

Probing the formation of bimetallic colloidal nanoparticles

Priscila Destro¹ (PG), Daniel A. Cantane¹ (PQ), Guilherme S. Honório¹ (IC), Luelc S. Costa¹ (PG), Débora M. Meira² (PQ), José M.C. Bueno² (PQ), Daniela Zanchet¹ (PQ)

1. Institute of Chemistry, State University of Campinas, P.O. Box 6154, 13083-970, Campinas, SP, Brazil

2. Department of Chemical Engineering, Federal University of São Carlos, P.O. Box 676, 13565-905 São Carlos, SP, Brazil

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* Corresponding author: daniela@iqm.unicamp.br (DZ)

Introduction

Bimetallic nanoparticles (NPs) are greatly attractive for different applications, such as catalysis, since a large number of physical and chemical properties may be accessed by tuning their composition besides size and morphology.¹ Although colloidal synthesis appears as a versatile alternative for designing novel functional bimetallic NPs, the precise control over parameters that affects the formation of bimetallic NPs in solution (nucleation and growth stages) is still unfulfilled.^{2,3} In situ X-ray absorption fine structure (XAFS) spectroscopy is a unique tool to understand, in real time, these fundamental chemical processes in solution.

Herein we report insights on the stages of nucleation and growth of bimetallic CuAu NPs in organic-phase by associating in situ time-resolved XAFS spectroscopy with complementary ex situ characterization at different stages. Time-resolved mapping of fundamental chemical processes during bimetallic nanostructures formation is still a challenge but can lead to an unprecedented control of NPs growth and properties.

Results and Discussion

Bimetallic CuAu nanoparticles were synthesized by a method previously reported.[2] A home-made reaction reactor was used for enabling the direct probing (*in situ*) of the formation of the CuAu NPs in solution by XAFS. Complementary, samples collected from solution at different temperatures were characterized by transmission electron microscopy (TEM), X rays diffraction (XRD) and UV-vis spectroscopy. Figure 1 shows a set of *in situ* XAFS spectra at both the Au L₃ (a) and Cu K (b) absorption edges, respectively, during the generation of bimetallic NPs.

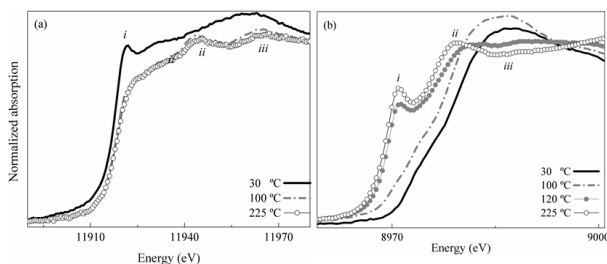


Figure 1: In situ XAFS spectra at the Au L₃ (a) and Cu K (b) absorption edges, at different reaction temperatures: 30 °C (solid), 100 °C (dot), 120 °C (solid-circle), and 225 °C (open-circle).

Focusing on the spectra features at the Au L₃-edge (Fig. 1a), it is noted a quickly depletion of signal intensity attributed to the Au(III) species, (i), concomitantly with the appearance of two shoulders 38^a Reunião Anual da Sociedade Brasileira de Química

(ii and iii) at lower temperature (100 °C). This result reveals that the Au(III) reduction and formation of Au–Au bonding occurred at the initial stage of the reaction. In contrast, the reduction of Cu(II) species were clear observed after reaching 120 °C (Fig. 1b, solid-circle), owing to the formation of a small pre-peak (i) and a shift in the position of the main peak from (iii) to (ii) energy. Upon increasing to the 225 °C temperature, the Cu reduction evolved and the spectrum (Fig. 1b, open-circle) resembled the metallic Cu. Previously XANES study⁴ found that the formation of Cu₁Au₃ bulk-alloy led to a small increase in the (i) feature (Fig.1a) compared to bulk Au due to charge-transfer of *d* electrons from Au to Cu. As a consequence, a decrease of the absorption pre-peak (i) and an increase of the main peak (ii) at the Cu K-edge (Fig. 1b) was also found, compared to Cu foil.⁴ Our results at the Au L₃ edge are in agreement with the formation of bimetallic CuAu NPs at 225 °C. However, the Cu K-edge results shows that under the reaction conditions used in this experiment (open to air) a large amount of unreduced Cu species were still present in solution. The analysis of a purified sample (not shown) corroborated that part of the Cu was indeed incorporated in the NPs, forming the alloy. Complementary TEM images, XRD patterns and UV-vis spectra taken at different temperatures also confirmed the initial formation of Au NPs (10 nm in size), followed by incorporation of Cu. While TEM shows a slightly increase of the mean NP size, the XRD patterns and UV-Vis spectra clearly showed shifts in peak positions associated to the incorporation of Cu. These results suggested that the formation of CuAu NPs occurred via solid-state diffusion mechanism at nanoscale, where Cu species diffuse into the Au NP cores.³

Conclusions

In summary, we showed that the formation of bimetallic CuAu NPs occurs by a multi-stages mechanism. Au NPs of 10 nm are early generated at low temperature followed by incorporation of Cu atoms at higher temperature through a solid-state diffusion mechanism, at nanoscale.

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¹Alonso, D.M., Wettstein, S.G., Dumesic, J.A., *Chem. Soc. Rev.*, **2012**, *41*, 8075–8098.

²Motl, N. E.; Ewusi-Annan, E.; Sines, I. T.; Jensen, L.; Schaak, R. E; *J. Phys. Chem. C*, **2010**, *114*, 19263.

³Chen, W., Yu, R., Li, L., Wang, A., Peng, Q, Li, Y., *Angew. Chem.*, **2010**, *122*, 2979–2983

⁴Kuhn, M., Sham, T.K., *Phys. Rev. B.*, **1994**, *49*, 1647.,