SUPPORTING INFORMATION

Dual Role of Azide as a Quencher and Stimulator of Singlet Oxygen Generation on Some Manganese Oxides

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EXPERIMENTAL METHODS

Preparation of Oxide Catalysts: Single-crystalline V_2O_5 nanostructures were grown using hot filament chemical vapor deposition (HFCVD) method directly on different substrates such as quartz or fluorine-doped ton oxide (FTO). δ-MnO_2 thin films were prepared by liquid-phase reduction of permanganate. The procedure consisted of dissolving 316 mg of potassium permanganate in 112 ml of deionized water. Next, 11 ml of 6M hydrochloric acid was slowly added to the reaction mixture under gentle stirring. A layer-by-layer coating of δ-MnO_2 occurred on fluorine-doped tin oxide (FTO) coated glass substrates that were attached to the walls of the reaction beaker. The remaining δ-MnO_2 precipitated as a powder. After nearly 2 hours of deposition, both the film and powder samples were thoroughly rinsed with deionized water and then dried at 40 °C for 2 hours in ambient air. H- δ-MnO_2 was prepared by reacting δ-MnO_2 with an aqueous HCl acid solution of pH = 3 for 24 hours. The powder was centrifuged, washed with water, and then dried at 40 ° C for 2 hours. All other oxide powders, including LiMn2O4 and $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$ (henceforth $LaSrMnO_3$), and La_2NiO_4 were purchased from commercial vendors (Sigma Aldrich and Alfa Aesar).

2.2. Structural and Optical Characterization: Photoluminescence (PL) studies were performed with a HORIBA Scientific LabRAM HR Evolution spectrometer in a backscattered geometry at room temperature using the 633 nm line of a He-Ne laser. A typical spectrum was recorded for a total acquisition time of 15 minutes in the energy range of 1.2 to 2.0 eV. All signals were recorded with the samples at room temperature and detected using a Si detector.

Detection and Quantification of Singlet Oxygen Generated: Singlet Oxygen was detected using two probes: Singlet oxygen sensor green (SOSG®) obtained from Invitrogen and 1,3 diphenylbenzofuran (DPBF) obtained from Sigma Aldrich. SOSG emission measurements were made with an excitation wavelength of 490 nm, and the emission intensity was recorded at 510 nm using a fluorimeter (Biorad). A stock solution was prepared on the same day as the test by dissolving 100 μg of SOSG in 33 μl of methanol, which produced a stock of 5 mM solution. Emission tests were performed in 1 ml of a 0.1 M Tris buffer prepared in D_2O or H_2O to avoid inadvertent pH changes during the addition of oxide powder. To this, SOSG from the stock solution was added so that the final concentration of the probe was 30 μM. Subsequently, 1 mg of oxide powder was added to the mixture in a glass vial, followed by the addition of azide at a concentration of 15 mM and increasing H_2O_2 concentrations. The mixture was shaken and then centrifuged. The intensity of SOSG in the supernatant was recorded after 5 minutes of incubation after each successive addition. After this, the solution was returned to the vial and different concentrations of H_2O_2 were added. The change in the emission intensity of the top solution was recorded again. All experiments were conducted under ambient temperature and pressure conditions. Testing with DPBF was similar, except that a 1:1 (v/v) ethanol: water mixture was used instead of Tris buffer due to the limited solubility of DPBF in water. All other conditions were the same. Emission measurements were made with an excitation wavelength of 325 nm, and the emission spectrum was recorded using a PL/Raman spectrometer (Horiba Instruments).

The concentration of ${}^1O_2$ was calculated from the intensity changes using the formula.

$$[1O_2] = \frac{I_{oxide \pm NaN_3} - I_{oxide \pm NaN_3 + H_2O_2}}{S_{Cali} \times \Phi_P}$$

Here, $I_{oxide \pm NaN_3}$ is the measured fluorescence intensity of DPBF in the presence of oxide with or without NaN_3. This was taken as the baseline intensity. $I_{oxide \pm NaN_3 + H_2O_2}$ is the intensity values measured after each addition of the H_2O_2 dose. S_{Cali} is the slope of the calibration curve (**Fig.S2**) of emission intensities obtained by varying the known concentrations of DPBF in the ethanol /

water mixture. Φ_P is the sensitivity factor that represents the probability of capture of ${}^1O_2$ by DPBF of certain concentration before deactivation of the excited state to ${}^3O_2$. For the DPBF concentration of 30 μM used here, Φ_P was 0.449.[1]

2.6. Electrochemical Characterization: The work function of δ-MnO_2 and H-δ-MnO_2 was calculated from their flat band potential, U_{FB}, which was determined from the electrochemical Mott-Schottky (M-S) plots. Impedance measurements of δ-MnO_2 and H-δ-MnO_2 films as the working electrode were performed in a standard three-electrode cell in an aqueous 0.1 M Tris buffer electrolyte in the presence and absence of azide. A platinum mesh served as the counter electrode and a standard calomel electrode (SCE), which has a potential of 0.242 V *versus* the standard hydrogen electrode (SHE), served as the reference electrode. The SHE has a work function of 4.44 eV with respect to the vacuum electron energy scale. The electrochemical capacitance of the oxide electrode was measured at various DC potentials by superimposition of an AC voltage of 5 mV amplitude at a frequency of 90 Hz using the CH Instruments 660E electrochemical workstation. The U_{FB} value was determined from the extrapolation of the linear region of the C^{-2} versus V plot to the voltage axis.

