

**Effect of Silver Nanoparticles on the Photophysics of Riboflavin: Consequences on the ROS Generation.**

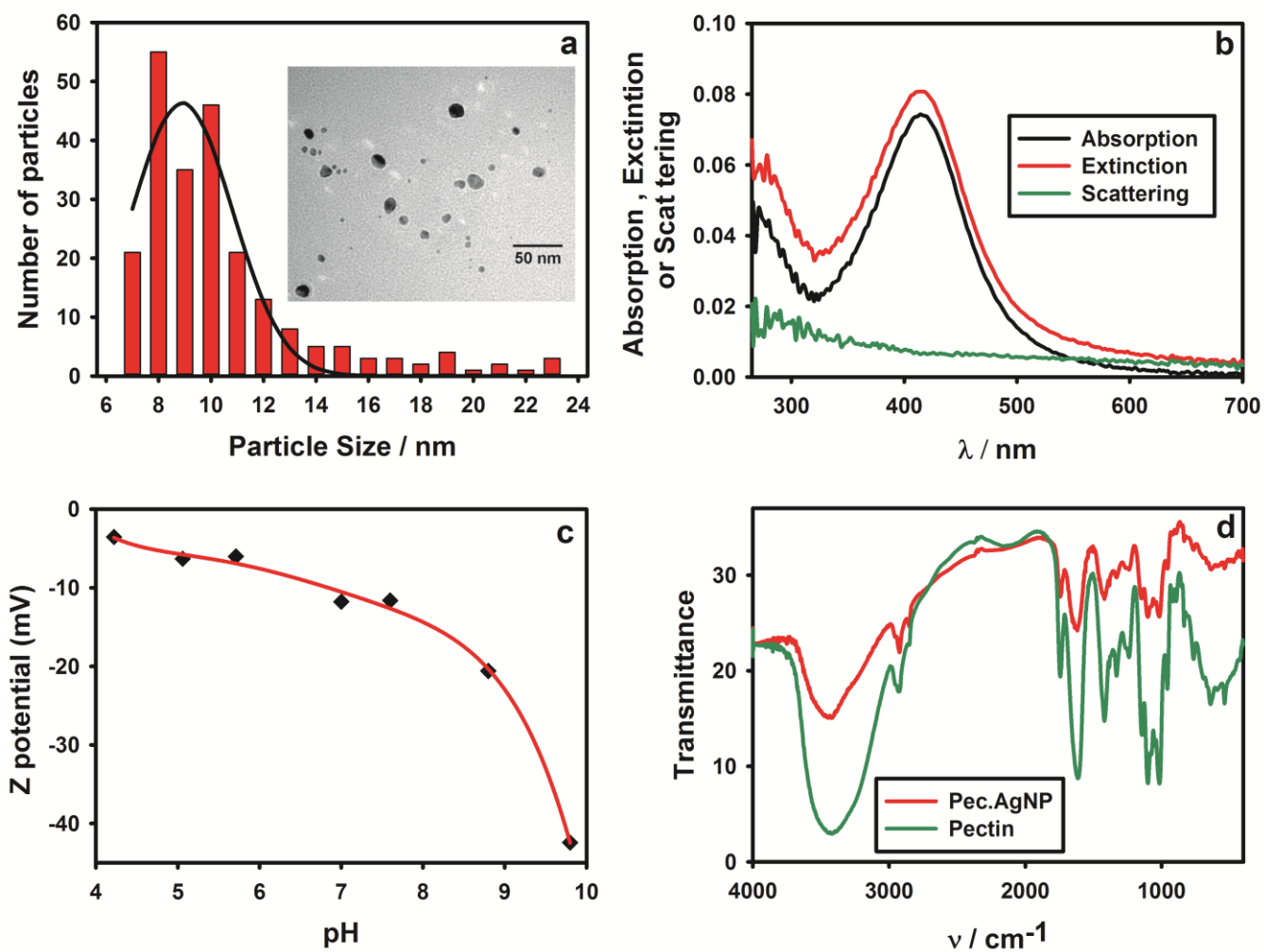
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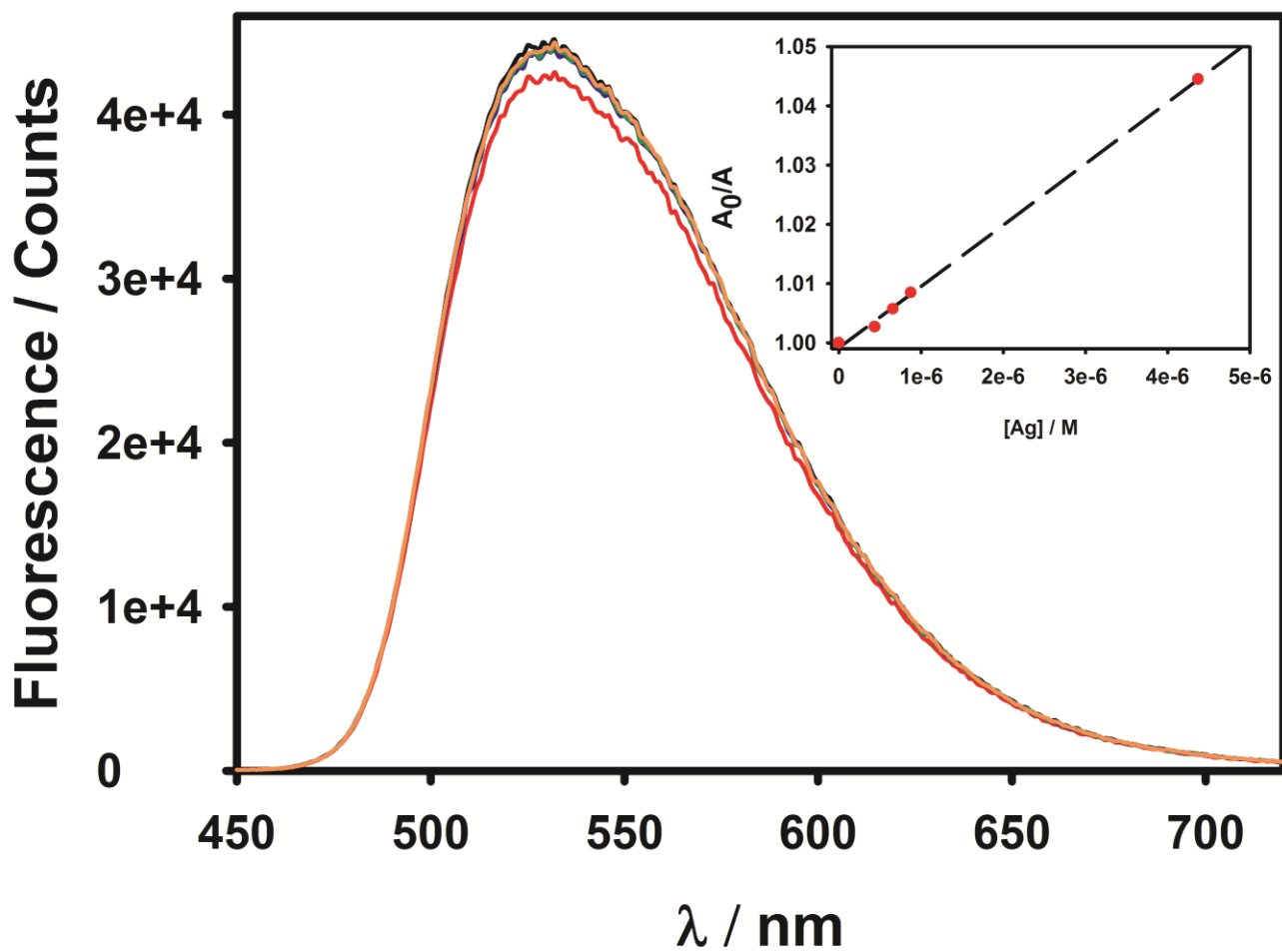
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**Figure S1:** a) Size distribution histogram of Pec.AgNP. Inset: TEM image of Pec.AgNP. b) UV-vis absorption, extinction, and scattering spectra of a 11.7 M suspension of Pec.AgNP. c) Zeta potential measurements of Pec.AgNP as a function of pH. d) FTIR spectra of pectin and Pec.AgNP.

