JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

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Tuning the Morphology of Gold Clusters by Substrate Doping

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S *Supporting Information*

ABSTRACT: The morphology of small metal clusters can have a big impact on their electronic, magnetic, and chemical properties. This has been shown earlier, for example, for Au_{20} clusters on MgO(001), where planar and tetrahedral geometries are possible for the gold atoms. While the planar geometry is more desirable for catalytic applications, it is disfavored in the usual situation. While earlier suggestions that have been made for tilting this balance in favor of the planar isomer are of considerable fundamental interest, they do not easily lend themselves to practical applications. Here, we suggest a conceptually simple but practicable way of achieving the same goal: viz., by doping the MgO substrate with Al atoms. We show, by performing density functional theory calculations, that this stabilizes the planar over the tetrahedral arrangement by an energy difference that is linearly proportional to the dopant concentration and is insensitive to the position of the dopant atom. The charge transferred to the Au cluster also depends monotonically on the doping concentration. This work is of interest for possible applications in the field of gold nanocatalysis.

Small metal clusters can exist as several structural isomers. Isomers that are close in energy may, however, differ drastically in their mechanical, chemical, magnetic, and thermal properties. Such effects become particularly noticeable when the morphology of the cluster is changed from a three-dimensional compact shape to a two-dimensional planar arrangement. This is true also when metal clusters are supported on an oxide substrate, as is frequently done when the clusters are intended to be used for particular applications such as in catalysis, magnetism, and photonics. In such cases, the substrate serves several purposes:[1] by anchoring the clusters, it prevents sintering; by remaining relatively inert electronically, it preserves the sharp electronic levels and consequent high magnetic moments of the cluster; in some cases, it can enhance desirable properties of the cluster by mediating charge transfer. One area in which the role of the substrate has been shown to be crucial is the use of small gold clusters as nanocatalysts. While bulk gold and extended gold surfaces are famously inert,[2] in recent years there has been the dramatic finding that nanosized gold clusters are catalytically active.[3,4] Moreover, this activity is enhanced[5] when the clusters are placed on an oxide substrate. A combination of experimental and theoretical work has shown that it is crucial for oxidation reactions that the cluster become charged (for example, from oxygen vacancies on an MgO substrate).[6] Due to electrostatic effects the magnitude of this charge transfer affects the wetting propensity and hence the cluster shape[7] and has a significant impact on adsorption energies and reaction rates.[8,9]

An example of a system where the interplay between cluster shape, charging effects, and reaction rates, has been convincingly demonstrated is the Au_{20} cluster on MgO(001). Possible low-energy isomers for this system include a three-dimensional tetrahedral cluster (T) and a two-dimensional planar cluster (P). Though the former structure is lower in energy in the gas phase as well as on a defect-free thick MgO substrate, it has been shown that the planar arrangement can be stabilized in two ways: by using as the support an ultrathin film of MgO on an underlying metal substrate[7−11] or by placing the system in an electric field with a strength of the order of 1 V/nm.[12] However, while both these ways of controlling cluster morphology are of considerable fundamental interest, they are perhaps not very practicable in actual applications. In this communication, we demonstrate, using first-principles density functional theory calculations, that the same goals can be achieved in a third way which is conceptually simple yet experimentally and technologically feasible: viz., by doping the MgO substrate with Al atoms.

Our calculations have been performed by solving the Kohn—Sham[13] equations with a plane wave basis, as implemented in the Quantum ESPRESSO code.[14] The energy cutoffs used were 30 and 240 Ry for wave functions and charge densities, respectively. Interactions between nuclei and electrons were described by ultrasoft pseudopotentials[15] that include scalar relativistic effects for Au, while exchange and correlation effects were treated within the generalized gradient approximation (GGA).[16] Calculations on gas-phase T clusters were performed using a cubical box of size of 16.9 Å, and a cuboid of size 20.1 × 20.1 × 9.5 Å was used for the P clusters. The calculations on supported clusters were performed using a 6 × 6 surface unit cell with four layers of the substrate as well as a vacuum region of thickness approximately equal to 14.2 Å (above the highest Au atom). All atomic coordinates were allowed to relax.

