Supporting Information for

Solution and surfactant-free growth of supported high index facet SERS active nanoparticles of Rhenium by phase demixing

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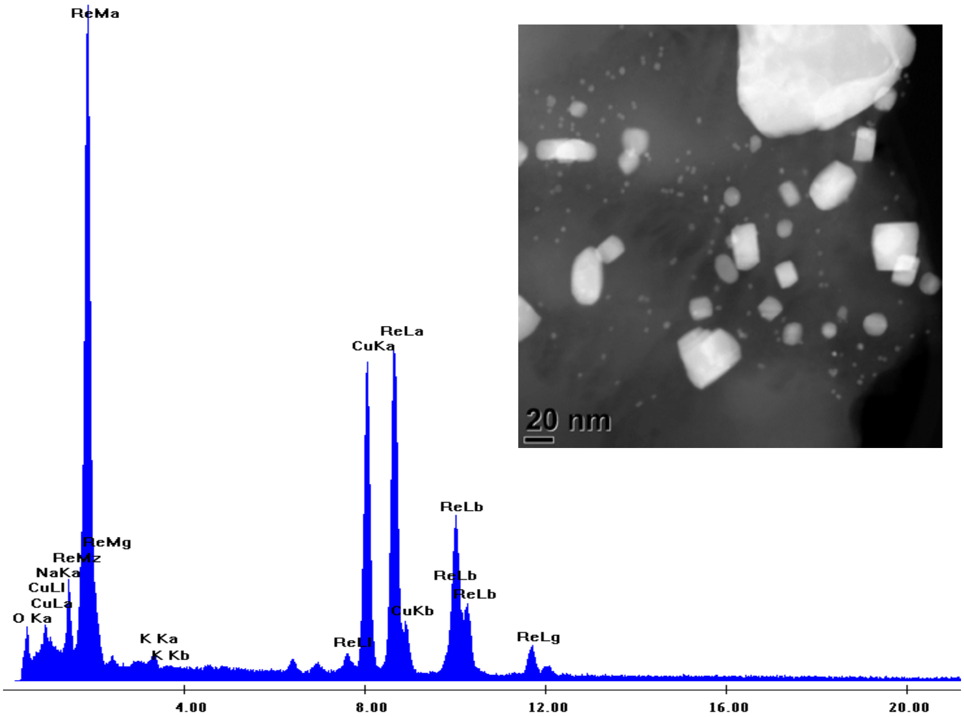

Figure S1. EDX analysis of a region of supported large crystals. The Cu signal comes from the holey carbon grid on which the material was deposited for imaging.