<b>[Ag] / M</b>	<b>Lifetime / ns</b>
0	4.73
4.55E-08	4.75
6.83E-08	4.75
7.88E-08	4.73
9.11E-08	4.75
1.18E-07	4.72
1.58E-07	4.72
4.55E-07	4.70
4.55E-07	4.75
6.83E-07	4.68
7.88E-07	4.72
9.11E-07	4.69
4.55E-06	4.73

**Table S1:** Fluorescence lifetimes of Rf in the absence and presence of Pec.Ag NP ( $\lambda^{\text{exc}} = 388 \text{ nm}$ ).



**Figure S2:** Fluorescence emission spectra ( $\lambda^{\text{exc}} = 420\text{nm}$ ) of Rf (16  $\mu\text{M}$ ) in the absence (black) and presence of various amounts of Pec.AgNP. The Ag concentrations are: 4.37  $\mu\text{M}$  (red), 0.87  $\mu\text{M}$  (blue), 0.65  $\mu\text{M}$  (green), 0.44  $\mu\text{M}$  (orange). Inset: Plot of  $(A_0/A)$  vs.  $[\text{Ag}]$ .  $A_0$  and  $A$  are the emission areas without and with nanoparticles, respectively.

## Calculation of the diffusion-controlled rate constant with the Smoluchowski equation

Rates of reaction at an interface, with one reactant immobilized at a spherical surface, as derived from the Smoluchowski equation are given by equation (S1)<sup>1</sup>

$$k_{q,P} = \frac{4\pi N_{AV} R_{P+Rf} D_{P+Rf}}{1000 n_{q/P}} e^{(-E_a/kt)} \quad (S1)$$

Where  $N_{AV}$  is the Avogadro constant,  $R_{P+Rf}$  is the encounter radius,  $D_{P+Rf}$  is the mutual diffusion coefficient given by the sum of  $D_P$  and  $D_{Rf}$ ,  $n_{q,P}$  is the average number of surface Ag atoms per particle. The pre-exponential factor represents the diffusion-controlled rate constant, and  $E_a$  is the activation energy of the reaction.

The average number of Ag atoms per particle calculated from the density of silver and the diameter of the particles is  $2.2 \times 10^4$ . Considering that the amount of surface Ag atoms for particles of 9 nm diameter is about 15%,<sup>2</sup> the average value of  $n_{q,P}$  yields  $3.35 \times 10^3$ . Taking  $R_{P+Rf} \sim R_P = 4.5 \times 10^{-7}$  cm,  $D_{P+Rf} \sim D_{Rf} = 2.6 \times 10^{-5}$  cm<sup>2</sup>s<sup>-1</sup>,<sup>3</sup> and  $n_{q,P} = 3.3 \times 10^3$ , the calculated diffusion-controlled rate constant between silver atoms and any species in solution is  $2.7 \times 10^7$  M<sup>-1</sup>s<sup>-1</sup>.

## References

- (1) Shield, S. R.; Harris, J. M. Reaction Kinetics at Dispersed-Colloid/Solution Interfaces: Benzophenone Triplet-State Quenching by Methylated Silica Particles. *J. Phys. Chem. B.* **2000**, *104*, 8527-8535.
- (2) Molleman, B.; Hiemstra, T. Surface Structure of Silver Nanoparticles as a Model for Understanding the Oxidative Dissolution of Silver Ion. *Langmuir.* **2015**, *31*, 13361-13372.
- (3) Zhang, H.; Zhao, J.; Liu, H.; Wang, H.; Liu, R.; Jifeng Liu. Application of Poly (3-methylthiophene) Modified Glassy Carbon Electrode as Riboflavin Sensor. *Int. J. Electrochem. Sci.* **2010**, *5*, 295 – 301.