One Step Synthesis of the Smallest Photoluminescent and Paramagnetic PVP-Protected Gold Atomic Clusters

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ABSTRACT Gold atomic clusters of only two and three atoms were prepared by a simple electrochemical technique based on the anodic dissolution of a gold electrode in the presence of PVP, and subsequent electroreduction of the Au-PVP complexes. These clusters show stable photoluminescent and magnetic properties, which make them the smallest and most elemental gold (0) building blocks in nature (after atoms) bringing new possibilities to construct novel nano/microstructures with large potential interest in biomedicine, catalysis, and so forth.

KEYWORDS Metal clusters, Au cluster, electrochemical synthesis, photoluminescent clusters, magnetic clusters, PVP-protected clusters.

Metal atomic clusters consist of groups of atoms between 2 and around 100−200 atoms, which have defined compositions and one or very few stable geometric structures.[1] An important aspect of these atomic clusters is related to their properties, which are usually very different from the bulk ones, offering exciting possibilities for their use in novel materials or devices. Although the synthesis and the study of the properties of clusters is more difficult than that of the usual larger nanoparticles,[2] their unique electronic and chemical properties have already drawn attention in many scientific areas. Applications in different fields, such as sensors,[3] photography,[4] catalysis,[5] biological labeling,[6] and electronics[7] have already been proposed.

The development of new methods for the production of small quantum dots (QDots) with nontoxic materials is of great importance, because semiconductors used at the moment for the preparation of QDots are based on toxic heavy metals, have large physical size comparable to proteins, and tend to photoblink.[8] The discovery of the fact that nanoparticles of less-toxic metals, like Au or Ag, become semiconductors when their dimensions are below ~2−3 nm (atomic clusters), offers a novel strategy to search for a new kind of highly fluorescent and nontoxic QDots.[9]

Catalysis using small gold clusters is of extensive interest not only in simulations studies but also in practical applica-tions.[10] Tsunoyama et al.[11] have studied the effect of electronic structures of Au-PVP clusters on aerobic oxidation catalysis obtaining higher catalytic activity with decreasing the core size.

On the other hand, small clusters can be thought as the most elemental gold building blocks in nature (after atoms) bringing new possibilities to construct novel nano/micro-structures.[12] Although very small Au clusters with similar photoluminiscent properties have been reported before by Jin et al.,[13] this was achieved by a two-step top-down approach consisting of thiol-etching of nanoparticles. The bottom-up strategic approach shown here is a simple one-step electrochemical process using a biocompatible polymer (PVP) as a capping-stabilizing agent.

Au clusters were synthesized in acetonitrile by a modifi-cation of the electrochemical technique used before for the production of nanoparticles[14] and large and relative poly-disperse gold clusters.[15]

For this particular synthesis, we employed poly(N-vi-nylpyrrolidone) (PVP), which acts as stabilizer of the gold clusters. PVP is a homopolymer, which contains an amide group in its monomer and it is known to be a good stabilizing agent for transition metal particles[16] and, at the same time, is biocompatible.[17] The new electrochemical method of producing PVP-protected gold atomic clusters presented here has several advantages, such as its simplicity, repro-ducibility, and effectiveness, having at the same time a good control of the cluster size.

Gold clusters were synthesized in an Autolab PGSTAT 20 potentiostat with a constant temperature of 25.0 ± 0.1 °C. Experiments were carried out in a standard Metrohm elec-

