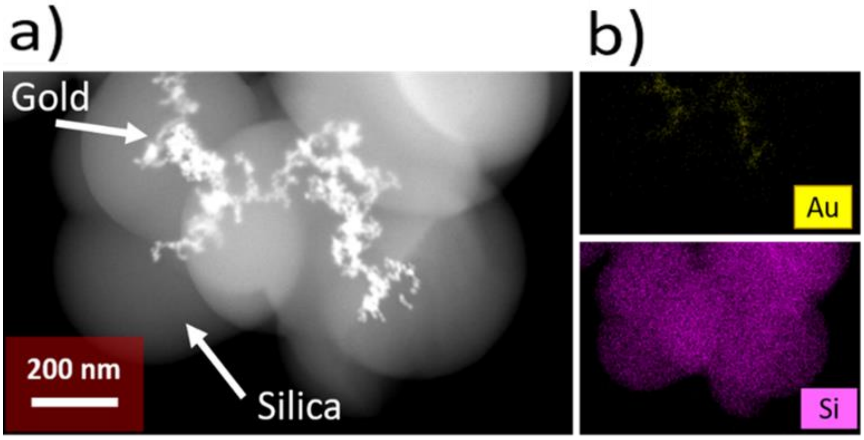

Figure S.1. a) HAADF-STEM revealing the distribution of silicon and gold atoms within the ionically imprinted gold/silica nanoparticles using a Z contrast. **b)** EDX mapping of Si, O and Au elements contained within the silica nanostructure.

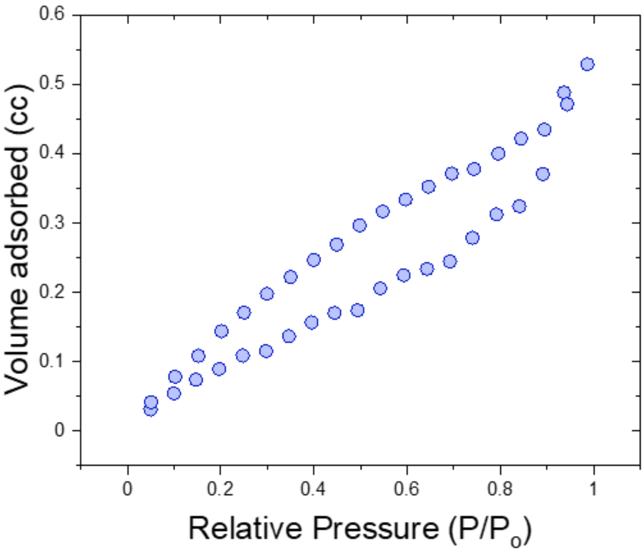

Figure S.2. Isotherms for the ionically imprinted gold/silica nanoparticles obtained during the BET process. Such isotherms were used to calculate the average surface area of the nanoparticles by using the BET equations, which correlates the relative pressure with the number of adsorbed gas molecules, which is related with the surface area of the material. In this case, the surface area of the present material was 108 m^2 g^{-1} [1].

