

## Optical response and electron dynamics of charged plasmonic nanoparticles

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### Abstract

There is a continuous effort in the plasmonics community to achieve a control of the optical response of metallic nanostructures via a proper design of their morphology [1, 2]. However, in the last years there has been an increasing interest in obtaining an active control of the response by application of external bias, or polarizing fields [3]. The modulation of the plasmon resonances in this active fashion has been recently achieved in electrochemistry by adding chemical reductants to the colloidal nanoparticle solution [4-6]. Similarly to the situation in 2D materials, such as graphene [7-9], the observed shift of the plasmon frequency has been often interpreted also in 3D particles as a result of the charge doping of the nanoparticles. Based on a full quantum mechanical description, we review this long-standing misconception in electrochemistry.

In this work, we study the electron dynamics and plasmon modes of small charged metallic clusters in vacuum with use of density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations. We obtain the electronic structure and trace the dynamics of well-defined nanoparticle clusters that allow to isolate and identify the effects of pure charging in the optical response of metallic nanostructures, with respect to the action of an external polarization or chemical effects. In particular, we show that the frequency shift of the plasmon mode is generally small when a nanoparticle is charged, and this shift has an opposite sign to that expected from the arguments based on the change of bulk electron density. Our results can be well understood based on the theory of dynamical screening [10-12] to describe the dependence of the dipolar plasmon resonance on the nanoparticle size. We also demonstrate that for negatively charged clusters, as soon as the Fermi level is promoted above the vacuum level, the extra charge decays at femtosecond (fs) time scales. Despite the small size of the systems considered in our model calculations (~5 nm in diameter), our results can be generalized to the case of larger nanoparticles as those commonly treated in electrochemistry. Counterintuitively, these results reveal that the plasmon energy shifts observed in electrochemical solutions of plasmonic nanoparticles cannot be explained without considering the effect of the dipole layer formed by the ions that screen the nanoparticle charge and the eventual modification of the surface electronic structure of the metal nanoobject by the chemisorbed species.

### References

- [1] Boardman, A. D.; Grimalsky, V. V.; Kivshar, Y. S.; Koshevaya, S. V.; Lapine, M.; Litchinitser, N.M.; Malnev, V. N.; Noginov, M.; Rapoport, Y. G. and Shalaev, V. M. *Laser. Photon. Rev.*, **10** (2010) 00012.
- [2] Liu, A. Q.; Zhu, W. M.; Tsai, D. P.; and Zheludev, N. I. *J. Opt.*, **14** (2012) 114009.
- [3] Chu, K. C.; Chao, C. Y.; Chen, Y. F.; Wu, Y. C.; Chen, C. C. *Appl. Phys. Lett.*, **89** (2006) 103107.
- [4] Dondapati, S. K.; Ludemann, M.; Müller, R.; Schwieger, S.; Schwemer, A.; Handel, B.; Kwiatkowski, D.; Djiango, M.; Runge, E.; Klar, T. A., *Nano Lett.*, **12** (2012) 1247–1252.
- [5] Mulvaney, P.; Perez-Juste, J.; Giersig, M.; Liz-Marzán, L. M.; Pecharroman, C. *Plasmonics*, **1** (2006) 61–66.
- [6] Daniels, J. K.; Chumanov, G., *J. Electroanal. Chem.*, **575** (2005) 203–209.
- [7] Ju, L.; Geng, B.; Horng, J.; Girit, C.; Martin, M.; Hao, Z.; Bechtel, H. A.; Liang, X.; Zettl, A.; Shen, Y. R.; Wang, F., *Nat. Nanotechnol.*, **6** (2011) 630–634.
- [8] Grigorenko, A. N.; Polini, M.; Novoselov, K. S. *Nat. Photonics.*, **6** (2012) 749–758.
- [9] Manjavacas, A.; García de Abajo, F. J. *Nat. Commun.*, **5** (2014) 3548.
- [10] Apell, P.; Ljungbert, Å., *Solid State Commun.*, **44** (1982) 1367–1369.
- [11] Liebsch, A, *Phys. Rev. B: Condens. Matter Mater. Phys.*, **48** (1993) 11317–11328.
- [12] Monreal, R. C.; Antosiewicz, T. J.; Apell, S. P. *New J. Phys.*, **15** (2013) 083044.