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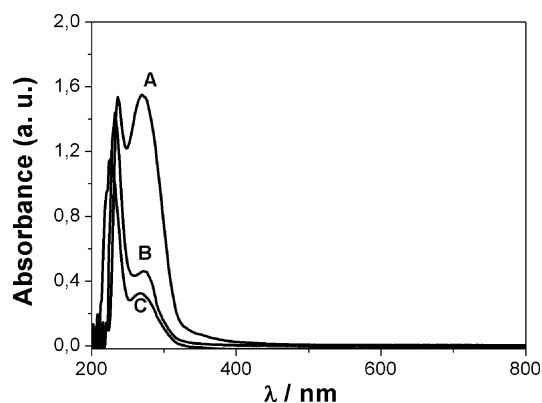
FIGURE 1. UV−vis spectra at different concentrations of PVP in acetonitrile: 1 mg/mL (sample A), 0.5 mg/mL (sample B), and 0.1 mg/mL (sample C). The spectra were registered using the appropriate amount of PVP in acetonitrile as blank in each sample.
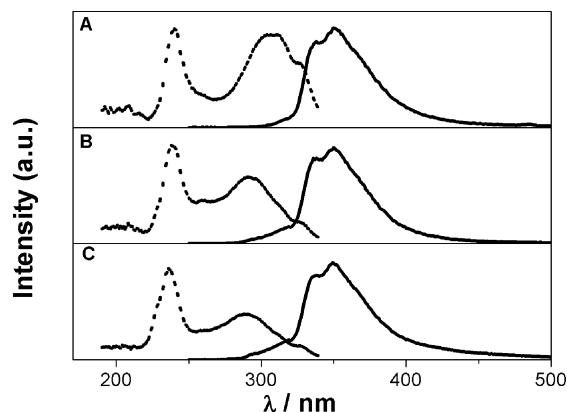

FIGURE 2. Excitation (dash lines)/emission (solid lines) scans of PVP-protected Au cluster samples A, B, and C in acetonitrile.
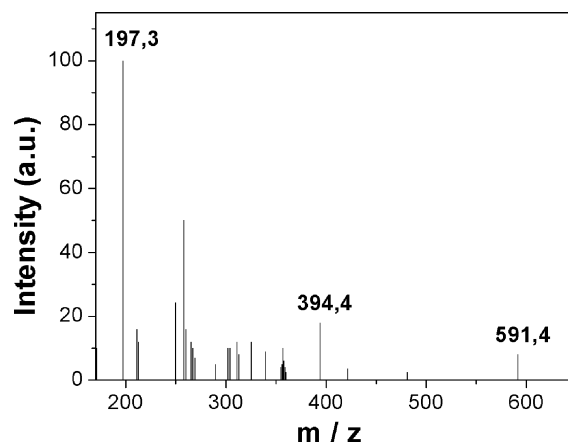

FIGURE 3. LDI-TOF mass spectrum of gold clusters.

trolysis beaker containing a sacrificial gold sheet as the anode (counter electrode), and a copper sheet of the same size as a cathode (working electrode). These two electrodes were placed vertically, face-to-face, inside the cell. An Ag/AgCl electrode was used as reference electrode. The conductive solution, consisting of PVP at different concentrations dissolved in acetonitrile, was deaerated by bubbling nitrogen for about 15 min, keeping an inert atmosphere during the whole process. Strong magnetic stirring was maintained during the galvanostatic electrolysis, which consists of the application of a current density of 100 mA cm^{-2} for 300 s. PVP is stable at the low potentials ($\sim$ −0.2 V vs Ag/AgCl) used in the galvanostatic synthesis. PVP concentrations (with a weight-average molecular weight of 10 000) used in the experiments were 0.1, 0.5, and 1 mg/mL. During the process, gold-cations, continuously generated in low concentrations in the anode, were complexed by the PVP. Electroreduction of these complexes generate Au(0) atoms along the PVP chains giving rise to the formation of very stable clusters.

It is known that particles below 1.5 nm do not show surface plasmon band and the spectrum consists of a continuous increase in absorbance with decreasing wavelength, because of the presence of a bandgap at the Fermi level.[18] For very small clusters (Au$_n$, where $n < 2−20$ atoms), discrete, molecule-like bands, similar to those observed in Figure 1 for the synthesized clusters, are expected.[19]

The absence of surface plasmon resonance is a characteristic for the samples obtained by the electrochemical synthesis here reported, which shows only three discrete bands centered at 240 nm (5.17 eV), 270 nm (4.59 eV), and 350 nm (3.54 eV), being the intensity of the absorption bands larger for higher concentrations of PVP. Almost no changes in the UV−vis spectra are observed after more than two years (see Supporting Information), which indicates the great stability of the synthesized clusters.

