Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

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Electronic Supplementary Information

The role of self-diffusiophoresis and reactive force during the propulsion of manganese-based catalytic micromotors

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1. Supporting videos

Movie S1. Growth of a gas bubble during the decomposition of H_2O_2 in the presence of $MnFe_2O_4@Fe_3O_4@graphite$ (UV light).

Movie S2. Movement of the micromotor $MnFe_2O_4@Fe_3O_4@graphite$ in a solution H_2O_2.

Movie S3. Growth of a gas bubble during the decomposition of H_2O_2 in the presence of $MnO@Fe_3O_4@Fe@graphite$ (visible light).

Movie S4. The cluster of nanoparticles (NPs) $MnO@Fe_3O_4@Fe@graphite$ does not move in a solution H_2O_2.

Movie S5. Movement of micromotor $MnO@Fe_3O_4@Fe@graphite$ in a solution H_2O_2 in a non-uniform magnetic field.

2. Supporting figures

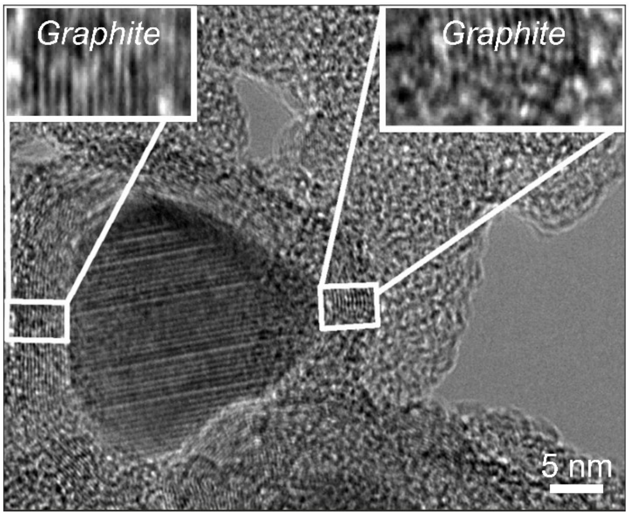

Figure S1. TEM image of NPs obtained after spraying in an electric arc. Particles of Fe and Mn are surrounded by graphite. Carbon layers in graphite are arranged regularly. The interplanar distance between the carbon layers is 3.38 Å, which exceeds the value for ideal graphite 3.34 Å.

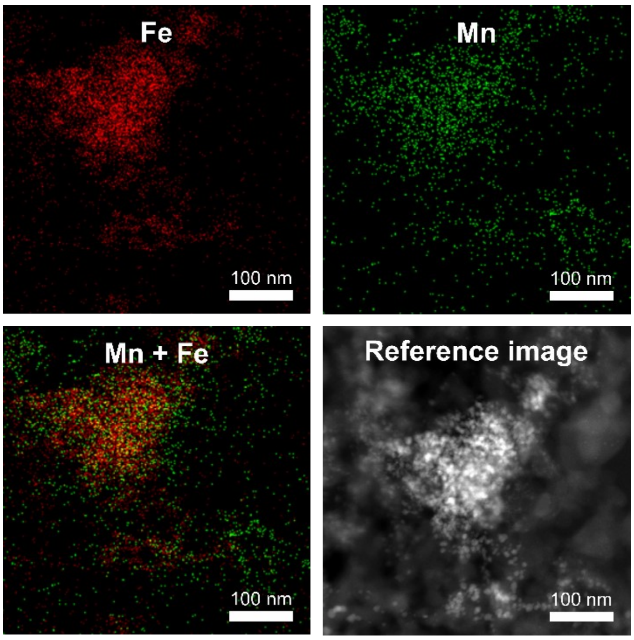

Figure S2. The EDS elemental mapping images. NPs are obtained by spraying the initial mixture in an electric arc. Manganese and iron are uniformly distributed throughout the volume of the material.

