



Short Communication

One-step/one-pot decoration of oxide microparticles with silver nanoparticles



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ABSTRACT

Hypothesis: Heterogeneous nucleation of silver oxide (Ag_2O) onto oxide microparticles (OMPs) followed by spontaneous thermal decomposition produce nanostructures made of OMPs decorated with silver nanoparticles (OMP|AgNPs).

Experiments: Colloidal chemistry methods have been used to produce the decoration of OMPs with silver nanoparticles (AgNPs), by carrying out the Ag_2O precipitation/thermal decomposition. The process is driven in water enriched acetone medium containing NaOH , NH_3 , AgNO_3 and SiO_2 MPs as substrate. Optical and morphological properties of OMP|AgNPs were characterized by using STEM, EDS, HRTEM and Raman spectroscopy.

Findings: A new synthetic method to decorate OMPs (TiO_2 , SiO_2) with metallic AgNPs in a single step/single pot reaction is proven effective to produce OMP|AgNPs either in aqueous or water enriched media.

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1. Introduction

As new properties of matter are discovered within the nano-scale, research is driven into the exploration of more complex nanostructures (NSs) which, in turn, rise up the complexity of synthetic process needed to produce them. Among metal nanoparticles (MNPs), those made of noble metals have been widely investigated because of their applications in areas such as catalysis (Pt, Au) [1,2] as well as due to their plasmonic [3] and surface enhancement Raman spectroscopy (SERS) properties (Au, Ag) [4–6]. The decoration of oxide microparticles (OMPs) with noble MNPs is an approach widely used to obtain hybrid NSs where the active surface for catalysis is noticeably enhanced. In such an approach a stable and low cost material (OMPs) is used to support the catalytic active material (NPs), often more expensive, in building up low cost NS catalysts [7]. The synthesis of OMP|MNPs structures requires the heterogeneous nucleation of MNPs onto OMPs surface to be achieved. This involves running against the small adhesive interaction between these materials, which results from the fact that surface tension values for metals are higher than those

for oxides [8]. This particular issue has been approached by using a variety of synthetic methods that can be grouped as follows: (a) those using, firstly, impregnation of OMPs by immersion in solutions containing noble metal complexes/cations (precursors), and then the MNP formation that results from precursors reaction either by chemical reduction [9–11] or by photochemical decomposition [12] or by calcination [13]; and (b) those employing a functionalization strategy, where a molecular linker with appropriate functional groups is used to chemically bind both, oxide MPs and metallic NPs [14,15]. It is worthwhile mentioning that all these approaches do involve, at least, two or more synthetic steps to achieve the decoration of oxide MPs.

Here we report a new synthetic approach to produce OMP|MNPs, where the decoration of OMP (SiO_2 and TiO_2) with silver nanoparticles (AgNPs) is achieved by means of a one-step/one-pot straightforward procedure.

2. Experimental section

All chemicals were of analytical grade and they were used as received without further purification: silver nitrate (AgNO_3), ammonia (NH_3), sodium hydroxide (NaOH), rhodamine 6G and acetone. Deionized purified water (Milli Ro-Milli Q system) was

