

Electronic Supplementary Information

Au/SiO₂ Nanoparticles in TiO₂:Sm³⁺ Films for Improved Fluorescent Sensing of Oxygen

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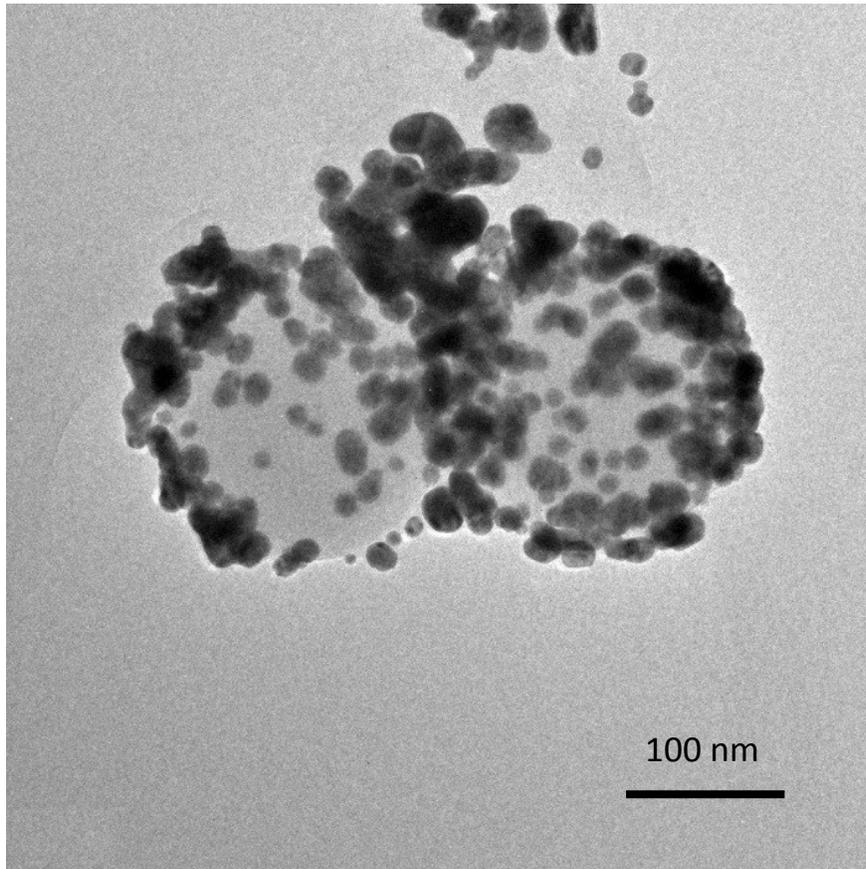


Fig. S1. Transmission electron microscopy image of settled Au/SiO₂ nanoparticles.

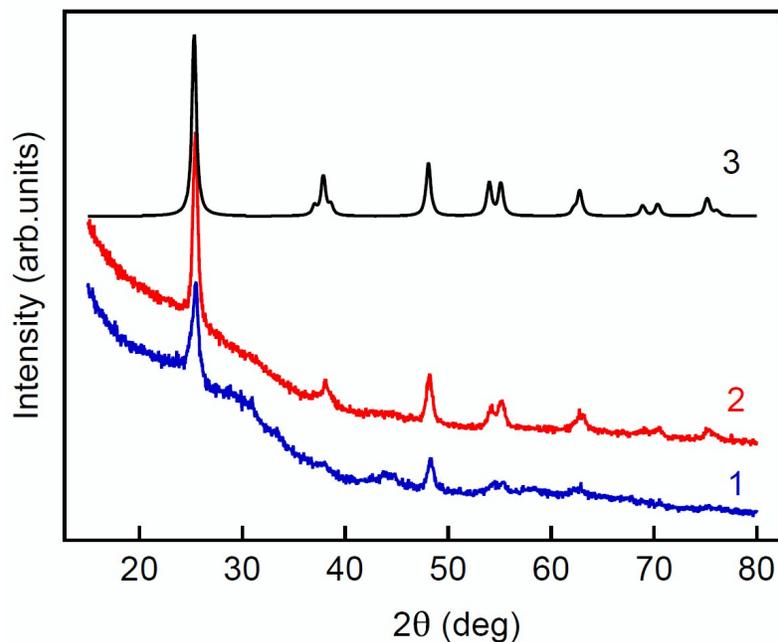


Fig. S2. Observed X-ray diffraction patterns for referent $\text{TiO}_2:\text{Sm}^{3+}$ film (1), $\text{TiO}_2:\text{Sm}^{3+}$ film decorated with Au/SiO_2 nanoparticles (2) and taken for TiO_2 anatase from Inorganic Crystal Structure Database collection code 93098 (3). Observed patterns were measured using grazing incidence XRD method, incident angle is 0.32° .