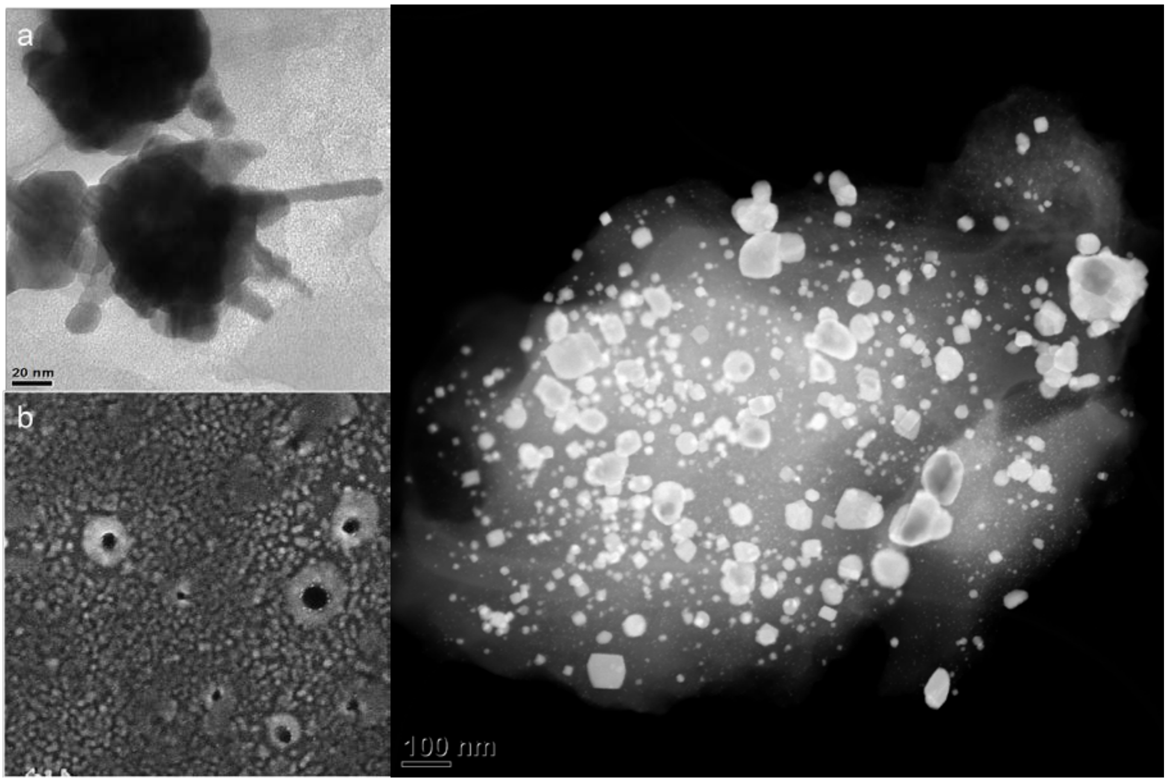

Figure S2. (a) HRTEM image of a localized clusters of Re in regions where circular, layered particles eventually results (see Fig. 1a in the main text), and (b) SEM image of the surface of the spin-cast, pyrolyzed support showing NP agglomeration around the rims of the holes. This confirms a similar overall process on at least two length scales, with crystals coarsening to rim edges, whose contact lines are themselves pinned, with their eventual ripening to a high index NP or supracrystal. On the right is a dark field STEM image of a high density of dispersed NPs and larger Re supracrystals within a carbon support.

S1 – Pyrolytic decomposition mechanism

It is now well known that the thermal degradation of cyclotriphosphazenes often produces cyclolinear and cyclomatrix materials [1-3]. In these cases the cross-linking of the polymeric chains of the cyclophosphazenes produces a high char yield. For the pyrolysis of the organometallic-metallic/cyclotriphosphazene mixtures, a similar mechanism to that of the analogous organometallic derivatives of polyphosphazenes could operate [4]. The high pyrolytic yields of these systems were attributed to their extensive coordination cross-linking upon heating. It is possible that during heating, the metallic ions be able to coordinate through the phenyl groups of the cyclic triphosphazene $[NP(O_2C_{12}H_8)]_3$, resulting in the formation of a cyclomatrix [5]. Subsequent oxidation of the organic matter gives rise to holes where the metallic rhenium begins to nucleate. During this carbonization process, carbon monoxide [6] is also produced which eventually reduces the perrhenate ions (VII) to Re (0).

References

1. D. E. Brown, K. Ramachandra, K. R. Carter, C. W. Allen, *Macromolecules* 2001, **34**, 2870.
2. J. Maynard, T. R. Sharp, J. F. Haw, *Macromolecules* 1991, **24**, 2794.
3. D. Kumar, A. D. Gupta, *Macromolecules* 1995, **28**, 6323.
4. C. Díaz, M. L. Valenzuela, *Macromolecules* 2006, **39**, 103.
5. C. Díaz, M. L. Valenzuela, L. Zuñiga, C. O'Dwyer, *J. Inorg. Organomet. Polym. Mater*. 2009, **19**, 507.
6. B. C. Tappan, M. H. Huynh, M. A. Hiskey, D. E. Chavez, E. P. Luther, J. T. Mang, S. F. Son, *J. Am. Chem. Soc*. 2006, **128**, 6589.