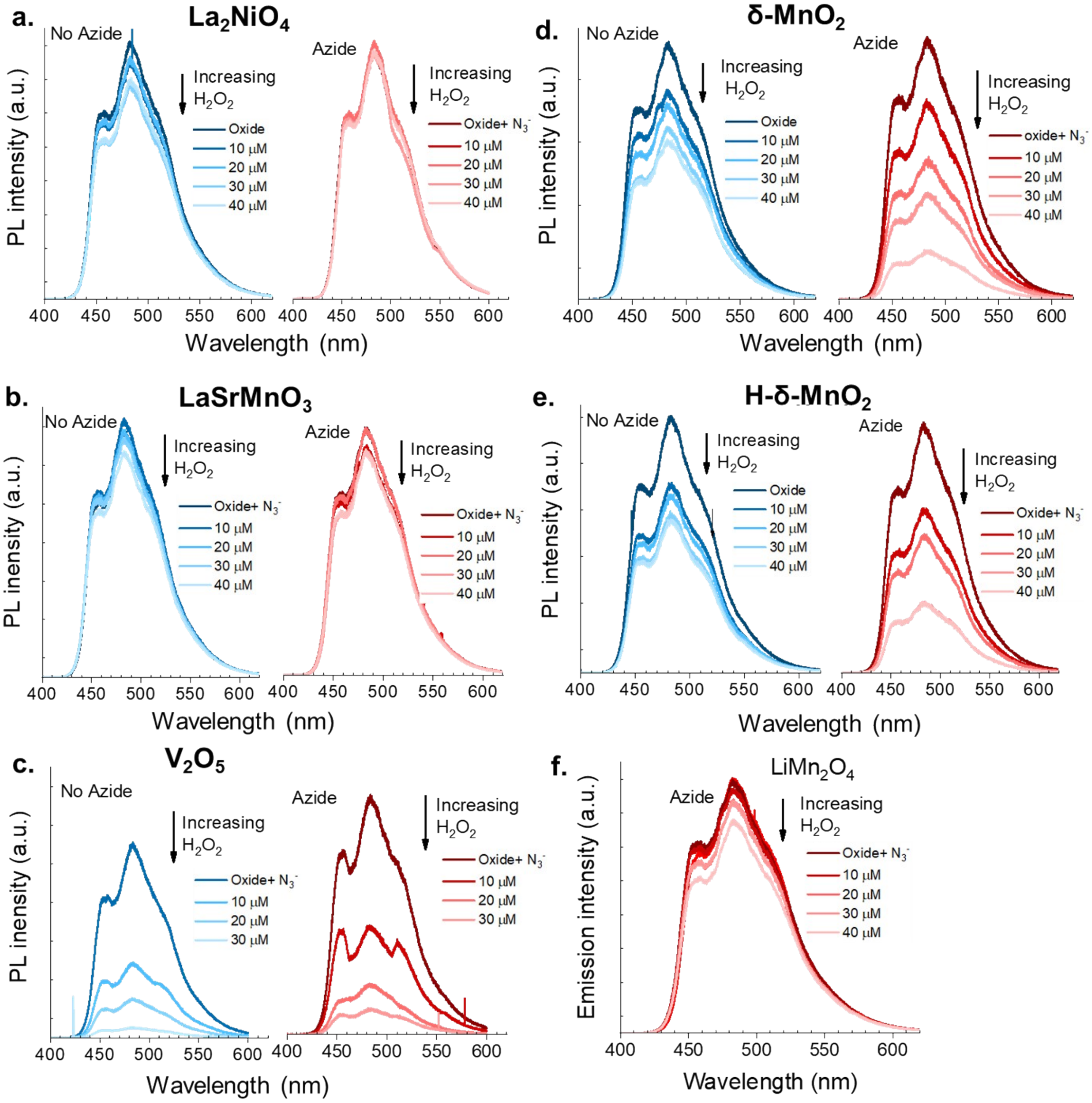

Figure S1. *Changes in the intensity of the $^1O_2$-sensitive DPBF emission with the addition of increasing concentrations of H_2O_2 to the electrolyte in the absence and presence of 15 mM NaN_3 and 1 mg of oxide powder of La_2NiO_4 (a), $LaSrMnO_3$ (b), V_2O_5 (c), δ-MnO_2 (d), H-δ-MnO_2 (e) and $LiMn_2O_4$ (f).*