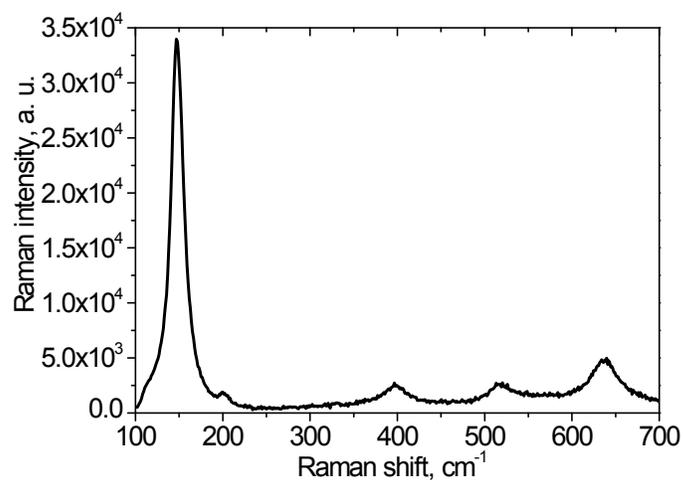


Fig. S3. The spectrum of Raman scattering from the $\text{TiO}_2:\text{Sm}^{3+}$ film decorated with Au/SiO_2 nanoparticles. Excitation wavelength was 514 nm.

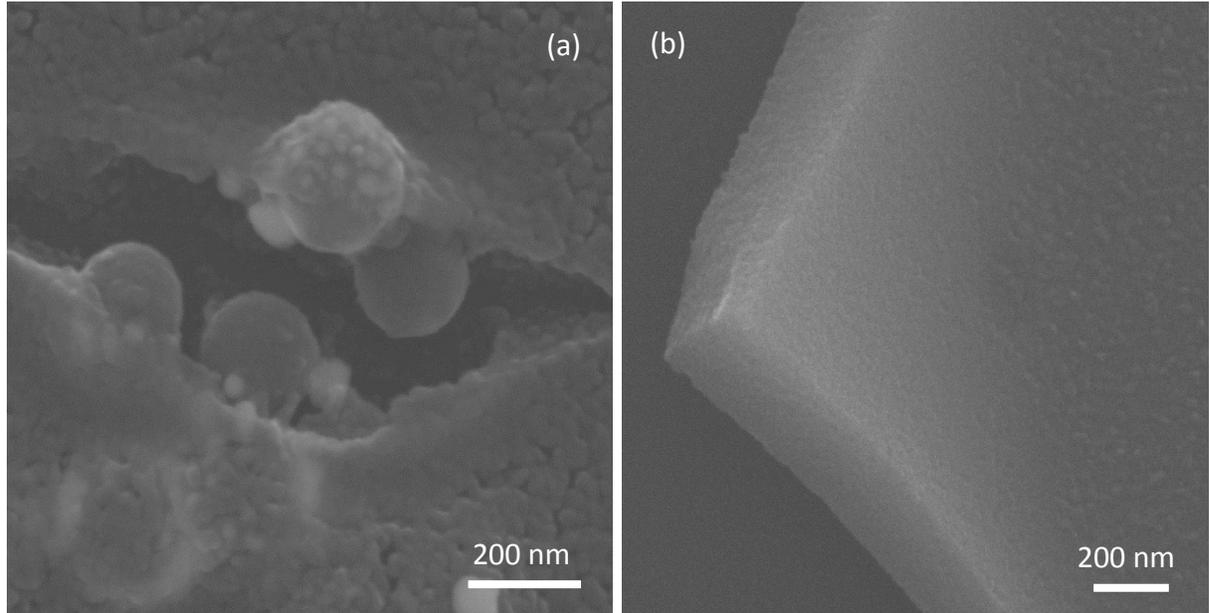


Fig. S4. Scanning electron microscopy images of cuts for films: (a) $\text{TiO}_2:\text{Sm}^{3+}$ decorated with Au/SiO_2 nanoparticles; (b) referent $\text{TiO}_2:\text{Sm}^{3+}$.