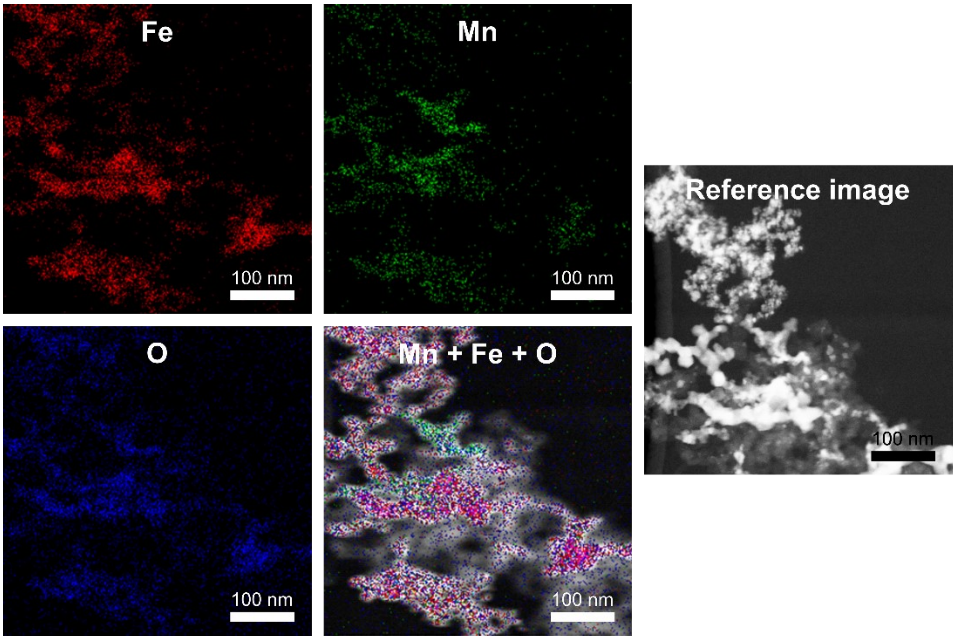

Figure S3. The EDS elemental mapping images. $MnO@Mn_3O_4@Fe_3O_4@graphite$ NPs were obtained after annealing the original NPs in a hydrogen atmosphere at 500 °C. In the volume of the material, areas are formed where iron and manganese are separated. Oxygen is more uniformly distributed, indicating that manganese and iron are in an oxidized state.

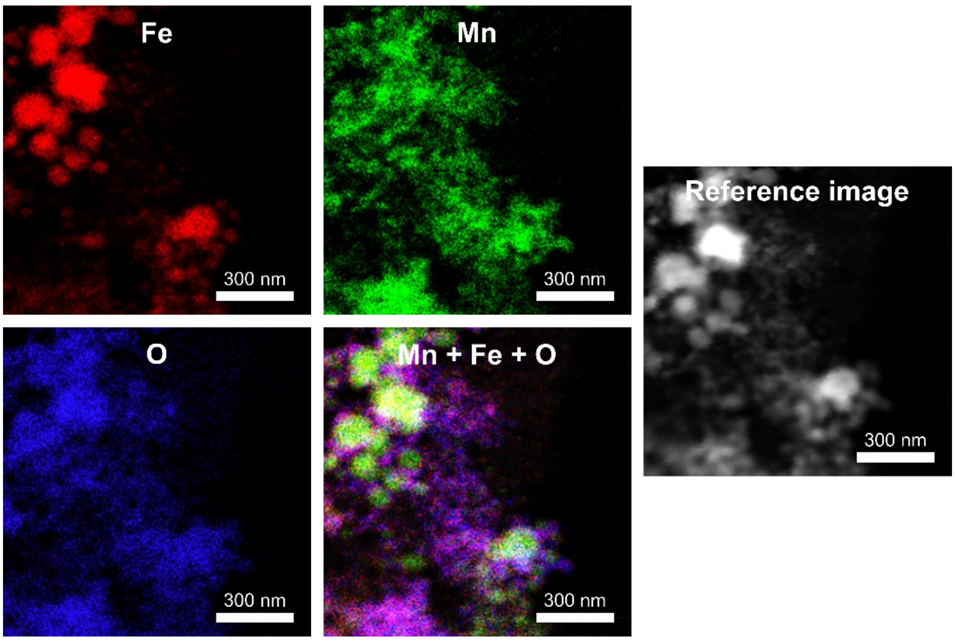

Figure S4. The EDS elemental mapping images. $MnO@Fe_3O_4@Fe@graphite$ NPs were obtained after annealing in a hydrogen atmosphere at 700 °C. Manganese is distributed uniformly throughout the volume of the material, but iron is concentrated in local areas.

