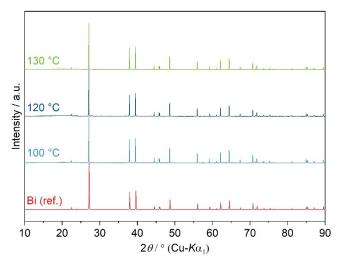
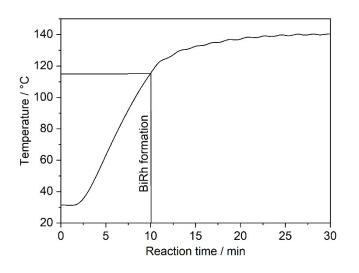
## In situ Investigation of the Formation Mechanism of α-Bi<sub>2</sub>Rh Nanoparticles in Polyol Reductions

Matthias Smuda, Jonas Ströh, Nicole Pienack, Azat Khadiev, Huayna Terraschke, Michael Ruck, and Thomas Doert\*

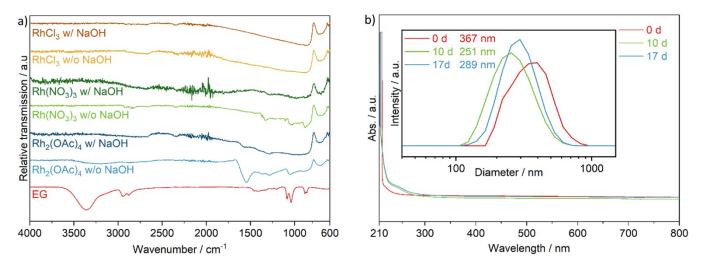


## **Supporting Information**

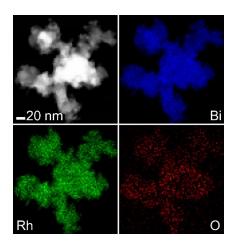
**Figure S1.** PXRD patterns of solid reaction products obtained by heating the supernatant obtained from the reaction of  $Bi(NO_3)_3$  and  $Rh_2(OAc)_4$  with added NaOH to 250 °C for 10 min. Bi (ref.) is the calculated diffraction pattern based on the crystal structure of Bi (ICSD entry CSD-64703).



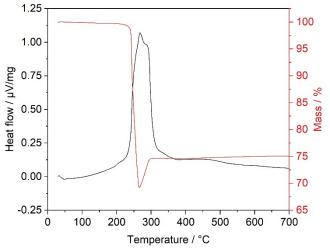
**Figure S2.** Temperature course throughout the reaction with an approximate suggestion of the BiRh formation point.



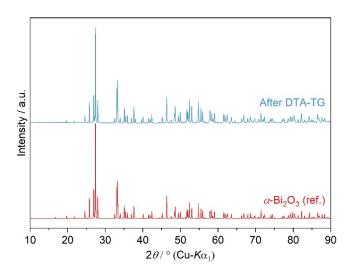
**Figure S3.** a) FT-IR spectra of the final products obtained by reacting  $Bi(NO_3)_3$  with different rhodium salts under neutral and alkaline conditions. b) UV-Vis spectrum and DLS measurement (inset) of  $Bi_2Rh$  re-dispersed in EG (0.04 mg/mL) after dispersion (0 d), 10 days and 17 days.



**Figure S4.** Elemental mapping of an intermediate obtained from the reaction of  $Bi(NO_3)_3$  and  $Rh_2(OAc)_4$  with added NaOH at 130 °C after 10 min reaction time.



**Figure S5.** DTA-TG measurement of  $Bi_3(C_2H_4O_2)_4(NO_3)$ .



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

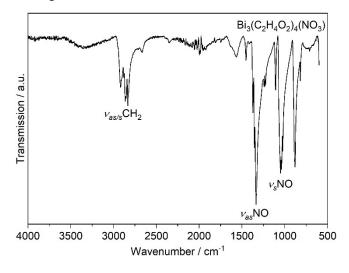
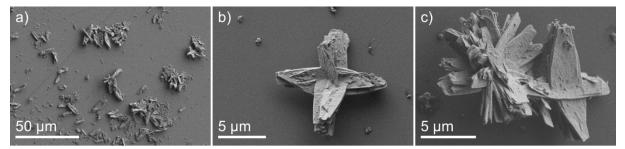
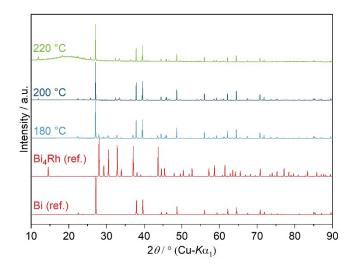


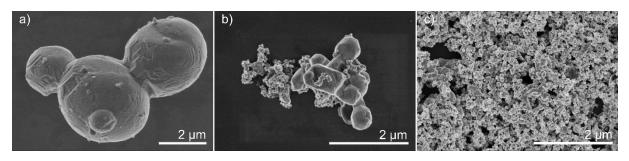
Figure S7. FT-IR spectrum of the obtained bismuth glycolate from pure  $Bi(NO_3)_3$  solution.



**Figure S8.** SEM images of particles obtained from the reaction of  $Bi(NO_3)_3$  and  $Rh(NO_3)_3$  in EG at 160 °C.



**Figure S9.** PXRD patterns of solid reaction products obtained by reacting the supernatant obtained from the reaction of  $Bi(NO_3)_3$  and  $RhCl_3$  at 250 °C for 10 min. Bi (ref.) and  $Bi_4Rh$  (ref.) are the calculated diffraction patterns based on the crystal structure of Bi (ICSD entry CSD-64703) and  $Bi_4Rh$  (ICSD entry CSD-58854), respectively



**Figure S10.** SEM images of particles obtained from the reaction of  $Bi(NO_3)_3$  and  $RhCl_3$  with added NaOH at 240 °C displaying spherical bismuth particles (a), a mixture of  $Bi_2Rh$ , rhodium and bismuth particles (b) and rhodium particles (c).