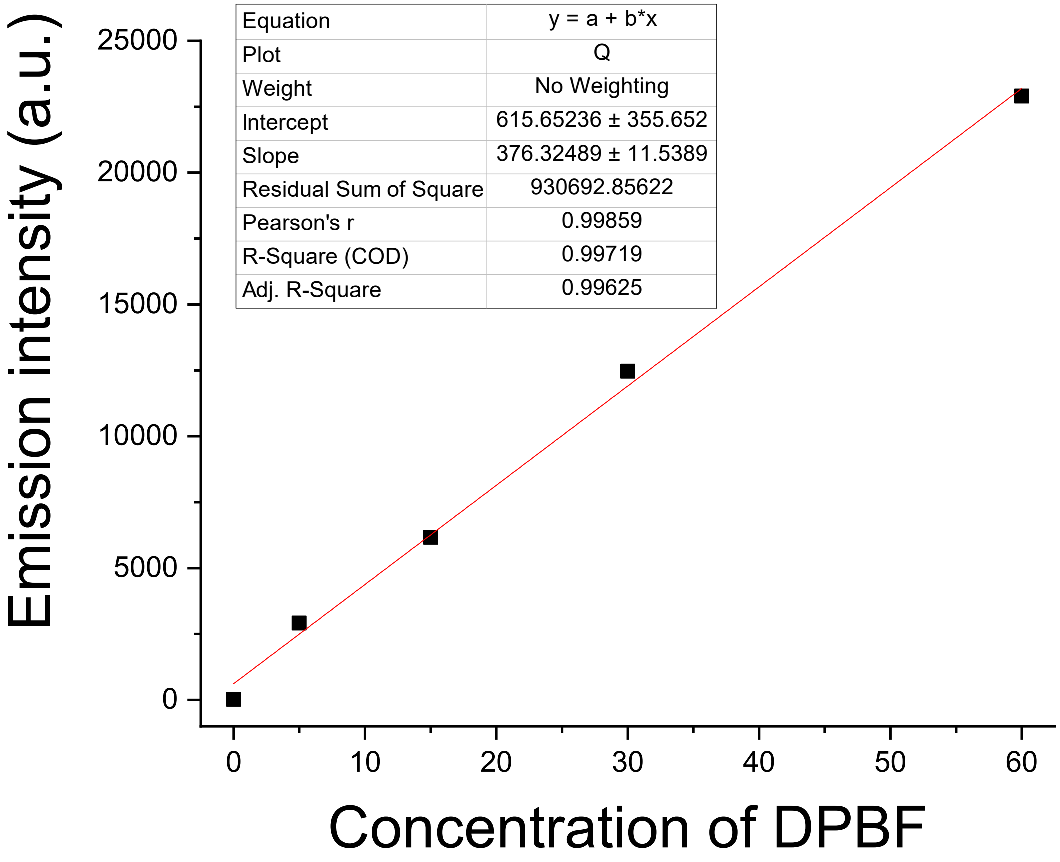

Figure S2. Calibration curve showing the changes in the emission intensity as a function of the varying concentration of DPBF in the ethanol/water mixture.

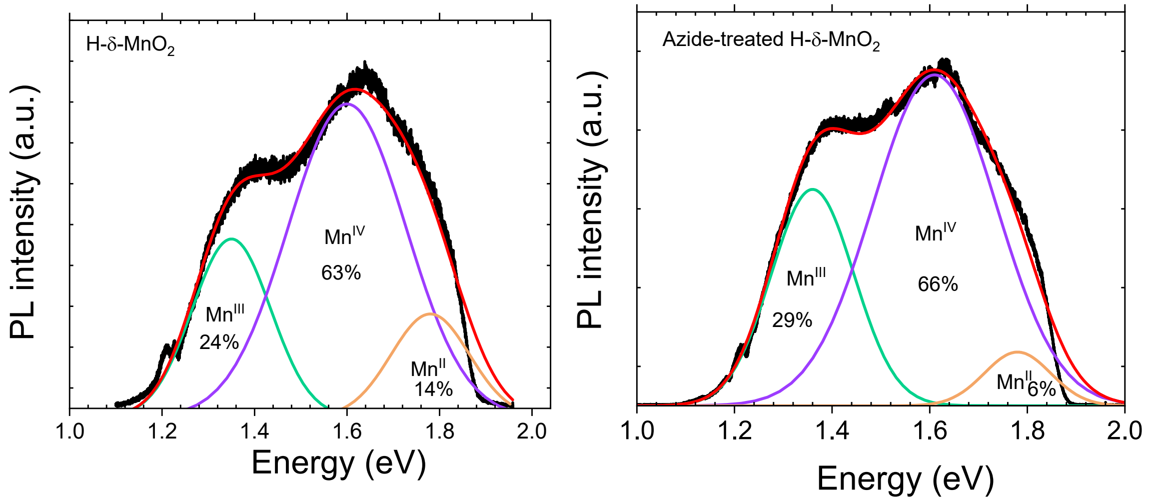

Figure S3. Photoluminescence spectrum of H-δ-MnO$_2$ showing changes in the characteristic peaks of Mn^{II}, Mn^{III}, and Mn^{IV} before and after exposure to azide ions.

1. T. Entradas, S. Waldron and M. Volk, *J. Photochem. Photobiol. B, Biol.*, 2020, **204**, 111787.