Clusters obtained show three fluorescence emission bands (Figure 2): 315 nm (3.94 eV), 335 nm (3.70 eV), and 350

nm (3.54 eV) by photoexcitation at 240 nm (5.17 eV) and 300 nm (4.13 eV). Quantum yield of the samples is $\Phi = 12.5\%$ (sample B) using as reference a 0.1 M solution of quinine sulfate dehydrate in H_2SO_4 $\Phi = 0.546$ as standard. It has to be mention that solutions containing PVP with gold salt do not show fluorescence. Therefore, fluorescence has to be associated with the formation of reduced Au clusters (the absence of Au ions in the samples has been checked as it will be described below). Almost no fluorescence changes are observed after more than 2 years for samples stored in air.

Mass spectra were performed with an Autoflex Spectrometer using a laser wavelength of 337 nm and a repetition frequency of 50 Hz. The spectra were acquired in the Reflection mode between 0−4 kDa of mass range. The samples were deposited on a steel plate and were analyzed after drying. LDI-TOF spectrum show three major peaks: m/z = 197, 394, and 591 corresponding to Au$_1$, Au$_2$, and Au$_3$, respectively (see Figure 3 and Supporting Information). No other peaks at higher mass were detected. The presence of only naked Au$_n$ clusters in the mass spectra indicates the weakly coordination of PVP to metal clusters.

It has been shown that the spherical Jellium model can provide an approximate description of the dependence of

sample A		sample B		sample C	
LT (ns)	RA (%)	LT (ns)	RA (%)	LT (ns)	RA (%)
1.14	13.4	1.12	8.6	1.06	6.6
3.44	28.1	4.11	38.5	4.07	38.6
10.4	58.5	10.6	53.0	11.0	54.7

the emission energy with the number of atoms, N, in gold clusters by the simple relation $E_g = E_{Fermi}/N^{1/3}$, where E_{Fermi} is the Fermi energy of bulk gold, and E_g is the band gap energy of the cluster assumed to be identical to the fluorescence emission energy.[20] On the basis of this model, the emission of Au_2 and Au_3 clusters should be observed at 4.22 and 3.68 eV, respectively, which approximately agrees with the observed emission energies, taken into account that this model does not consider the influence of the capping (PVP) on the cluster emission energies. These results also agree with the mass spectra and with the fact that the synthesized clusters are too small to be observed by TEM (results not shown).

It has to be mentioned that Jin et al.[13] also reported the synthesis of Au_2 and Au_3 clusters by a two step top-down approach, via thiol etching, with similar absorption and photoluminiscent properties. They assigned the absorption and photoluminiscence bands to the Au_3 cluster assuming that the detection of Au_1 and Au_2 clusters by mass spectrometry could be due to the laser-induced dissociation of the parent trimers. However, in our case we have observed that the relative intensities of the absorption bands change with the amount of PVP (see Figure 1), which clearly indicates that the absorption bands should correspond to two different species instead of being two bands of the same species. We can then assume that Au_2 and Au_3 are the main species in the samples with absorption bands located at 270 nm (5.17 eV) and 350 nm (4.59 eV), respectively, being both species much more abundant in sample A than in samples B and C. The band at 240 nm can be associated with a charge transfer band from the metal to the PVP.

Photoluminescence decay curves of PVP-protected Au clusters excited at 280 nm require a sum of three exponentials to be adequately fitted (see Supporting Information) with time constants given in Table 1 for the different samples. Relaxation times of the order of nanoseconds indicate that photoluminescence takes place through an allowed-spin process.

