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SCINT 2024

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NA18

Radioprotective Properties of Oxide Nanocrystals

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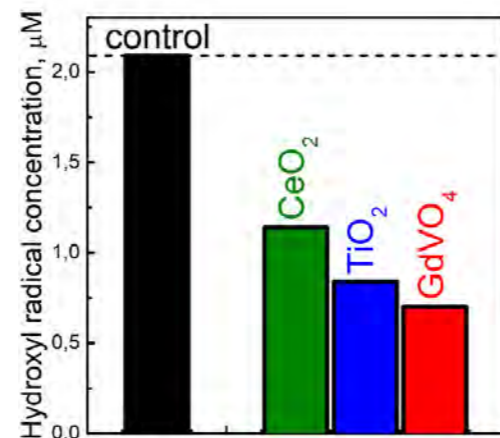
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Cellular respiration in living cells generates biologically active molecules known as reactive oxygen species (ROS). Among these ROS, superoxide anions, hydrogen peroxide, and hydroxyl radicals are produced within mitochondria and play pivotal roles in cellular metabolism. However, an elevation in hydroxyl radical ($\cdot\text{OH}$) levels, the most potent oxidants among ROS, can instigate various pathological processes within cells, ranging from heightened lipid peroxidation of cell membranes to DNA damage. Hydroxyl radicals are generated through water radiolysis during X-ray or gamma irradiation of cells. Their extremely high reactivity, coupled with an average lifespan of only a few nanoseconds in a biological environment, poses a considerable challenge for the cell's internal defense mechanisms in effectively neutralizing them. In response, we propose the utilization of three distinct types of oxide nanocrystals - containing variable valence ions (CeO_2 , TiO_2 , and GdVO_4) - as promising materials for the efficient neutralization of hydroxyl radicals.

These nanocrystals, CeO_2 , TiO_2 , and GdVO_4 , exhibit remarkable capabilities in scavenging hydroxyl radicals generated in water solutions during X-ray irradiation. Their hydroxyl radical-neutralizing properties are intricately linked to the high concentration of reduced variable valence ions (such as Ce^{3+} in CeO_2 , Ti^{3+} in TiO_2 , and $\text{V}^{4+}/\text{V}^{3+}$ in GdVO_4), which possess the ability to donate electrons during hydroxyl radical neutralization reactions. Small oxide nanocrystals, characterized by the presence of structural imperfections like oxygen vacancies, enable the reduction of neighboring variable valence ions, as validated by XPS experiments for all three types (CeO_2 , TiO_2 , and GdVO_4).

The proficiency of these small oxide nanocrystals containing variable valence ions (CeO_2 , TiO_2 , and GdVO_4) in efficiently neutralizing hydroxyl radicals in aqueous solutions highlights their potential as effective antioxidants and radioprotectors within living cells. This promising avenue opens new possibilities for cellular defense and therapeutic applications.

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Neutralizing of $\cdot\text{OH}$ radicals formed during radiolysis of water solutions containing synthesized nanocrystals.

NA19

On the origin of the light yield enhancement in polymeric composites scintillators loaded with dense nanoparticles

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Fast emitting plastic scintillators are currently highly requested for advanced applications where high signal-to-noise detections is required in a short time window as like for rare event in high energy physics experiments, or to acquire high quality image for diagnostics at low doses of radiotracers.[1] Polymeric composite nanoscintillators are proposed in tandem with traditional dense inorganic crystals to realize heterostructures exploiting the benefits from both the building block materials, i.e. fast time response and high light yield (LY). [2] However, the density of plastic scintillators is low, thus they show a limited stopping power of high energy radiation and low light output intensity. Additional dyes as wavelength shifter can be used to harvest more efficiently the energy deposited in the matrix and then populate the final emitters through energy transfer mechanisms. However, this strategy results in a delayed system's time response. The loading of the polymeric host with high-Z nanoparticles is another strategy proposed to enhance the stopping power of plastics and sensitize their scintillation but preserving the fast time response. To point out the mechanism behind the LY enhancement in composites, we investigate the scintillation properties of polymeric composites based on polystyrene doped with POPOP as scintillating dye. This is then modified i) by adding the p-terphenyl (TP) as wavelength shifter and ii) by loading with hafnium dioxide (HfO_2) nanoparticles ($\rho=9.68 \text{ g cm}^{-3}$). The scintillation mechanism is modelled considering the energy transfer processes involved as a function of the material composition and studied by photoluminescence and scintillation spectroscopy. Notably, the light yield scintillation enhancement of 200% achieved with the loading of HfO_2 nanoparticles is comparable to the one obtained using the wavelength shifting dye while preserving the scintillator fast time response. We ascribe this effect to a locally enhanced release of energy in proximity of the nanoparticles. The locally increased density of diffusing charges boosts their recombination probability to form the emissive POPOP molecular excitons, thus increasing the material light yield. Our findings indicate that the loading with optically inert dense nanoparticles could be an excellent strategy to surpass the limits of the currently employed fast emitting conjugated materials by finely controlling the punctual release of energy to manipulate the charges recombination kinetics at the nanoscale.

1. J. Perego, "Highly luminescent scintillating hetero-ligand MOF nanocrystals with engineered Stokes shift for photonic applications" *Nature communications* 13.1, 3504 (2022)

2. M. Orfano, "Fast emitting nanocomposites for high-resolution ToF-PET imaging based on multicomponent scintillators", *arXiv preprint arXiv:2309.14968* (2023)

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