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Manipulation of Energy Migration towards Long-lived Mn^{2+} Upconversion Emission and Enhanced Singlet Molecular Oxygen Generation

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Nanosensitizers having long-lived upconversion emission under near-infrared (NIR) excitation offer great advantages in terms of reduced background noise and prolonged signal detection for deep tissue therapy of cancer. Herein, we demonstrated a systematic mechanism of energy migration towards achieving the long-lived Mn^{2+} upconversion emission in the multilayered core-shell-shell lattice of $NaGdF_4:Yb^{3+},Tm^{3+},Ca^{2+}/NaGdF_4:Yb^{3+},Ca^{2+}/NaGdF_4:Mn^{2+}$ upconversion nanoparticles, following the $Yb^{3+} \rightarrow Tm^{3+} \rightarrow Gd^{3+} \rightarrow Mn^{2+}$ intermetal ions energy transfer pathway. Besides, a rational design of nanosensitizer was displayed based on incorporating the Er^{3+} ion into the intermediate shell of multishell nanoparticles (NPs), which was subsequently conjugated with Rose Bengal (RB) sensitizer to enable the enhancement in singlet molecular oxygen ($^1O_2$) generation under excitation at 980 nm NIR Laser. The higher energy intense emission in the UV-blue visible region from Tm^{3+} was achieved through optimization of Ca^{2+} amount in the core-shell NPs, followed by its subsequent energy migration to Mn^{2+} ion incorporated at the outer shell. The Mn^{2+} ions were strategically doped in the outer shell of NPs to leverage the catalytic activities of Mn^{2+} for H_2O_2 decomposition and decrease the backward energy transfer to Tm^{3+} ion, which led to a long lifetime of Mn^{2+} (~34 ms), arising from the spin-forbidden $^4T_{1g} \rightarrow {}^6A_{1g}$ transition within $3d^5$ configuration. It is noteworthy that the nanosensitizer demonstrated high $^1O_2$ (~0.39 μM) generation even though at a very low concentration (5 μg/mL) under a laser power of 2 $mWcm^{-2}$. Additionally, the hydrogenase-like catalytic activities of Mn^{2+} exhibited significant oxygen production through the decomposition of H_2O_2 (Figure 1). Hence, these findings might contribute to the development of convenient multifunctional nanosensitizers for multimodal bioimaging and therapeutic features, including efficient $^1O_2$ generation and catalytic decomposition of H_2O_2 (found excessively in tumor environment) to oxygen for alleviating the hypoxia.

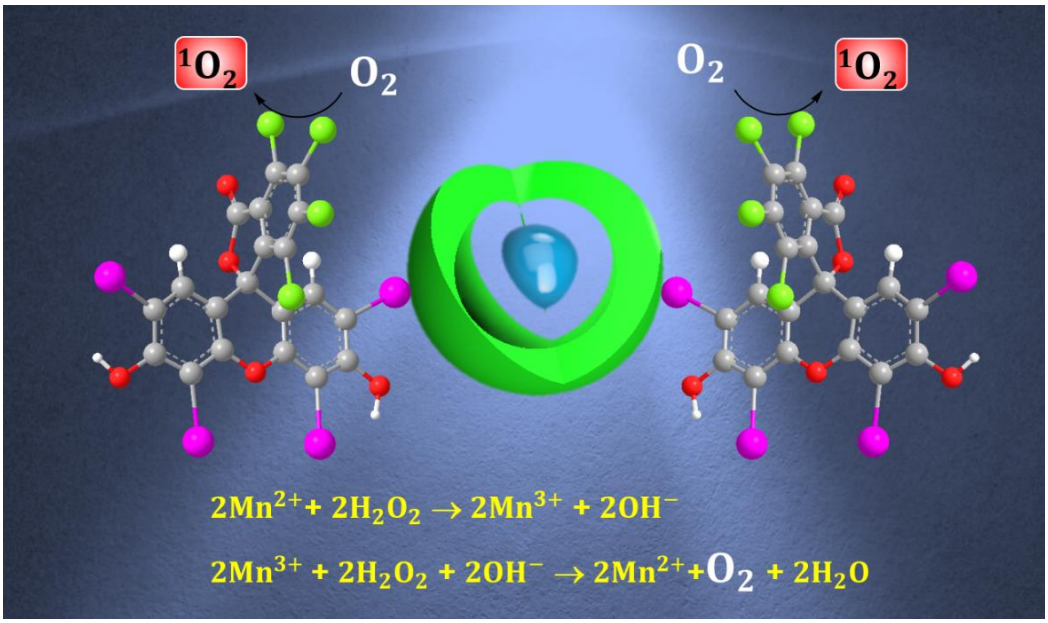

Figure 1. Illustration of singlet oxygen generation and decomposition of H2O2 by hydrogenase-like catalytic activities of NPs.

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References

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