Photoluminiscence results can be explained assuming that the shorter decay time (~1 ns) comes from the emission of the charge transfer state (see later). The lifetime about 10 ns can be associated with the emission of the Au_3 clusters and the lifetime of ~4 ns from the Au_2 clusters. Upon excitation, the three states are populated and, in the case of clusters, a very fast ICT (internal charge transfer) process (not visible in the nanosecond time scale) occurs before emission. The small lifetime of 3.4 ns in sample A, in comparison to
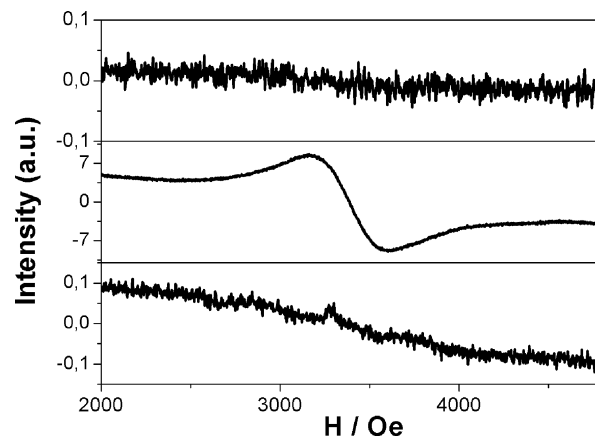
FIGURE 4. EPR curves for PVP-protected Au clusters. From top to bottom curves correspond to samples B, A, and C.

samples B and C, continues to be associated to the Au_2 cluster emission but now is quenched by energy transfer to the Au_3 cluster, present in a high concentration in this sample.

According to the Jellium model, Au_3 clusters should have the following electronic structure ($1S^2 2P^1$), and therefore they should exhibit some kind of paramagnetic behavior, contrary to Au_2 clusters ($1S^2$), which should display a diamagnetic behavior. Figure 4 shows the results of electron paramagnetic resonance (EPR) measurements carried out at 9 GHz and 120 K. The presence of a paramagnetic-like behavior is clearly observed only for sample A, which should contain a major proportion of the trimer cluster. However, samples B and C containing mainly dimers are diamagnetic.

These results agree with recent rigorous theoretical calculations[21] showing that indeed gold dimers have zero magnetic anisotropy energy (MAE) whereas Au_3 is weakly magnetic with a MAE of only 8 meV. Therefore, this paramagnetic behavior can only be detected at high concentrations, like those provided in sample A.

Different conditions of the electrochemical synthesis were used to see how the experimental parameters affect the cluster size. It was observed[22] that temperature and synthesis time are crucial to obtain clusters with 2 and 3 atoms. As an example, raising the temperature to 50 °C samples obtained are composed of a mixture of larger clusters (from Au_2 to Au_{11}). In this case samples are still photoluminiscent, but emission is now centered in the range from 350 to 520 nm upon electronic excitation at different wavelengths. The variation of the emission spectrum with the excitation wavelength clearly indicates the presence of a large gold cluster mixture in the sample as it is found by mass spectrometry (see Supporting Information). When not only the temperature but also the time of the synthesis is increased to 600 s, one can finally observe the formation of gold nanoparticles, which are easily detected by the appearance of the typical pink-purple color. UV−vis spectra of such samples show the characteristic plasmon band at 550 nm,
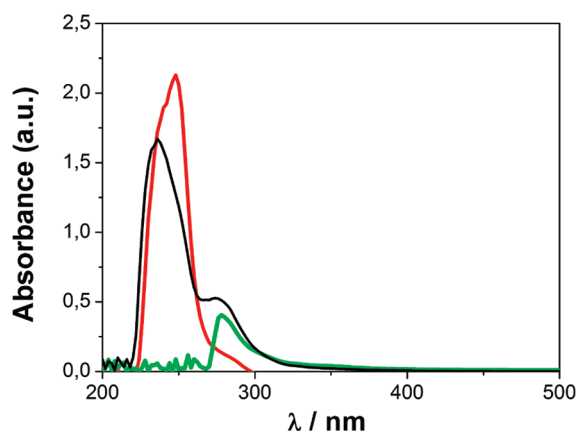
FIGURE 5. UV−vis absorption spectra of the original PVP-protected Au clusters in acetonitrile (black line), the resulting hexane solution after thiol exposuring (green line), and the acetonitrile solution after thiol exposure (red line).
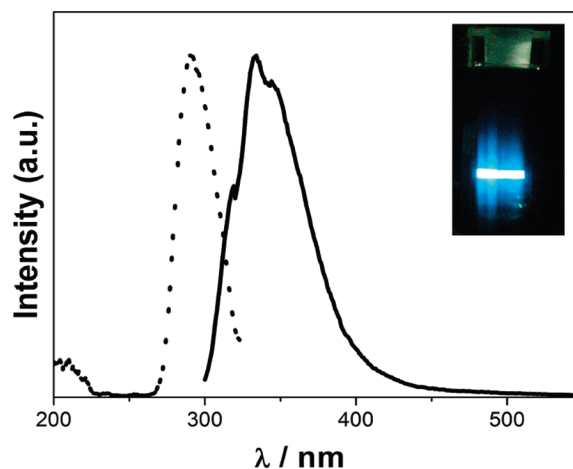