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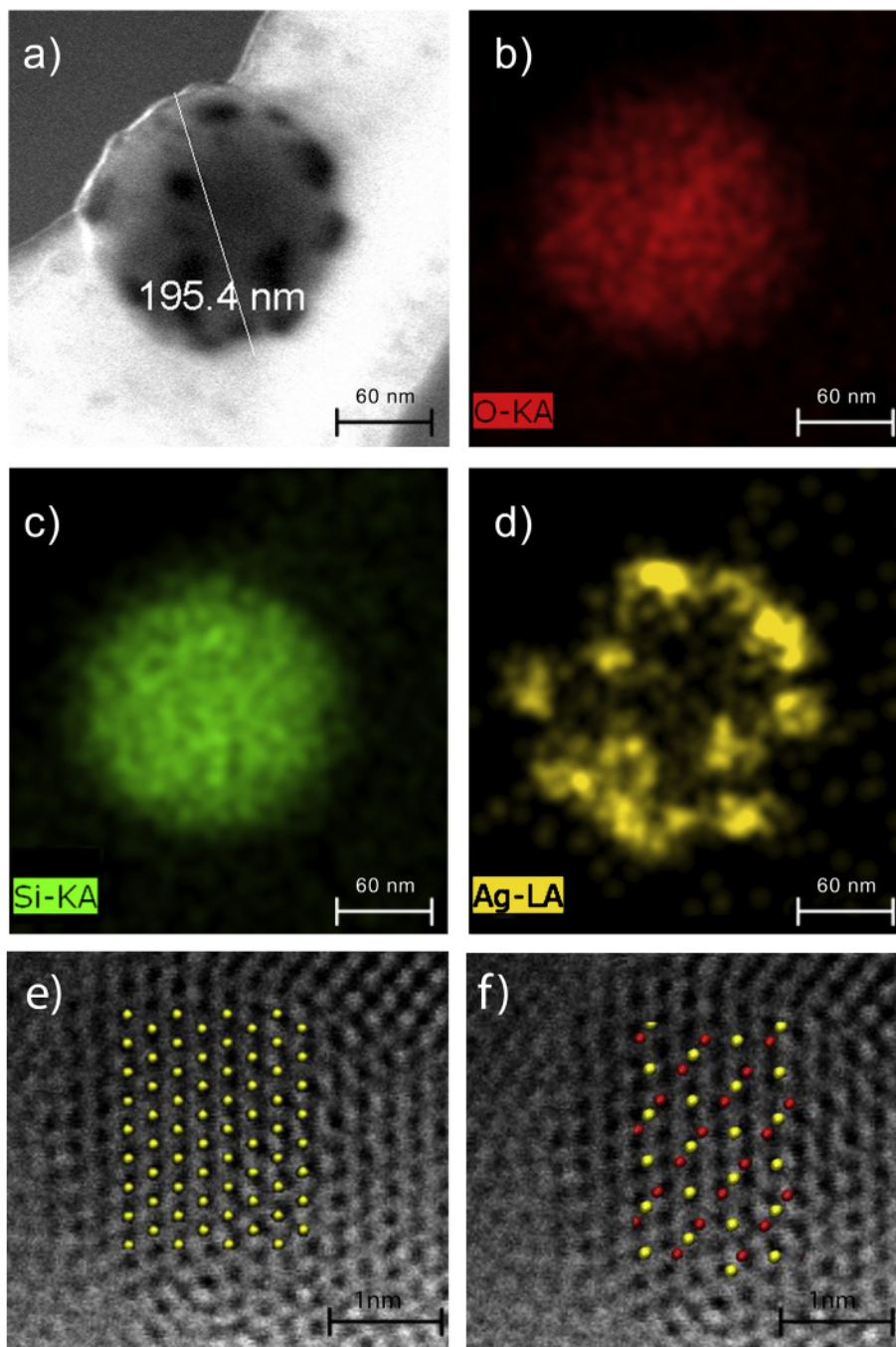


Fig. 1. A representative $\text{SiO}_2\text{MP|AgNPs}$ produced in acetone/water medium: (a) STEM image. EDS maps for: (b) K-oxygen, (c) K-silicon and (d) L-silver. Comparison of a magnified HRTEM bright field image with ball models (superimposed) corresponding to: (e) metallic fcc Ag with a lattice parameter of 4.08 Å, and (f) Ag_2O crystalline structure with a lattice parameter of 4.72 Å.

used in preparing solutions (resistivity of $18.2 \times 10^6 \Omega \text{ cm}$). Soluble silver salts solutions (AgNO_3) were kept in darkness to prevent any photochemical reaction involving the silver ion (Ag^+).

