



## Short Communication

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



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## ARTICLE INFO

## Article history:

Received 12 March 2014

Accepted 17 April 2014

Available online 28 April 2014

## Keywords:

Nanostructures

Synthesis

Silver oxide

Thermal decomposition

Metal-oxide adhesion

## ABSTRACT

**Hypothesis:** Heterogeneous nucleation of silver oxide (Ag<sub>2</sub>O) 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<sub>2</sub>O precipitation/thermal decomposition. The process is driven in water enriched acetone medium containing NaOH, NH<sub>3</sub>, AgNO<sub>3</sub> and SiO<sub>2</sub>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<sub>2</sub>, SiO<sub>2</sub>) 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.

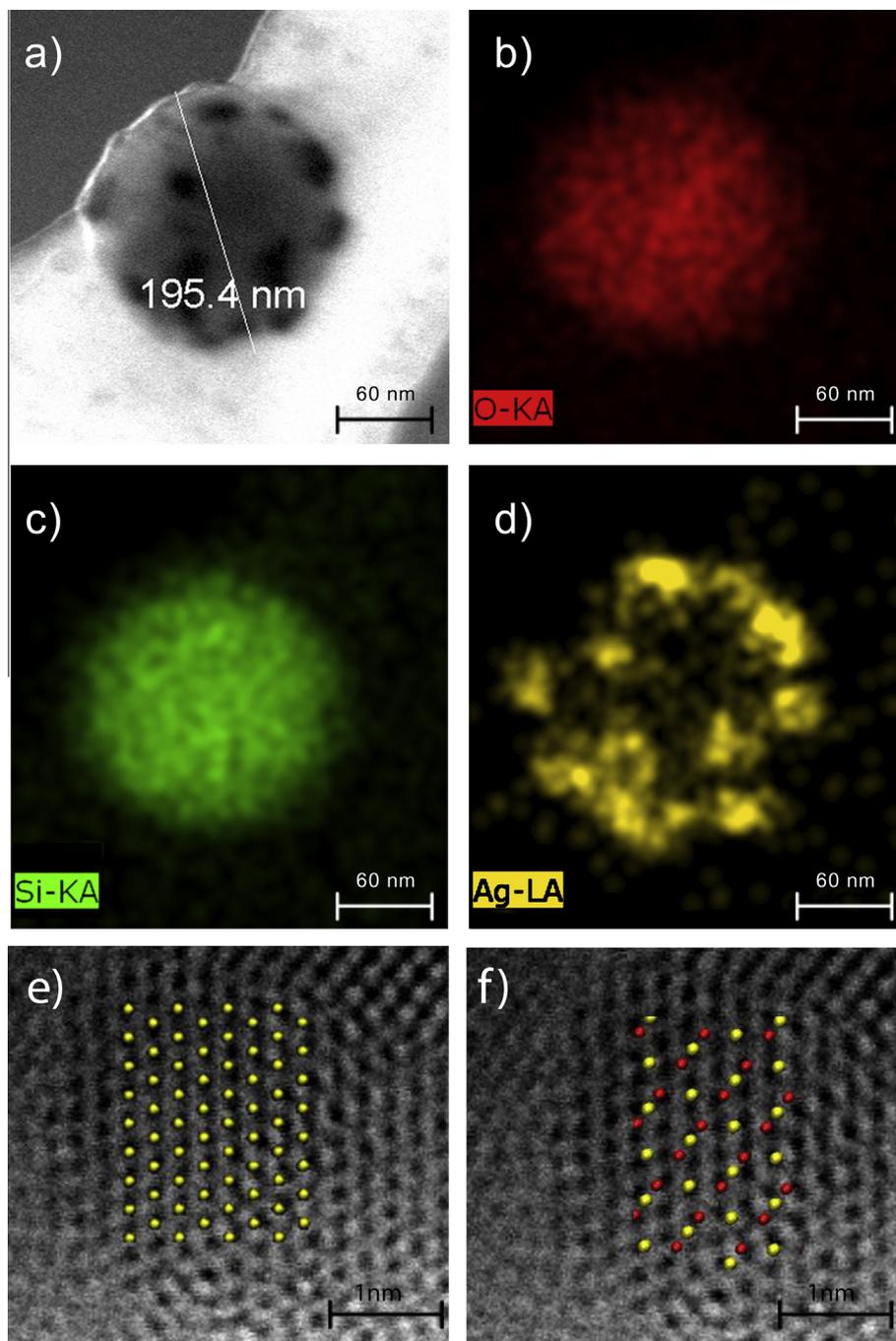
Here we report a new synthetic approach to produce OMP|MNPs, where the decoration of OMP (SiO<sub>2</sub> and TiO<sub>2</sub>) with silver nanoparticles (AgNPs) is achieved by means of a one-step/one-pot straightforward procedure.