FIGURE 6. Fluorescence/excitation spectra of dodecanethiol protected gold clusters in hexane. Excitation spectrum (dash line) recorded at $\lambda_{em} = 333$ nm and fluorescence (solid line) by excitation at $\lambda_{exc} = 290$ nm.

and the formation of gold nanoparticles of approximately 6 nm is now clearly seen by TEM (see Supporting Information).

To further examine the physicochemical properties of gold clusters, the samples containing Au_2 and Au_3 were mixed with a concentrated solution of dodecanethiol (1 M) in hexane for 24 h stirring at 40 °C. During this process, dodecanethiol is expected to replace multivalent PVP ligands because of the higher affinity of the sulfur for gold. The optical absorption and fluorescence spectra of the resulting solution were compared with the previous ones. The spectra shown in Figure 5 indicate that the PVP is successfully replaced by dodecanethiol.

After thiol exchange, two characteristic absorption bands at 270 and 350 nm corresponding to Au_2 and Au_3, respectively, were observed in the hexane solution proving the successful replacement. The excitation peak at 240 nm disappears (see Figure 6), but it has no effect on the emission spectra. This observation provides strong evidence that the original fluorescence emission is due to intrinsic properties of the gold clusters and the absorption/excitation peak at 240 nm arises from metal−ligand charge transfer transitions. Although one should expect changes in the excitation/emission spectra after thiol exchange based on the general different bonding properties of PVP and thiols to gold, the very small observed changes in the position of the peaks (<approximately 10%) are in agreement with recent theoretical calculations by Day et al.[23] predicting only a minor change of about 10% displacement of the absorption peaks for Au dimers compared with monothiolated gold dimer anions. The fact that the UV−vis and fluorescence spectra of the gold clusters do not show changes after the thiol exposure is also a proof of the stability of the synthesized gold clusters. It has to be noticed that the photoluminescence observed in these thiolate clusters is very different from Au(I) thiolate complexes, in which the photoluminiscence is very weak and they do not emit at room temperature, as it was reported by Bardaji et al.[24]

Next, the stability of PVP-protected Au clusters was checked against reduction and oxidation by $NaBH_4$ and H_2O_2, respectively. The addition of these agents to the cluster solutions has no effects on their fluorescence and absorption spectra indicating again the stability of the clusters and that there are no gold ions in the samples.

Very recently Sakamoto et al[25] have reported differences in the photoluminescence behavior of Au_n clusters embedded in polyvinyl acetate films depending on the number of atoms. Contrary to clusters with $n \approx 19$ or 20, for clusters with $n < 12$ they observe fluorescence quenching by oxygen, which they associate with the instability of the smaller clusters. Our results show that this is not the case, and that much small clusters, like Au_2 and Au_3 reported here, are very stable without oxygen quenching having fluorescence lifetimes comparable with those reported for larger clusters.[20]

Conclusions. In summary, we have reported a new simple one-step bottom-up method for preparing fluorescent and paramagnetic PVP-protected gold atomic clusters. The different fluorescent and magnetic properties suggest that these properties are very sensitive to the cluster size, because large changes in those properties are observed with only one atom difference between the clusters, which can be easily predicted by the simple spherical Jellium model.