$\text{SiO}_2\text{MP|AgNPs}$ were obtained from a reactive water/acetone solution/suspension of 0.1 mM AgNO_3 , 0.2 mM NaOH, 20 mM NH_3 and 2.3×10^{12} SiO_2MPs per liter suspension (final volume = 100 mL).

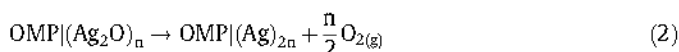
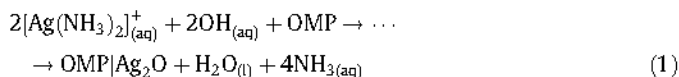
Selected experimental samples were characterized with Cs-Corrected Transmission Electron Microscopy (TEM, JEM-200ARMF JEOL's microscope operating at 200 kV) and Hitachi STEM-5500 microscope operating at 30 kV. The elemental distribution on the NSs was studied by Energy-dispersive X-ray Spectroscopy (EDS) line scanning and mapping. Raman spectra were recorded on a

Horiba Jobin Yvon LabRAM HR Raman spectrometer by using a He-Ne laser (632.82 nm) as excitement source. Raman measurements were performed by using a quartz cell containing either suspensions of SiO_2MPs or of $\text{SiO}_2\text{MP|AgNPs}$ in presence of Rhodamine 6G (50 μM).

3. Results and discussion

The strategy of the method here reported is based on the assumption that noble metal oxides/hydroxides will exhibit better adhesion forces onto foreign oxide surfaces than the noble metal itself. The synthetic scheme is completed by a recently reported

piece of knowledge [16,17]: aqueous/water-enriched silver oxide (Ag_2O) undergoes spontaneous thermal decomposition to produce AgNPs. Therefore, the synthesis itself is a straightforward reaction that involves two processes taking place simultaneously: the Ag_2O precipitation onto OMPs (Eq. (1)), and its spontaneous decomposition (Eq. (2)).



The experimental conditions were controlled to achieve, on the one hand, the heterogeneous nucleation of Ag_2O onto OMP surface to be favored over its homogeneous nucleation (1); and, on the other hand, the thermal activation to be appropriate in driving the decomposition of Ag_2O deposited onto oxide MPs ($\text{OMP}|\text{Ag}_2\text{O}$) that finally produces $\text{OMP}|\text{AgNPs}$ (2). The Ag_2O precipitation is easily obtained from the addition of strong alkali into aqueous solutions of soluble salts of $\text{Ag}(\text{I})$. By performing this procedure at 2°C , Ag_2O does precipitate and remain stable; whereas at room temperature (c.a. 25°C) the Ag_2O precipitation is followed by a slow thermal decomposition to form AgNPs [16]. Ag_2O precipitation is affected by ammonia which forms coordination complexes with $\text{Ag}(\text{I})$ and can selectively dissolve the silver oxide. Thus, ammonia is used in presence of OMPs to disfavor the Ag_2O homogeneous nucleation over the Ag_2O heterogeneous nucleation onto OMPs' surface. Given its influence on the Ag_2O precipitation, ammonia also influences the Ag_2O thermal decomposition, too [16]. Another factor used in controlling the Ag_2O precipitation, and in turn its thermal decomposition, is the change of the average dielectric constant of the formation media, as it has been recently reported [16]. It will be shown below that a fine control over the amount of silver deposited on OMPs can be achieved by driving the Ag_2O precipitation/decomposition in water-enriched environments, e.g. water/acetone solutions [16].