## 2. Experimental section

All chemicals were of analytical grade and they were used as received without further purification: silver nitrate (AgNO<sub>3</sub>), ammonia (NH<sub>3</sub>), 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)  $\text{Ag}_2\text{O}$  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 ( $\text{AgNO}_3$ ) were kept in darkness to prevent any photochemical reaction involving the silver ion ( $\text{Ag}^+$ ).

$\text{SiO}_2\text{MP|AgNPs}$  were obtained from a reactive water/acetone solution/suspension of 0.1 mM  $\text{AgNO}_3$ , 0.2 mM NaOH, 20 mM  $\text{NH}_3$  and  $2.3 \times 10^{12}$   $\text{SiO}_2\text{MPs}$  per liter suspension (final volume = 100 mL).

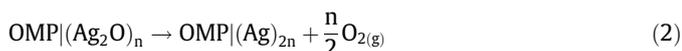
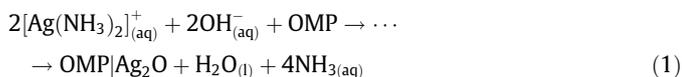
Selected experimental samples were characterized with Cs-Corrected Transmission Electron Microscopy (TEM, JEM-200ARMF JEOL's microscope operating at 200 kV) and Hitachi STEM-5500 microscope operating at 30 kV. The elemental distribution on the NSs was studied by Energy-dispersive X-ray Spectroscopy (EDS) 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  $\text{SiO}_2\text{MPs}$  or of  $\text{SiO}_2\text{MP|AgNPs}$  in presence of Rhodamine 6G (50  $\mu\text{M}$ ).

### 3. Results and discussion

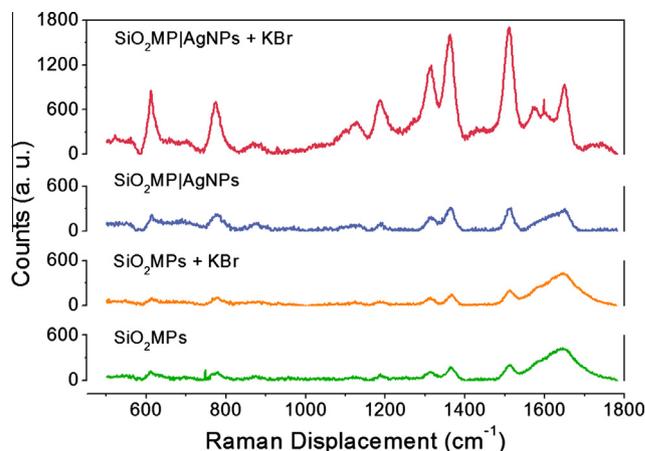
The strategy of the method here reported is based on the assumption that noble metal oxides/hydroxides will exhibit better adhesion forces onto foreign oxide surfaces than the noble metal itself. The synthetic scheme is completed by a recently reported

piece of knowledge [16,17]: aqueous/water-enriched silver oxide ( $\text{Ag}_2\text{O}$ ) undergoes spontaneous thermal decomposition to produce AgNPs. Therefore, the synthesis itself is a straightforward reaction that involves two processes taking place simultaneously: the  $\text{Ag}_2\text{O}$  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  $\text{Ag}_2\text{O}$  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  $\text{Ag}_2\text{O}$  deposited onto oxide MPs ( $\text{OMP}|\text{Ag}_2\text{O}$ ) that finally produces  $\text{OMP}|\text{AgNPs}$  (2). The  $\text{Ag}_2\text{O}$  precipitation is easily obtained from the addition of strong alkali into aqueous solutions of soluble salts of Ag(I). By performing this procedure at 2 °C,  $\text{Ag}_2\text{O}$  does precipitate and remain stable; whereas at room temperature (c.a. 25 °C) the  $\text{Ag}_2\text{O}$  precipitation is followed by a slow thermal decomposition to form AgNPs [16].  $\text{Ag}_2\text{O}$  precipitation is affected by ammonia which forms coordination complexes with Ag(I) and can selectively dissolve the silver oxide. Thus, ammonia is used in presence of OMPs to disfavor the  $\text{Ag}_2\text{O}$  homogeneous nucleation over the  $\text{Ag}_2\text{O}$  heterogeneous nucleation onto OMPs' surface. Given its influence on the  $\text{Ag}_2\text{O}$  precipitation, ammonia also influences the  $\text{Ag}_2\text{O}$  thermal decomposition, too [16]. Another factor used in controlling the  $\text{Ag}_2\text{O}$  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  $\text{Ag}_2\text{O}$  precipitation/decomposition in water-enriched environments, e.g. water/acetone solutions [16].

