Metal clusters of small atomicity synthesized by kinetic control with outstanding physicochemical properties

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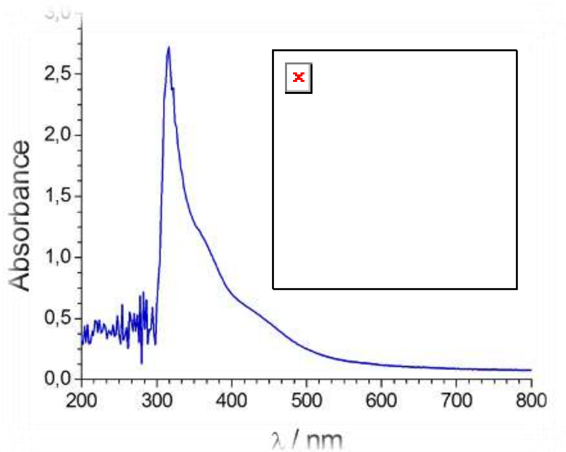
Typical metal nanoparticles show scaling behavior properties. However, when particle size is reduced below ≈ 2 nm (clusters of atoms) quantum confinement break the scaling laws and the properties of metal clusters become dramatically different from the nanoparticles [1].

In general, clusters can be divided into (i) large clusters –consisting of a core formed by a number of metal atoms in the number range ~10-20 to 10-200 atoms and a protecting shell of strong ligands such as phosphines or thiols and (ii) small clusters – formed by a small number of atoms ~2 to 10-20, which - contrary to what is commonly assumed- do not need any strong stabilizing ligand and have almost all of their atoms on the surface [1]. We will show here that such small clusters can be synthesized *wet chemical techniques* without using binding ligands. The key point to achieve the preparation of such "naked" clusters is the use of the *kinetic control method* [2]. Using such method our research group has synthesized very monodisperse clusters of different metals (mainly Ag, Au, Cu and Pt), with sizes in the range 2 to ≈ 30 atoms [3]. As an example, we show in Figure 1 (left) the UV-Vis absorption spectrum of Au_9 clusters (the inset shows for comparison the plasmon band of Au nanoparticles). It can be seen that the absorption is similar to semiconductors and this similar behavior can be used to get information of the cluster's size. Figure 1 (right) shows the corresponding Tauc plot, indicating that such clusters behave as a direct-like semiconductor with a bandgap (HOMO-LUMO gap) = 2.6eV. Taking into account the Jellium model this gap would should correspond to a cluster with N=9 atoms $[N=(E_F/E_g)^3=(5.4/2.6)^3=9]$. We will also report here some of their exceptional physicochemical properties, mainly in the fields of catalysis [4] and therapeutics [5].



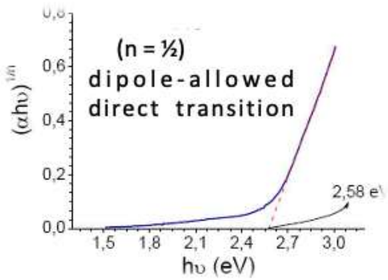


Figure 1: Left: UV-Vis absorption spectrum of Au_9 clusters (inset shows, for comparison, the plasmonic absorption of Au nanoparticles). Right: Tauc plot of the cluster absorption indicating a clear dipole-allowed direct transition (n=1/2).

REFERENCES

[1] See e.g. Y. Piñeiro et al. in Metal Nanoparticles and Clusters, Ed. F.L. Deepak, Springer 2018. Chapter 1 "*From Nano-to Angstrom Technology*" , pp 1.
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[3] See e.g. S. Huseyinova, et al. J. Phys. Chem. C 120 (2016) 15902.
[4] See e.g. A. Corma et al. Nat. Chem. 5 (2013) 775.
[5] See e.g. V. Porto et al. Adv. Mat. 30 (2018) 1801317.