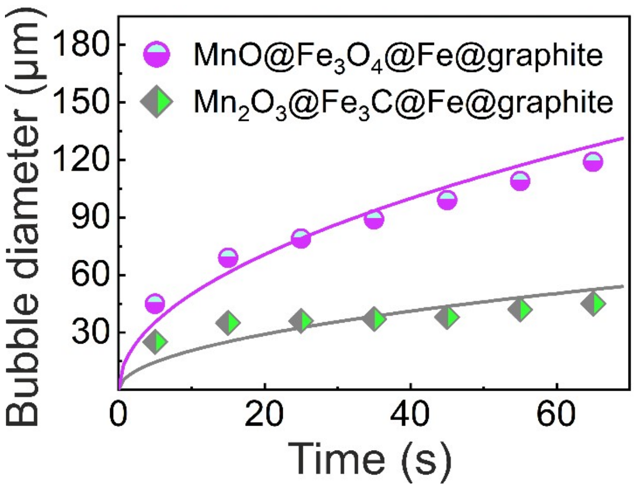

Figure S5. Dependence of the bubble growth rate on time during the catalytic decomposition of H_2O_2. NPs were obtained by annealing in a hydrogen atmosphere.

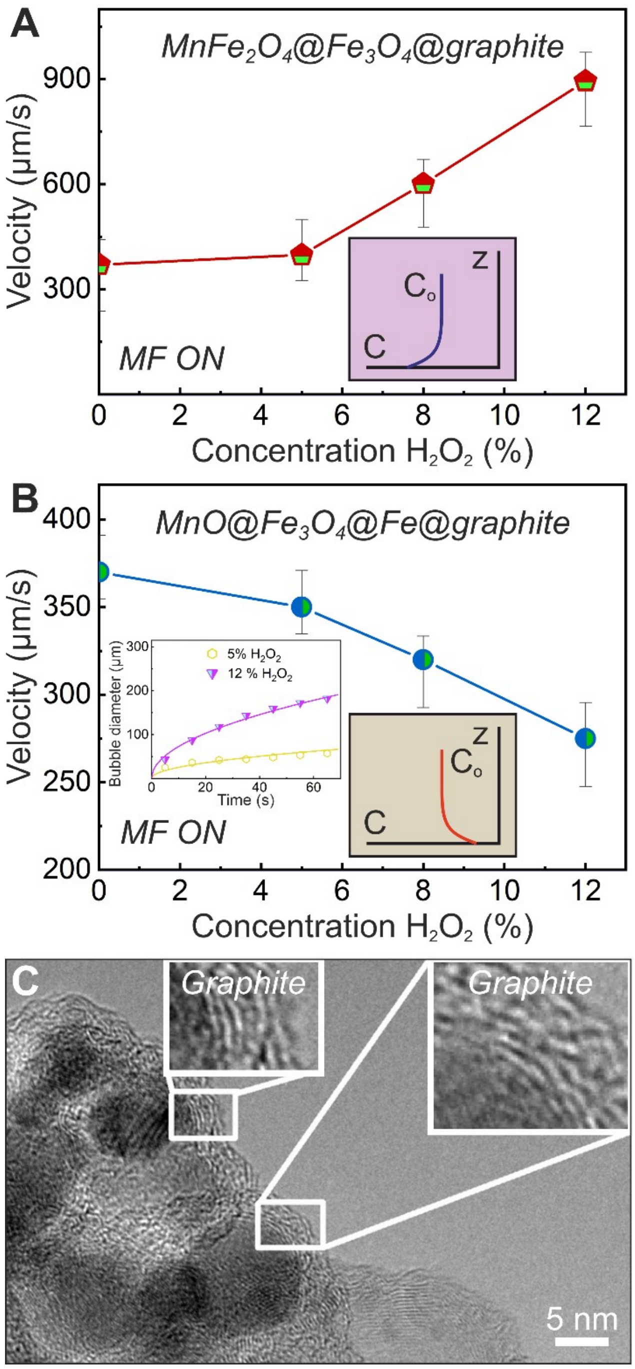

Figure S6. Movement of micromotors in a non-uniform magnetic field (MF) in a solution H_2O_2. (A) Effect of H_2O_2 concentration on the velocity of $MnFe_2O_4@Fe_3O_4@graphite$ (the inset shows concentration profile H_2O_2 for positive adsorption; $25 \pm 3\mu m$). (B) Effect of H_2O_2 concentration on the velocity of $MnO@Fe_3O_4@Fe@graphite$ (insets: dependence of bubble growth rate on H_2O_2 concentration; negative adsorption; $23 \pm 4\mu m$). (C) TEM $MnO@Fe_3O_4@Fe@graphite$.

3. Materials and methods

3.1. Materials

Powders of graphite (20 μm, Merck), manganese (≥99.9%, Merck), and iron (60 μm, 99%, Merck) were used to synthesize nanoparticles. Deionized water was used to prepare all solutions. Hydrogen peroxide (H_2O_2) (37%) was used as fuel.

3.2. Nanoparticle synthesis

Manganese-based magnetic nanoparticles were used to obtain micromotors. Nanoparticles were synthesized by anode sputtering in a buffer gas (helium) at 50 Torr. The anode was a graphite rod 8 mm in diameter with a hole 4 mm in diameter, which was filled with Mn-Fe-C powder with a component ratio Mn:Fe:C =7:3:5. After spraying in an electric arc, the vapors condensed on a cooled screen. At the final stage of synthesis, the nanoparticles were annealed in a muffle furnace for two hours. In this case, the temperature varied in the range from 500 to 1000°C. After cooling to room temperature, the nanoparticles were removed from the oven.

3.3. Nanoparticle properties

TEM images for nanoparticles were obtained using JEOL JEM-220FS transmission electron microscopy with lattice-fringe resolution of 0.1 nm and accelerating voltage of 200 kV. XRD analysis was performed using a Bruker D8 diffractometer.

3.4. Micromotors