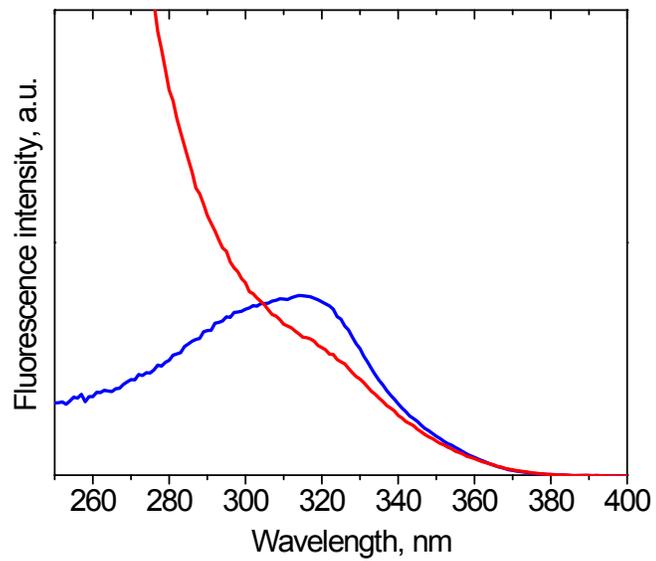


Fig. S5. Fluorescence excitation spectra of films: (red line) $\text{TiO}_2:\text{Sm}^{3+}$ decorated with Au/SiO_2 nanoparticles; (blue line) referent $\text{TiO}_2:\text{Sm}^{3+}$. Detection wavelength was 612 nm.

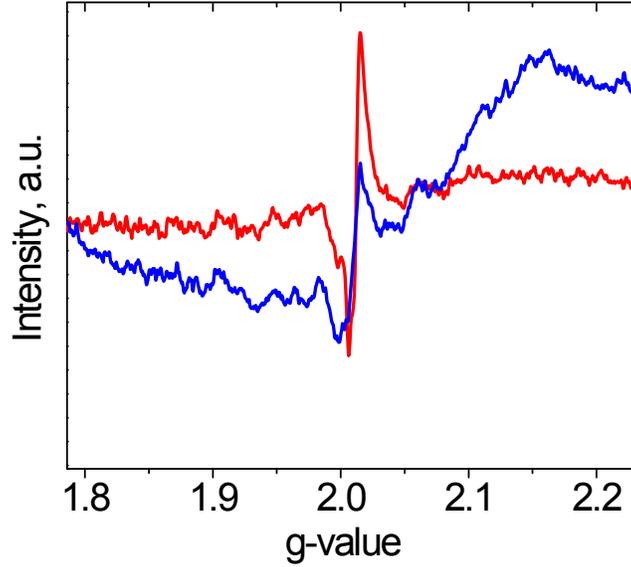


Fig. S6. Electron paramagnetic resonance spectra of films: (red line) $\text{TiO}_2:\text{Sm}^{3+}$ decorated with Au/SiO_2 nanoparticles; (blue line) referent $\text{TiO}_2:\text{Sm}^{3+}$.

Comment on the decay kinetics of Sm^{3+} fluorescence and equation (3) of the main text

$$I(t) = I_0 e^{-\frac{t}{\tau_0} - c\sqrt{\frac{t}{\tau_0}}} + I_1 \int_0^\infty dk \rho(k) \int_0^t dt' k e^{-kt'} e^{-\frac{t-t'}{\tau_0} - c\sqrt{\frac{t-t'}{\tau_0}}} \quad (3).$$

The first term describes the decay of instantly excited Sm^{3+} ions involving both natural decay (with lifetime τ_0 fixed at 300 μs) as well as a Förster-type energy transfer to lattice defects (Fig.2a, energy transfer 3). This term is responsible for the fast initial decay (faster than the natural lifetime). The second term takes into account delayed excitation of Sm^{3+} ions. Here $\rho(k)$ is a probability density function defined so that the product $\rho(k)dk$ gives the fraction of traps which transfer energy (Fig. 2c, energy transfer 2) to Sm^{3+} centers at the rates of $k \dots k + dk$. The two integrations in the second term of Eqn. (3) describe convolution and averaging.

The distribution $\rho(k)$ is unknown. As a first approximation and in accordance with some experimental findings, we consider that the binding energies of the trapped electrons follow an

exponential distribution $\rho(E) = \frac{1}{\Delta E} \exp\left(-\frac{E}{\Delta E}\right)$, where ΔE characterizes the spread of the

distribution. On the other hand, the probability of de-trapping could follow the Arrhenius law

$k = s \exp\left(-\frac{E}{k_B T}\right)$, where k_B is the Boltzmann constant, T is temperature and s is an attempt-to-escape frequency. Assuming $s \approx \text{const}$, one can easily prove that the resulting k -distribution is $\rho(k) = \frac{R}{s^R} k^{R-1}$ (for $k = 0 \dots s$), where $R = k_B T / \Delta E$. Hence, the two parameters s and R determine the scale and shape of the distribution $\rho(k)$. For this particular distribution one can also analytically evaluate the first integral in Eqn. 3 (after swapping the order of integration):

$$\int_0^{\infty} dk \rho(k) k e^{-kt} = \frac{R \Gamma(R+1) - \Gamma(R+1, st)}{s^R t^{R+1}},$$

where Γ denotes the (incomplete) gamma function. The remaining integral in Eqn. 3 has to be evaluated numerically (using a fast Fourier transform, for instance).