$\text{TiO}_2\text{MPs}$  and  $\text{SiO}_2\text{MPs}$  were used as substrates in carrying out  $\text{Ag}_2\text{O}$  deposition/decomposition process. In spite of the spectroscopic/microscopic evidence that indicates the existence of (1)–(2) processes sequence over the surface of  $\text{TiO}_2\text{MPs}$  (ESI-3), the broad shape distribution of  $\text{TiO}_2\text{MPs}$  does blur the interpretation of results. On the contrary,  $\text{SiO}_2\text{MPs}$  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  $\text{SiO}_2\text{MPs}$  are used as substrate. In addition, the degree of control over the heterogeneous nucleation of  $\text{Ag}_2\text{O}$  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  $\text{SiO}_2\text{MP}$  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  $\text{SiO}_2\text{MPs}$  are homogeneously decorated (ESI-4, Fig. 7). A further confirmation of the presence of metallic Ag onto  $\text{SiO}_2\text{MP}$  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  $\text{SiO}_2\text{MP}|\text{AgNPs}$  (top, red and blue lines) as compared to  $\text{SiO}_2\text{MPs}$  (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  $\text{Ag}_2\text{O}$  crystalline structure, respectively. The close resemblance of HRTEM image and fcc Ag with a lattice parameter of 4.08 Å is clearly conclusive: there is metallic silver onto  $\text{SiO}_2\text{MP}$  surface. Therefore, in absence of any reducing agent, this whole evidence corroborates that  $\text{SiO}_2\text{MP}|\text{AgNPs}$  are produced effectively by  $\text{Ag}_2\text{O}$  heterogeneous nucleation and thermal decomposition within a one-step/one-pot synthesis.

Aiming at testing possible applications of the  $\text{SiO}_2\text{MP}|\text{AgNPs}$  produced as Raman enhancing NSs, its influence on Rhodamine 6G was characterized. Fig. 2 shows Raman spectra of Rhodamine 6G in solutions containing either  $\text{SiO}_2\text{MPs}$  (control results) or  $\text{SiO}_2\text{MP}|\text{AgNPs}$ , for different ionic strength conditions. As it is expected for a substrate like  $\text{SiO}_2\text{MPs}$  without SERS properties, no remarkable change of the Raman spectra is detected for Rhodamine whether  $\text{SiO}_2\text{MPs}$  are aggregated (with KBr) or not (Fig. 2, orange and green spectra). In presence of  $\text{SiO}_2\text{MP}|\text{AgNPs}$ , 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  $\text{SiO}_2\text{MP}|\text{AgNPs}$  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<sup>3b</sup>. 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  $\text{Ag}_2\text{O}$  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 ( $\text{SiO}_2$  or  $\text{TiO}_2$ ), 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 ( $\text{SiO}_2$  or  $\text{TiO}_2$ ) 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.

### Acknowledgments

We thank Claudia Nome from IPAVE, CIAP for her technical assistance in TEM, to the personnel of LAMARX-FaMAF from the Universidad Nacional de Córdoba for their assistance in SEM characterization, to Martin Fox Douglas for his advice in graphic design, and to Martin Harvey for his proof reading. M.A.M., O.A.D.-G, L.A.P., N.P., R.M., and A.S. thank Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for their fellowship. This research has been supported by the CONICET, the Fondo para la Investigación Científica y Tecnológica (FONCyT) of Argentina, Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT) Program BID, and the Secretaría de Ciencia y Tecnología (SECYT- UNC) by means of different grants: PME(2006) 1544, PIP (2012) 112-201101-00430, PIP (2012) 112-200801-000983, PICT (2012) 2286, PICT (2010) 1233. The authors are indebted for support to the following: Welch Foundation Agency (project AX-1615: Controlling the Shape and Particles Using Wet Chemistry Methods and Its Application to Synthesis of Hollow Bimetallic Nanostructures), and the National Science Foundation (NSF) (PREM grant number DMR-0934218, NSF Grant 1103730: Alloys at the Nanoscale; The Case of Nanoparticles Second Phase) and to Facilities of Kleberg Advanced Microscopy Center (KAMC) and NIH RCMI Nanotechnology and Human Health Core (Grant 5G12RR013646-12) at The University of Texas at San Antonio (UTSA).

### 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. Hebalkar, 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.