TiO_2 MPs and SiO_2 MPs were used as substrates in carrying out Ag_2O deposition/decomposition process. In spite of the spectroscopic/microscopic evidence that indicates the existence of (1)–(2) processes sequence over the surface of TiO_2 MPs (ESI-3), the broad shape distribution of TiO_2 MPs does blur the interpretation of results. On the contrary, SiO_2 MPs have an advantageous characteristic: they are all spheres (ESI-4), a crucial morphological feature that helps to unravel aspects of deposition/decomposition sequence. Therefore, the discussion here will be focused on results obtained in our experiments where SiO_2 MPs are used as substrate. In addition, the degree of control over the heterogeneous nucleation of Ag_2O onto OMP surface can be enhanced by decreasing both the strong alkali concentration and the average dielectric constant of formation media [16]. Fig. 1a shows a STEM image of a NS, prepared by carrying out the synthesis in acetone/water environment, which exhibits the characteristic SiO_2 MP spherical shape, as well as zones with very high electronic contrast all over the surface. The element distribution over the NS was mapped by tracing the X-ray signature of O, Si and Ag (EDS results in Fig. 1b–d, respectively). In contrast to the homogeneous spherical distribution of O and Si, Ag exhibits a heterogeneous pattern distribution that strongly resembles the high contrast pattern already observed in the SEM image (Fig. 1a). Similar NSs were observed in the different fields of the sample, indicating that SiO_2 MPs are homogeneously decorated (ESI-4, Fig. 7). A further confirmation of the presence of metallic Ag onto SiO_2 MP surface is obtained with HRTEM. Although Fig. 1e and f show for comparison purposes only high magnification bright field images, the complete sequence of dark and bright field images for increasing magnification is shown in

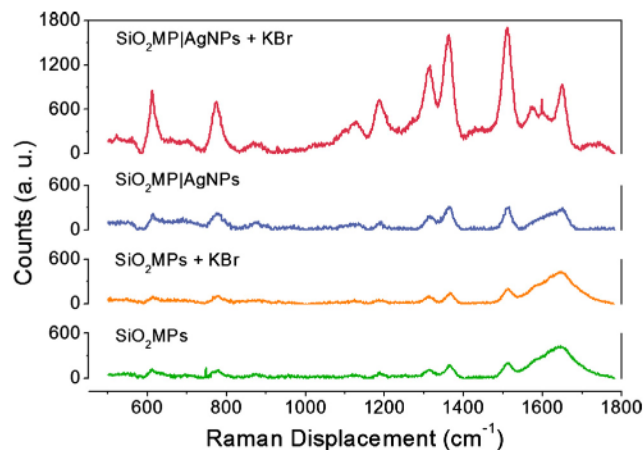


Fig. 2. Rhodamine 6G Raman spectroscopy results in presence of SiO_2 MP|AgNPs (top, red and blue lines) as compared to SiO_2 MPs (bottom, orange and green lines) under different ionic strength conditions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

supporting material (ESI-4, Fig. 8). Fig. 1e and f also show ball models corresponding to fcc Ag and Ag_2O crystalline structure, respectively. The close resemblance of HRTEM image and fcc Ag with a lattice parameter of 4.08 \AA is clearly conclusive: there is metallic silver onto SiO_2 MP surface. Therefore, in absence of any reducing agent, this whole evidence corroborates that SiO_2 MP|AgNPs are produced effectively by Ag_2O heterogeneous nucleation and thermal decomposition within a one-step/one-pot synthesis.

Aiming at testing possible applications of the SiO_2 MP|AgNPs produced as Raman enhancing NSs, its influence on Rhodamine 6G was characterized. Fig. 2 shows Raman spectra of Rhodamine 6G in solutions containing either SiO_2 MPs (control results) or SiO_2 MP|AgNPs, for different ionic strength conditions. As it is expected for a substrate like SiO_2 MPs without SERS properties, no remarkable change of the Raman spectra is detected for Rhodamine whether SiO_2 MPs are aggregated (with KBr) or not (Fig. 2, orange and green spectra). In presence of SiO_2 MP|AgNPs, only a very modest change in the Rhodamine spectral profile is detected (Fig. 2, blue), probably due either to a small surface enhancement effect associated with small AgNPs present in the NSs or to a low concentration of NSs in the solution. However, the addition of KBr drives the SiO_2 MP|AgNPs to undergo agglomeration, resulting in a noticeable enhancement of the Rhodamine Raman spectrum (Fig. 2, red), probably related to the generation of hot-spots in the aggregated NSs^{3b}. This behavior is consistent with the presence of a plasmonic material (Ag) in the NS in complete agreement with the evidence above discussed.