Compared with the previous methods to obtain these extremely small cluster sizes, the electrochemical synthesis is much simpler and quicker, providing a good control of the cluster size. Furthermore, the photoluminiscent gold clusters are very stable against strong reducing and oxidizing agents, and no changes on their optical properties are observed after more than two years of its preparation. At the same time Au_3 clusters display a paramagnetic-like behavior recently theoretically predicted for these very small Au clusters.

The PVP-capped Au clusters here described can be considered as the smallest and the most elemental Au(0) building blocks in nature (after atoms) bringing new possibilities

to construct novel nano/microstructures, which will be of great interest for applications in different fields, such as biomedicine, catalysis, and so forth.

Supporting Information Available. UV−vis spectra, mass spectra, photoluminescence decay curves, and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

(1) Lee, H. M.; Ge, M.; Sahu, B. R.; Tarakeshwar, P.; Kim, K. S. *J. Phys. Chem. B* **2003**, *107*, 9994.

(2) (a) Donkers, R. L.; Lee, D.; Murray, R. W. *Langmuir* **2004**, *20*, 1945. (b) Lee, D.; Donkers, R. L.; Wang, G.; Harper, A. S.; Murray, R. W. *J. Am. Chem. Soc.* **2004**, *126*, 6193. (c) Negishi, Y.; Takasugi, Y.; Sato, S.; Yao, H.; Kimura, K.; Tsukuda, T. *J. Am. Chem. Soc.* **2004**, *126*, 6518. (d) Negishi, Y.; Nobusada, K.; Tsukuda, T. *J. Am. Chem. Soc.* **2005**, *127*, 5261. (e) Shichibu, Y.; Negishi, Y.; Tsukuda, T.; Teranishi, T. *J. Am. Chem. Soc.* **2005**, *127*, 13464. (f) Guillén-Villafuerte, O.; García, G.; Anula, B.; Pastor, E.; Blanco, M. C.; López-Quintela, M. A.; Hernández-Creus, A.; Planes, G. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4266. (g) Bertino, M. F.; Sun, Z. M.; Zhang, R.; Wang, L. S. *J. Phys. Chem. B* **2006**, *110*, 21416. (h) Ledo-Suárez, A.; Rivas, J.; Rodríguez-Abreu, C. F.; Rodríguez, M. J.; Pastor, E.; Hernánez-Creus, A.; Oseroff, S. B.; López-Quintela, M. A. *Angew.Chem, Int. Ed.* **2007**, *119*, 8979. (i) Antonello, S.; Holm, A. H.; Instuli, E.; Maran, F. *J. Am. Chem. Soc.* **2007**, *129*, 9836.

(3) Shang, L.; Dong, S. *J. Mater. Chem.* **2008**, *18*, 4636.

(4) Belloni, J. *Radiat. Phys. Chem.* **2003**, *67*, 291.

(5) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647.

(6) Lin, C.-A.; Yang, T.-Y.; Lee, C.-H.; Huang, S. H.; Sperling, R. A.; Zanella, M.; Li, J. K.; Shen, J.-L.; Wang, H.-H.; Yeh, H.-I.; Parak, W. J.; Chang, H. *ACS Nano* **2009**, *3*, 395.

(7) Adams, D. M.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C.; Kagan, C. R.; Kamat, P. V.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-Beyerle, M. E.; Miller, J. R.; Newton, D. M.; Rolison, D. R.; Sankey, O.; Schanze, K. S.; Yardley, J.; Zhu, X. *J. Phys. Chem. B* **2003**, *107*, 6668.

(8) Nirmal, M.; Dabbousi, B. O.; Bawendi, M. G.; Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E. *Nature* **1996**, *383*, 802.

(9) Schaeffer, N.; Tan, B.; Dickinson, C.; Rosseinsky, M. J.; Laromaine, A.; McComb, D. W.; Stevens, M. M.; Wang, Y.; Petit, L.; Barentin, C.; Spiller, D. G.; Cooper, A. I.; Lèvy, R. *Chem. Comun.* **2008**, *34*, 3986.

