

## Intermatrix Synthesis of Ag, AgAu and Au nanoparticles by Galvanic Replacement Strategy for bactericidal and electrocatalytically active nanocomposites

### Electronic Supplementary Information (ESI) for RSC New Journal of Chemistry

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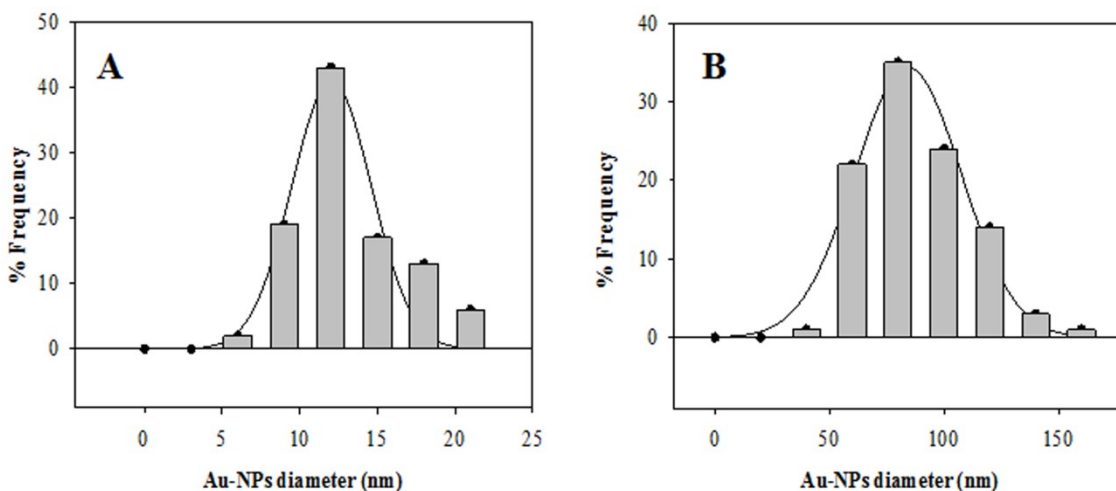
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### ESI.1: Size distribution Histogram of Au-FMNPs synthesized by Intermatrix Synthesis using NaBH<sub>4</sub> (A) and Ascorbic Acid (B) as reducing agent.



### ESI.2. Intermatrix Synthesis (IMS) of Ag-functional metal nanoparticles (FMNPs) on gel-type cationic polymeric matrix with formaldehyde as neutral reducing agent for interior and external location of FMNPs.

The understanding of the fundamental origins of the physical properties of Nanocomposites (NCs) through systematic studies of the controlled FMNPs distribution (size and interparticle distance) makes valid the idea of incorporating FMNPs in the interior of a stabilizer matrix. In order to achieve this, some

researchers have used a methodology very similar to IMS but for the selection of the reducing agent and the principles their studies are based on.

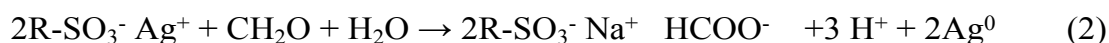
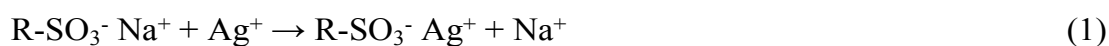
Thus, the preparation of nanocomposites microspheres containing Ni-FMNPs is accomplished via chemical surface modification<sup>4,5</sup>. This method takes advantage of the hydrolysis ability of the certain polymeric host, and subsequent ion exchange and annealing in hydrogen atmosphere induces both reduction of the doped metallic ions and reformation of the initial polymeric structures via dehydration. As IMS, the particle size and homogenous distribution of the embedded Ni-NPs can be controlled. This procedure can be extended to the preparation of other types of FMNPs in order to obtain photonic or magnetic NCs materials.

Regarding the potential applications of NCs with interior distribution of FMNPs; it is necessary to introduce new alternative preparation procedures. IMS seems to be a suitable to obtain this distribution by a more environmentally friendly methodology; as the use of high temperature, organic solvents or even the use of hydrogen fluxes are not needed.