4. Conclusions

The one-step/one-pot synthetic method presented here has been proven effective to produce the decoration of oxide microparticles with silver nanoparticles ($\text{OMP}|\text{AgNPs}$). This synthetic route is easily implemented and involves simple and safe procedures. Results are consistently explained by assuming a chemical scheme involving heterogeneous Ag_2O precipitation and subsequent decomposition to produce AgNPs. This alternative method requires low-cost starting materials and low-energy consumption; to obtain $\text{OMP}|\text{AgNPs}$ of easy purification and by-products ($\text{H}_2\text{O}_2/\text{O}_2$) environmentally harmless. The OMP used as substrates (SiO_2 or TiO_2), both relevant materials with different applications (medicine, solar devices, catalysts, etc.), can be easily transformed into a hybrid NS with plasmonic behavior. The nature of the OMPs used (SiO_2 or TiO_2) seems to play no important role with exception of

the reactivity during the synthesis, a feature that suggests this method might be feasible of being used with OMPs of elements different from Si and Ti.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2014.04.039>.

References

- [1] W.T. Wallace, B.K. Min, D.W. Goodman, *Top. Catal.* 34 (2005) 17.
- [2] D. Tongsakul, S. Nishimura, K. Ebitani, *ACS Catal.* 3 (2013) 2199.
- [3] M.-C. Daniel, D. Astruc, *Chem. Rev.* 104 (2004) 293.
- [4] A.I. Henry, J.M. Bingham, E. Ringe, L.D. Marks, G.C. Schatz, R.P. Van Duyne, *J. Phys. Chem. C* 115 (2011) 9291.
- [5] E.C. Le Ru, P.G. Etchegoin, *Principles of surface enhanced Raman spectroscopy and related plasmonic effects*, Elsevier, Amsterdam, 2009.
- [6] J.L. Castro, J.F. Arenas, M.R. Lopez-Ramirez, J. Soto, J.C. Otero, *J. Colloid Interface Sci.* 396 (2013) 95.
- [7] S. Liu, S.Q. Bai, Y. Zheng, K.W. Shah, M.Y. Han, *Chem. Cat. Chem.* 4 (2012) 1462.
- [8] Q. Fua, T. Wagner, *Surf. Sci. Rep.* 62 (2007) 431.
- [9] N. Zhang, F. Xue, X. Yu, H. Zhou, E. Ding, *J. Alloys Compd.* 550 (2013) 209.
- [10] N.Y. Hebbalkar, S. Acharya, T.N. Rao, *J. Colloid Interface Sci.* 364 (2011) 24.
- [11] M.S.M. Peterson, J. Bouwman, A. Chen, M. Deutsch, *J. Colloid Interface Sci.* 306 (2007) 41.
- [12] K. Chen, X. Feng, R. Hu, Y. Li, K. Xie, Y. Li, H. Gu, *J. Alloys Compd.* 554 (2013) 72–79.
- [13] Y.X. Gan, X. Zeng, L. Su, L. Yang, B.J. Gan, L. Zhang, *Mater. Res. Bull.* 46 (2011) 1828.
- [14] B.E. Brinson, J. Britt Lassiter, C.S. Levin, R. Bardhan, N. Mirin, N.J. Halas, *Langmuir* 24 (2008) 14166.
- [15] L. Chen, X. Han, J. Yang, J. Zhou, W. Song, B. Zhao, W. Xu, Y. Ozaki, *J. Colloid Interface Sci.* 360 (2011) 482.
- [16] O.A. Douglas-Gallardo, R. Moiraghi, M.A. Macchione, J.A. Godoy, M.A. Pérez, E.A. Coronado, V.A. Macagno, *RCS Adv.* 2 (2012) 2923.
- [17] A.A. Semenova, E.A. Goodilin, Y.D. Tretyakov, *Mendeleev Commun.* 21 (2011) 312.