(10) (a) Lee, S.; Molina, L. M.; López, M. J.; Alonso, J. A.; Hammer, B.; Lee, B.; Seifert, S.; Winans, R. E.; Elam, J. W.; Pellin, M. J.; Vajda, S. *Angew. Chem. Int. Ed.* **2009**, *48*, 1467. (b) Huang, J.; Akita, T.; Faye, J.; Fujitani, T.; Takei, T.; Haruta, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 7862. (c) Kacprzak, K. A.; Akola, J.; Häkkinen, H. *Phys. Chem. Chem. Phys.* **2009**, *11*, 6359.

(11) Tsunoyama, H.; Ichikuni, N.; Sakurai, H.; Tsukuda, T. *J. Am. Chem. Soc.* **2009**, *131*, 7086.

(12) Xiong, Y.; Washio, I.; Chen, J.; Sadilek, M.; Xia, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 4917.

(13) Jin, R.; Egusa, S.; Scherer, N. F. *J. Am. Chem. Soc.* **2004**, *126*, 9900.

(14) (a) Rodríguez-Sánchez, M. L.; Blanco, M. C.; López-Quintela, M. A. *J. Phys.Chem. B* **2000**, *104*, 9683. (b) Rodríguez-Sánchez, M. L.; Rodríguez, M. J.; Blanco, M. C.; Rivas, J.; López-Quintela, M. A. *J. Phys. Chem. B* **2005**, *109*, 1183. (c) Rodríguez, M. J.; Vázquez-Vázquez, C.; Mouriño, A.; Torneiro, M.; Blanco, M. C.; Rivas, J.; López-Quintela, M. A. Electrochemical Synthesis of Silver Nanoparticles. In *Colloids and Interfaces*; Valente, A., Seixas de Melo, J., Eds.; SPQ: Coimbra, 2007; pp 103−108 (ISBN: 978-989-8124-01-2).

(15) Rodríguez-Vázquez, M. J.; Blanco, M. C.; Lourido, R.; Vázquez-Vázquez, C.; Pastor, E.; Planes, G. A.; Rivas, J.; López-Quintela, M. A. *Langmuir* **2008**, *24*, 12690.

(16) (a) Hoppe, C. E.; Lazzari, M.; Pardiñas-Blanco, I.; López-Quintela, M. A. *Langmuir,* **2006**, *22*, 7027. (b) Han, M. Y.; Quek, C. H.; Huang, W.; Chew, C. H.; Gan, L. M. *Chem. Mater.* **1999**, *11*, 1144. (c) Lo, S. H. Y.; Wang, Y.-Y.; Wan, C.-C. *J. Colloid Interface Sci.* **2007**, *310*, 190.

(17) Cai, X.; Chen, S.; Chen, L. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2177.

(18) Issendorff, B. von.; Cheshnovsky, O. *Annu. Rev. Phys. Chem.* **2005**, *56*, 549.

(19) Woehrle, G. H.; Warner, M. G.; Hutchison, J. E. *J. Phys. Chem. B* **2002**, *106*, 9979.

(20) Zheng, J.; Zhang, C.; Dickson, R. M. *Phys. Rev. Lett.* **2004**, *93*, No. 077402.

(21) Ferrnández-Seivane, L.; Ferrer, J. *Phys. Rev. Lett.* **2007**, *99*, 183401.

(22) Santiago Gonzalez, B. Synthesis and properties of electrochemical synthesized gold atomic clusters. Master's thesis, Universidad de Santiago de Compostela, Santiago de Compostela, Spain, June 2008.

(23) Day P. N.; Nguyen K. A.; Patcher R. *J. Chem. Theory Comput.* [Online early access]. DOI: 10.1021/ct100139t.

(24) Bardají, M.; Calhorda, M. J.; Costa, P. J.; Jones, P. G.; Laguna, A.; Reyes Pérez, M.; Villacampa, M. D. *Inorg. Chem.* **2006**, *45*, 1059.

(25) Sakamoto, M.; Tachikawa, T.; Fujitsuka, M.; Majima, T. *Langmuir* **2009**, *25* (24), 13888.