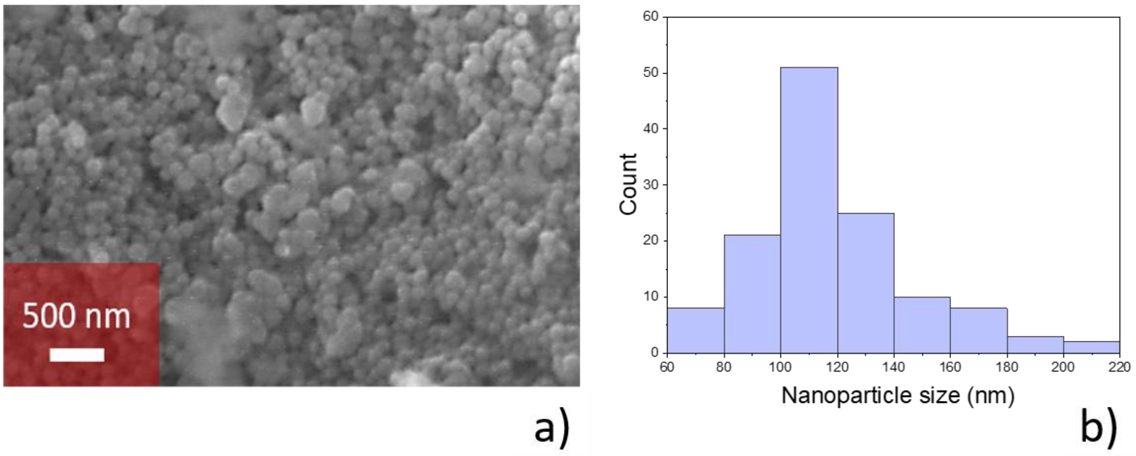

Figure S.3. a) SEM visualization of the ionically imprinted gold/silica nanoparticles employed for the measurement of chloride ions. **b)** The SEM micrograph in a) was employed for the determination of the nanoparticle size by measurement of these ionically imprinted gold/silica nanoparticles using ImageJ. 40% of the -particles have a typical size in the range of 100 – 120 nm and the mean size was 118±29 nm.

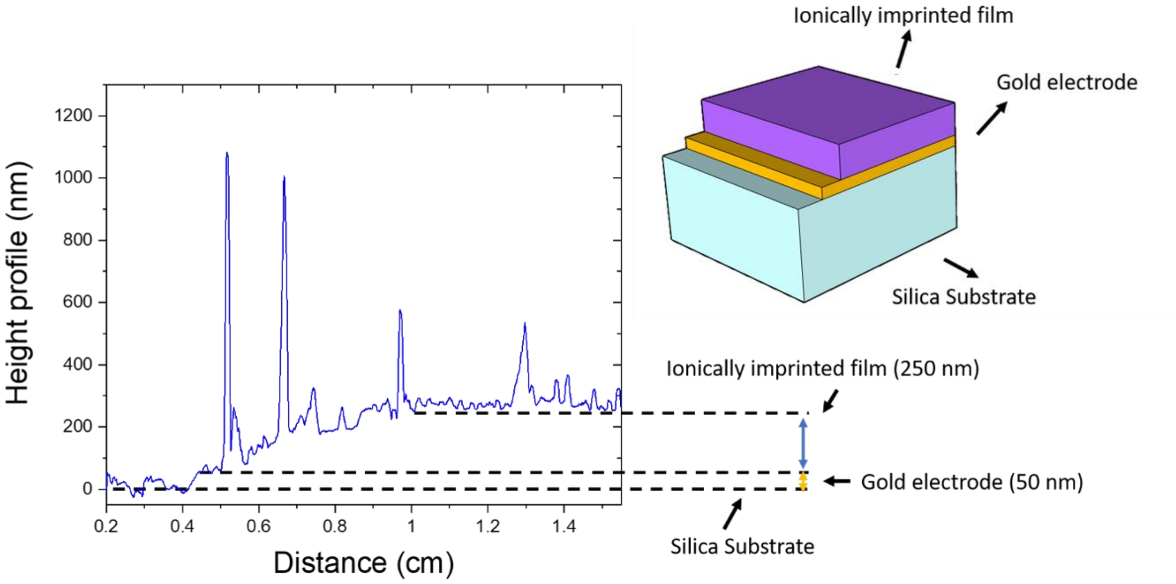

Figure S.4. Profile of the full device containing the gold/silica core/shell imprinted nanoparticles grafted onto a 50 nm thick gold electrode on a silica substrate as measured by a stylus profilometer. In the first part of the profile (up to 0.4 cm) the stylus is placed on the silica substrate, and the height profile is closed to 0 nm. The thickness of the full device containing the gold/silica core/shell imprinted nanoparticles is the measured, with a size closed to 300 nm, including the 50 nm thick gold electrode deposited by plasma sputtering. The inset shows a schematic diagram of this sensing film, illustrating the structure of the full device.

