# In situ Investigation of the Formation Mechanism of $\alpha-\mathrm{Bi}_{2} \mathbf{R h}$ Nanoparticles in Polyol Reductions 

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## Supporting Information



Figure S1. PXRD patterns of solid reaction products obtained by heating the supernatant obtained from the reaction of $\mathrm{Bi}\left(\mathrm{NO}_{3}\right)_{3}$ and $\mathrm{Rh}_{2}(\mathrm{OAc})_{4}$ with added NaOH to $250^{\circ} \mathrm{C}$ for 10 min . Bi (ref.) is the calculated diffraction pattern based on the crystal structure of Bi (ICSD entry CSD-64703).


Figure S2. Temperature course throughout the reaction with an approximate suggestion of the BiRh formation point.


Figure S3. a) FT-IR spectra of the final products obtained by reacting $\mathrm{Bi}\left(\mathrm{NO}_{3}\right)_{3}$ with different rhodium salts under neutral and alkaline conditions. b) UV-Vis spectrum and DLS measurement (inset) of $\mathrm{Bi}_{2} \mathrm{Rh}$ re-dispersed in EG ( $0.04 \mathrm{mg} / \mathrm{mL}$ ) after dispersion ( 0 d ), 10 days and 17 days.


Figure S4. Elemental mapping of an intermediate obtained from the reaction of $\mathrm{Bi}\left(\mathrm{NO}_{3}\right)_{3}$ and $\mathrm{Rh}_{2}(\mathrm{OAc})_{4}$ with added NaOH at $130^{\circ} \mathrm{C}$ after 10 min reaction time.


Figure S5. DTA-TG measurement of $\mathrm{Bi}_{3}\left(\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}_{2}\right)_{4}\left(\mathrm{NO}_{3}\right)$.


Figure S6. Powder pattern of the powder obtained after combustion of the bismuth glycolate during DTA-TG.


Figure S7. FT-IR spectrum of the obtained bismuth glycolate from pure $\mathrm{Bi}\left(\mathrm{NO}_{3}\right)_{3}$ solution.


Figure S8. SEM images of particles obtained from the reaction of $\mathrm{Bi}\left(\mathrm{NO}_{3}\right)_{3}$ and $\mathrm{Rh}\left(\mathrm{NO}_{3}\right)_{3}$ in EG at $160^{\circ} \mathrm{C}$.


Figure S9. PXRD patterns of solid reaction products obtained by reacting the supernatant obtained from the reaction of $\mathrm{Bi}\left(\mathrm{NO}_{3}\right)_{3}$ and $\mathrm{RhCl}_{3}$ at $250^{\circ} \mathrm{C}$ for 10 min . Bi (ref.) and $\mathrm{Bi}_{4} \mathrm{Rh}$ (ref.) are the calculated diffraction patterns based on the crystal structure of Bi (ICSD entry CSD64703) and $\mathrm{Bi}_{4} \mathrm{Rh}$ (ICSD entry CSD-58854), respectively


Figure S10. SEM images of particles obtained from the reaction of $\mathrm{Bi}\left(\mathrm{NO}_{3}\right)_{3}$ and $\mathrm{RhCl}_{3}$ with added NaOH at $240^{\circ} \mathrm{C}$ displaying spherical bismuth particles (a), a mixture of $\mathrm{Bi}_{2} \mathrm{Rh}$, rhodium and bismuth particles (b) and rhodium particles (c).

