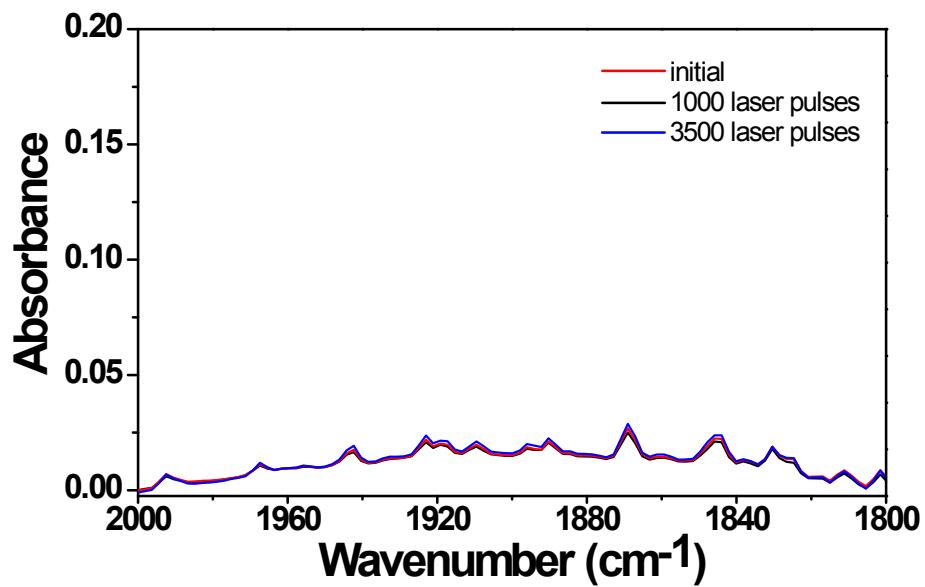
Conditions:  $\lambda_{\text{irr}} = 355$  nm, 5 mJ/pulse.



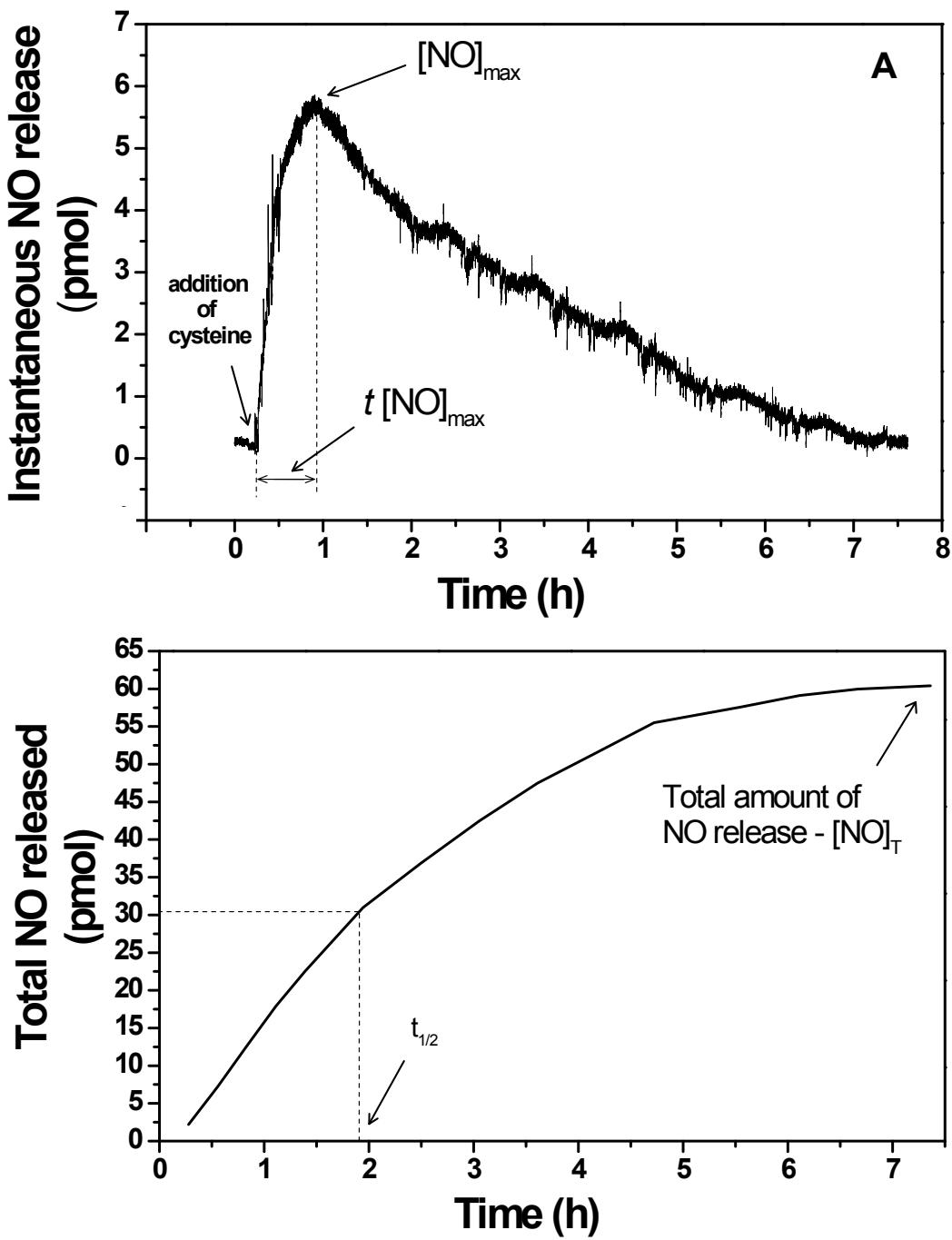
**Fig. S6.** Spectral changes during photolysis of a solution containing oxyMb and a ruthenium-free CS film. Conditions: 1 cm<sup>2</sup> of ruthenium-free CS film and 5.8 μM of oxyMb in a phosphate buffer solution (pH 7.4, 100 mM); 1000 laser pulses,  $\lambda_{\text{irr}} = 355$  nm, 5 mJ/pulse, T = 2 °C.



**Fig. S7.** **(A)** Spectral changes during a second cycle of irradiation of **CS<sub>50</sub>-RuNOisn** ( $\lambda_{\text{irr}} = 355 \text{ nm}$ , 5 mJ/pulse). The inset shows the changes in the absorbance at  $1935 \text{ cm}^{-1}$  during photolysis. **(B)** Second regeneration of photolyzed **CS<sub>50</sub>-RuNOisn** after reaction with 1.0 mM nitrite.



**Fig. S8** – Photolysis of a ruthenium-free starch-based film dipped in aqueous nitrite solution. Conditions: Film immersed in solution of sodium nitrite (10.0 mM) for 20 min. Photolysis:  $\lambda_{\text{irr}} = 355$  nm, 5mJ/ pulse, a pulse every 2 seconds.



**Fig. S9. (A)** Real time NO release profile and **(B)** plot of  $t[NO]$  vs. time for cysteine-initiated NO release from **RuNOisn**. Conditions: 1.77  $\mu$ mol of **RuNOisn**, TRIS buffer 0.150 M, 5 mM EDTA, pH 7.4 at 37 °C.  $[NO]_{\max}$  = maximum flux of NO release;  $t[NO]_{\max}$  = the time until  $[NO]_{\max}$ .