The nanoparticles agglomerated with each other in an aqueous solution of hydrogen peroxide due to the dipole-dipole interaction between them. The characteristic linear size of the clusters was 25 μm. The clusters had an asymmetrical shape. Agglomerates of nanoparticles were micromotors, they could move in a solution of hydrogen peroxide. Since the nanoparticles included a ferromagnetic element (iron), the micromotors had pronounced magnetic properties, as a consequence they moved in a non-uniform magnetic field. To create a magnetic field, a permanent neodymium magnet (NdFeB) was used. The magnetic field strength was measured using the magnetometer TD8620 (Changsha Tunkia). The magnetic field strength in the area of micromotor movement was 50 mT, and the magnetic field gradient was 20 T/m.

3.5. Micromotor motion analysis

The motion of micromotors was studied in an aqueous solution of H_2O_2. The thickness of the liquid film was 2 mm and was bounded by two quartz plates on both sides. Microscope Olympus IX73 was used to visualize the process of micromotor motion. The video was captured using the ADF camera (85 fps). To estimate the velocity of micromotor motion, Tracker software (Java) was used. Each experiment was repeated at least five times.

3.6. Gas bubble growth rate

To analyze the intensity of gas generation, the growth rate of gas bubbles was measured. All the tests were carried out at room temperature ($22\ ^{\circ}C$). During the experiments, the light wavelength changed (UV light $365 \pm 25\ nm$, blue light $480 \pm 10\ nm$, green light $540 \pm 10\ nm$). To measure the growth rate of gas bubbles, a microscope Olympus IX73 was used, that was equipped with the camera ADF (85 fps). For the decomposition of H_2O_2, cluster of nanoparticles placed on a glass plate were used. Due to the adsorption of the cluster on the glass surface, it remains motionless during the entire period of measuring the growth rate of the gas bubble. Nucleation of gas bubbles occurred in the cavities of the cluster, and the bubbles adjoined the surface of the cluster in the growth process. After some period of time, the bubble separated from the surface of the cluster under the influence of the Archimedes force. The growth rate of the gas bubble was measured only during the period of time when the gas bubble adjoined the surface of the cluster.