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BIOSENSORS FOR PANDEMICS

Green synthesis of plasmonic metal nanoparticles for biosensor applications

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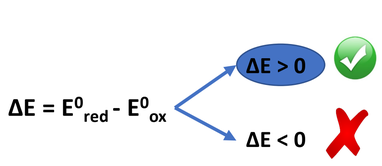
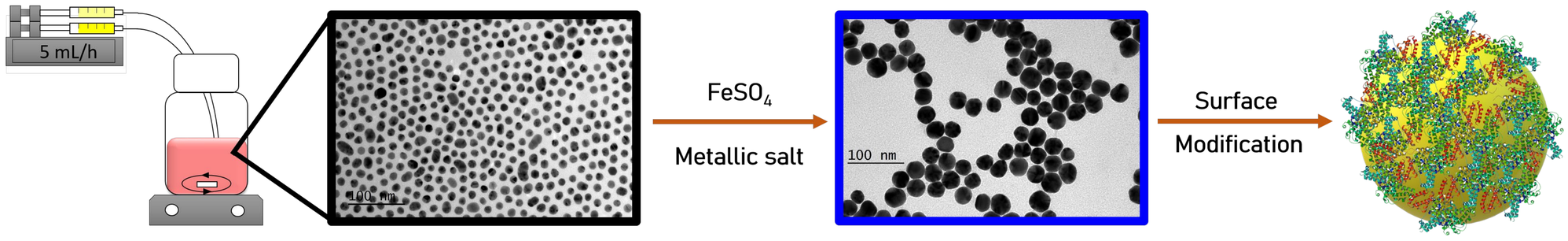
Since the first Faraday's report about the properties of noble metal nanomaterials,[1] the scientific community has invested great efforts and knowledge to control and enforcement of these new materials at the nanoscale. Nowadays, there are plenty applications based on metallic nanoparticles[2](NPs), from sensing or catalyst until biomedical imaging or therapy. There are innumerable methods to synthetize NPs with controlled size, shape and morphology. Among the different key factors in the synthesis of nanoparticles, the selection of the correct reduction agent plays an important role in this process. Several molecular reducing agents have been employed, but less attention was placed on the use of metal cations as reducing agents. Bearing this in mind, a new seeded-growth method to fabricate gold or core@shell nanoparticles was developed. Small gold NPs are overgrowth thanks to the redox potential of iron (II) or [Fe-citrate]$^{-}$ complex. It is a fast reaction at room temperature without polymers or surfactants. Furthermore, the surface modification of this material with proteins, thiolate molecules etc. is really easy due to the weak bond between the capping agent (citrate) and the NPs.[3]



Half-reaction			E^0 (V)
[Fe-citrate] + 1e$^-$	→	[Fe-citrate]$^-$	+0.372
Pt^{2+} + 2e$^-$	→	$Pt_{(s)}$	+0.758
Fe^{3+} +1e$^-$	→	Fe^{2+}	+0.77
Ag^{+} +1e$^-$	→	$Ag_{(s)}$	+0.80
Pd^{2+} + 2e$^-$	→	$Pd_{(s)}$	+0.92
Au^{3+} + 3e$^-$		$Au_{(s)}$	+ 1.52



Au NPs

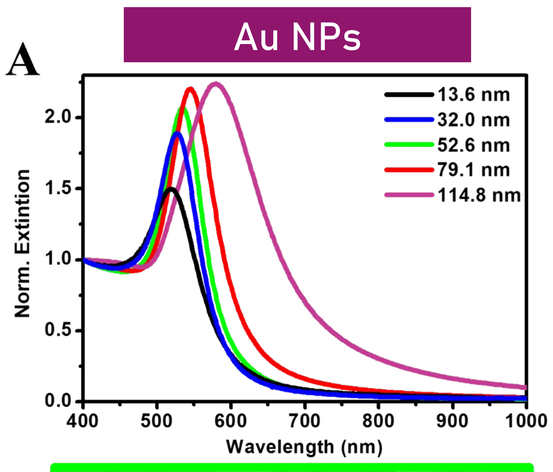


Fig. 1. Normalized Vis-NIR spectra of Au nanoparticles of different sizes obtained after several additions of gold (III) and iron (II) to a Au seed dispersion (Black line). TEM images of: B) Au NPs after the second overgrowth (54.5 ± 3.0 nm), C) Au NPs after third overgrowth, (79.8 ± 3.8 nm) of NPs and D) Au NPs after fourth overgrowth (114.8 ± 6.7 nm).

Au@Ag NPs

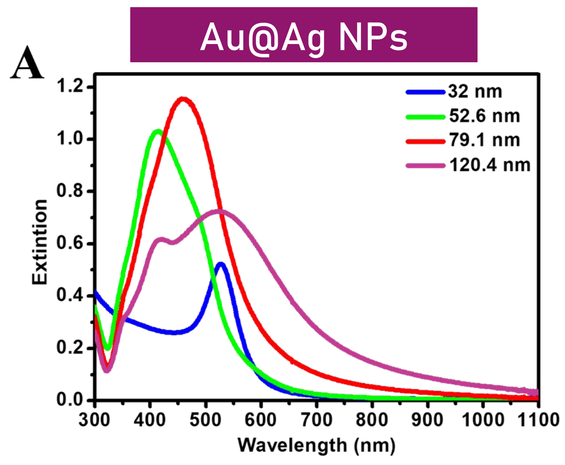


Fig. 2. Vis-NIR spectra of Au and Au@Ag nanoparticles of different sizes obtained after several additions of silver (I) and iron (II) to a Au seed dispersion (Blue line). TEM images of: A) Au@Ag NPs after one overgrowth (52.6 ± 3.7 nm), B) Au@Ag NPs after second overgrowth, (79.1 ± 6.2 nm) of NPs and C) Au NPs after third overgrowth (120.4 ± 9.4) nm.

Au@Pd NPs

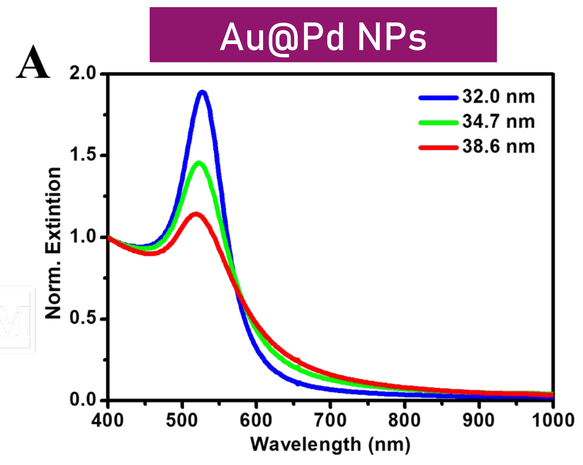


Fig. 3. Vis-NIR spectra of Au and Au@Pd nanoparticles of different sizes obtained after several additions of palladium (II) and iron (II) to a Au seed dispersion (Green line). TEM images of: B) Au@Pd NPs after the first overgrowth (34.7 ± 2.6 nm), C) Au@Pd NPs after second overgrowth, (38.6 ± 2.9 nm).

CONCLUSIONS

This work is the first proof in demonstrating that Fe (II) is a suitable reducing agent to synthesize of metallic NPs (Au and Ag) with tight size control at room temperature. Is also highly eco-friendly, once iron (II) sulphate is not toxic, the reaction conditions are soft and the times of synthesis are decreased compared with the traditional ones.

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