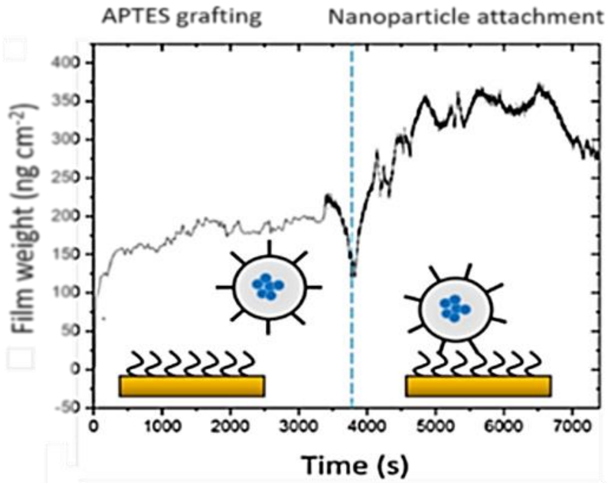

Figure S.5. Quartz microbalance monitoring of the weight changes of the gold electrodes during the functionalisation process with the self-assembled film and the silica/gold nanoparticles. Initially, the gold electrode was functionalised with a self-assembled monolayer containing 16-mercaptohexadecanoic acid after the exposure of the films to the nanoparticles, an increase in the weight of 294±3 ng cm^{-2} was observed.

Table S.1. Table comparison between the selectivity coefficients achieved in the present work and the reported values in the literature calculated by the matched potentials method in [2]. Here, smaller values represent a higher selectivity.

Anion	Present work $Log(K_{Cl,j}^{pot})$	Reported results $Log(K_{Cl,j}^{pot})$	Ref
SO_4^{2-}	-2.4	-2	[2]
NO_3^-	-2.1	+0.2	[2]
HCO_3^-	-2.6	-2.6	[2]
Br^-	-2.0	+0.2	[2]
F^-	-2.1	-	[2]
OH^-	-6.4	-	[2]

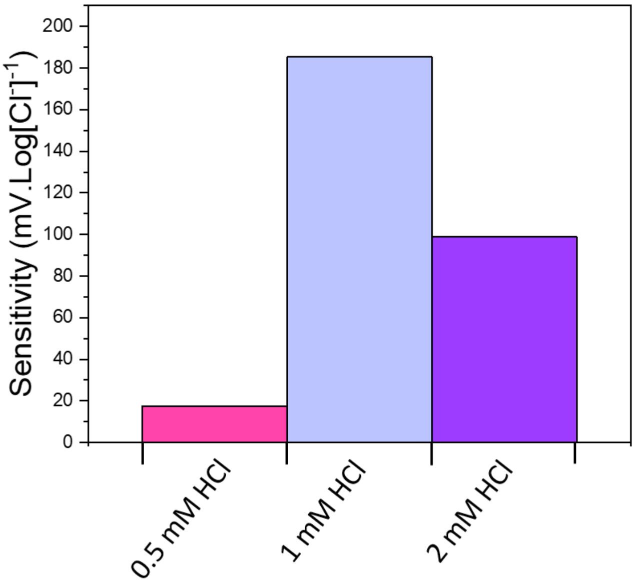

Figure S.6. Comparison of the profile of sensitivities achieved for different Ionically imprinted gold/silica nanoparticles synthetized using different concentrations of HCl as the template ion. Lower sensitivities were achieved in the case of 0.5 and 2 mM with sensitivities-17.4 and -99.1 mV.Log[Cl$^-$]$^{-1}$, respectively. On the contrary, an optimal composition was obtained using 1 mM HCl, achieving a maximum sensitivity of -186.7 mV.Log[Cl$^-$]$^{-1}$.