As discussed before, Donnan Effect (DE) affects the diffusion of ionic species through a charged matrix. In order to obtain an interior distribution of FMNPs on a cationic exchanger matrix; IMS second stage must include a non-ionic reducing agent such as formaldehyde. The loading of silver ions into the matrix is represented by Equation 1. As the negatively charged sulfonic groups of the gel-type cationic polymer are distributed through the entire matrix; so will be the Ag<sup>+</sup> ions due to diffusion and electrostatic interaction with them.

Formaldehyde reduction rate would be too slow at room temperature due to low or neutral pH. Therefore, the second stage of IMS included 2M of formaldehyde in aqueous alkaline solution. These conditions make formaldehyde a suitable reducing agent for silver.<sup>6,7</sup>

IMS of Ag-FMNPs on a gel-type cationic polymeric resin using formaldehyde as neutral reducing agent is presented in equations (1) and (2).



Equation 4 shows the typical IMS NPs – precursor loading stage, in this case of silver ions due to the exchange of  $\text{Na}^+$  to  $\text{Ag}^+$ . Consequently, Equation 2 presents the formation of Ag-FMNPs. The silver content in the final NCs was around  $159\text{mg Ag} \times \text{g}^{-1} \text{NC}$ , which corresponds to 70% efficiency of silver loading during IMS stage 1. In order to confirm the Ag-NPs intern distribution in the gel-type polymer, SEM characterization and EDS analysis were performed to the samples. As it can be seen in Figure 1, the element mapping and the LineScan EDS analysis verify this. Moreover, distribution is consistent and conclusive of DE influence during the appearance of the FMNPs in the second stage of IMS.

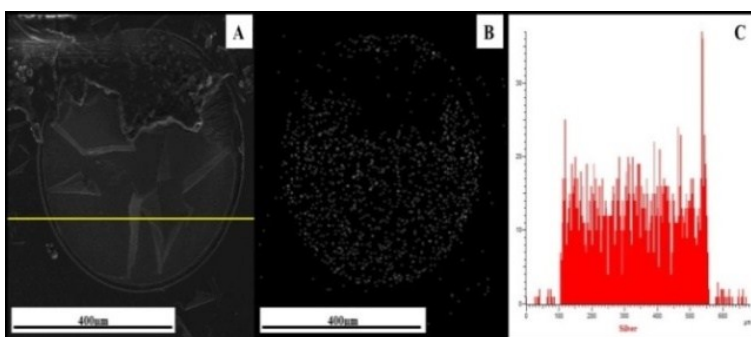
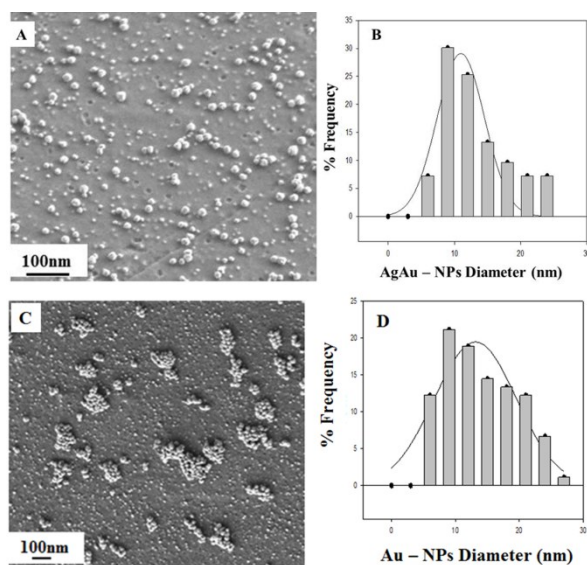


Figure 1: A) Cross section of Ag-FMNPs containing nanocomposite with B) Element Mapping and C) EDS -LineScan analysis showing the interior distribution of Ag-FMNPs due to IMS with formaldehyde as reducing agent

**ESI.3: Scanning Electron Microscopy Images and Diameter Size Distribution Histogram for AgAu-FMNPs (A;B) and Au-FMNPs(C,D) obtained by Galvanic Replacement Strategy during IMS.** In both cases, the NPs are well distributed over the surface of the polymer bead; showing that by this synthetic methodology the advantageous distribution offered by IMS is as well accomplished. The average diameter for AgAu-FMNPs is  $11.0 \pm 0.7$  nm and for Au-FMNPs is  $13.1 \pm 0.9$  nm.



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