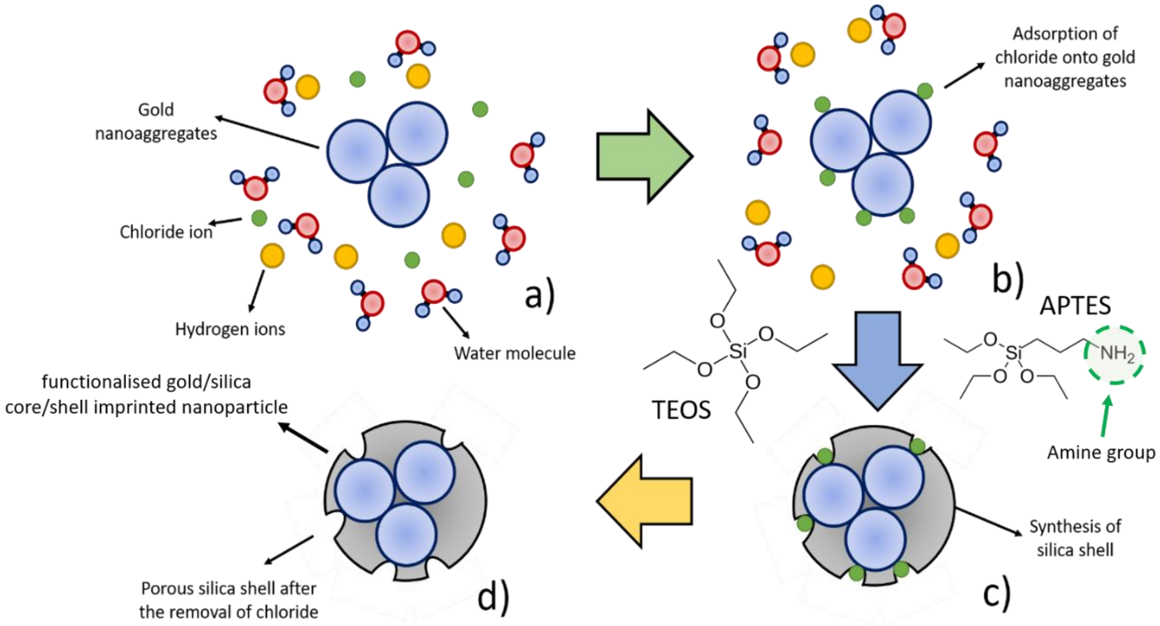

Figure S.7. Schematic representation of the role of gold nanoaggregates during the synthesis of the gold/silica core/shell imprinted nanoparticles. **a)** Initially, the gold nanoaggregates are dispersed in an aqueous solution, and the template chloride are introduced. **b)** Due to the affinity of such gold nanoaggregates towards the chloride ions, such ions selectively adsorb onto the surface of the gold nanoaggregates. Such adsorption will prevent the formation of nanoimprinted silica nanoparticles with selectivity towards other components present in the solution (e.g. hydrogen ions, water) due to the core-shell structure here synthetized. **c)** After adding the TEOS and APTES monomers to the solution, a shell containing the functionalised silica monomers with the amine groups provided by the APTES. This shell is porous, with a radius circa.1.4 nm and contains the chloride ions initially, since they have been used as a template. **d)** The chloride ions contained within the nanopores formed by the functionalised silica shell are removed by washing, leaving a functionalised gold/silica core/shell imprinted nanoparticle that can be used for the sensing of chloride ions.

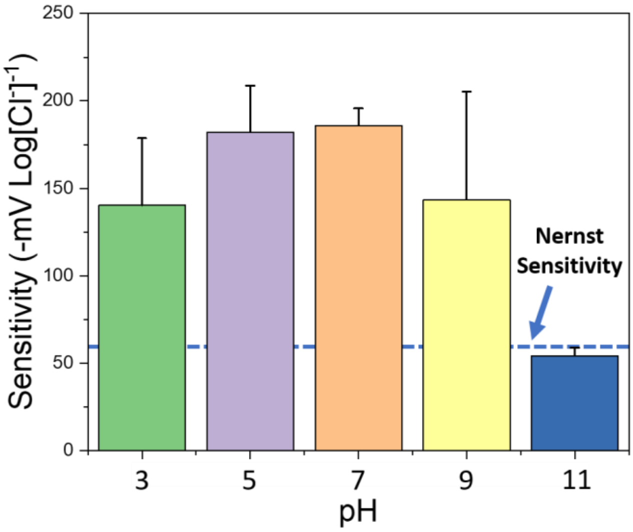

Figure S.8. Sensitivity towards chloride ions of the ion sensing devices containing the gold/silica ionically imprinted nanomaterials when subjected to different pH values. Such pH was tailored using NaOH and H_2SO_4. The Nernst sensitivity limit has been indicated.

Reference

1. Lowell, S., et al., *Surface Area Analysis from the Langmuir and BET Theories*, in *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*, S. Lowell, et al., Editors. 2004, Springer Netherlands: Dordrecht. p. 58-81.
2. Xiao, K.P., et al., *A Chloride Ion-Selective Solvent Polymeric Membrane Electrode Based on a Hydrogen Bond Forming Ionophore.* Analytical Chemistry, 1997. **69**(6): p. 1038-1044.