In order to validate our computational approach, we have first performed calculations on previously studied systems. Our results confirm that, in the gas phase and on a four-layer-thick MgO(001) substrate, the T morphology is favored over P, by 1.52 and 0.60 eV, respectively. In the latter case, we find that the Au T cluster acquires a negative charge of 0.60 e and the P cluster has a charge of 0.91 e. These results are all very similar to those of previous authors.[8]

We now consider possible morphologies of an Au_{20} cluster placed on an MgO(001) substrate where some of the Mg atoms

Received: November 8, 2010
Published: February 14, 2011

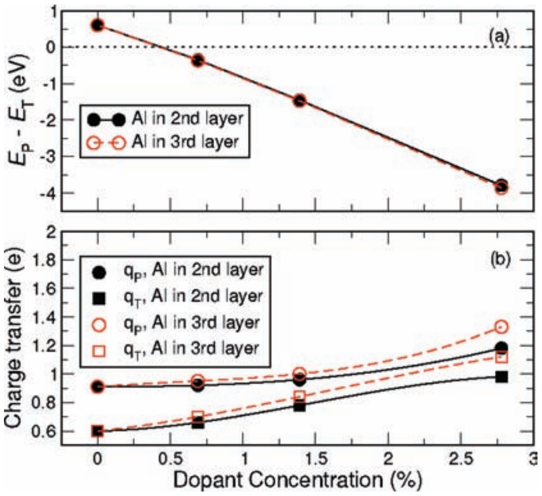

Figure 1. (a) Approximately linear relationship observed between the dopant concentration of Al in MgO and the stability of the planar structure over the tetrahedral structure ($E_P - E_T$), where E_P and E_T are the total energies of the supported clusters P and T, respectively. (b) Charge transfer values q_P and q_T for clusters P and T for different concentrations and positions of Al in Al-doped MgO. In all cases the Al atom is directly below the cluster.

Table 1. Calculated Values of Binding Energies, BE_P and BE_T, of Planar and Tetrahedral Au_{20} Clusters, Respectively, for Different Positions and Concentrations (concn) of Dopant Al Atoms in Al-Doped MgO Substrates

Al position	concn (%)	BE_P (eV)	BE_T (eV)
II layer	2.78	12.167	6.921
	1.39	7.415	4.444
	0.69 (below)	5.122	3.256
	0.69 (away)	4.940	3.072
III layer	2.78	11.646	6.266
	1.39	7.219	4.226
	0.69 (below)	5.008	3.124
	0.69 (away)	4.922	3.064
pure MgO	0	2.851	1.936

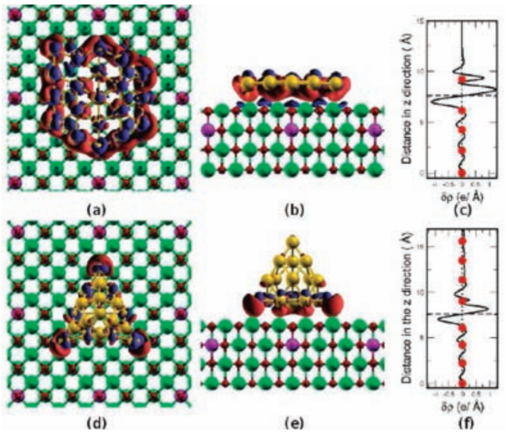

Figure 2. Charge transfer isosurfaces for the (a) top view and (b) side view of Au_{20} P and (d) top view and (e) side view of Au_{20} T, deposited on 2.78% Al-doped MgO. The green, red, magenta, and yellow spheres represent Mg, O, Al, and Au atoms, respectively. The blue and pink isosurfaces show the regions of charge depletion and charge accumulation, respectively. The isosurfaces shown correspond to (a, b) 0.0013 e/Å^3 and (d, e) 0.0025 e/Å^3. The planar integrals of the charge difference along the *z* direction for (c) Au_{20}(P)/Al-doped MgO and (f) Au_{20}(T)/Al-doped MgO are shown. The dots in (c) and (f) show the atomic positions along the *z* direction and are aligned with the atoms in the side view of the isosurface plots.

have been substituted with Al atoms. We considered two cases: Al replacing a Mg atom in (i) the second layer and (ii) the third layer. We considered three doping concentrations in each of these cases: viz., 0.69%, 1.39%, and 2.78%. We also considered two possible positions of the Al atom in the 0.69% Al-doped MgO: one in which the Al atom is directly below the Au cluster and another in which the Al atom is positioned away from the cluster. Doping with Al results in delocalization of the extra electron of Al in the MgO bulk and causes the Fermi level to shift to the conduction band of the system.

This lowers the work function of the system. One may then speculate that the system would release its electrons more easily to Au clusters than pure MgO and the clusters would gain a higher negative charge, possibly stabilizing the P cluster over the T isomer; below we demonstrate that this is indeed what happens.

Our results for the difference in energies between the P and T supported clusters and the charge state of the clusters are summarized in parts a and b of Figure 1, respectively. The binding energy (BE) of the cluster to the subtrate is calculated as the energy required to separate the supported cluster into the substrate and the cluster in the gas phase. It is computed as $\mathrm{BE(P/T)} = E[\mathrm{Au_{20}(P/T)}] + E[\text{Al-doped MgO}] - E[\mathrm{Au_{20}(P/T)}$ on Al-doped MgO], where E is the total energy of the corresponding system. These values are given in Table 1. With increasing concentration of the dopant in the MgO substrate, we observe an increase in BE. This is slightly reduced when the dopant atom is moved from the second to the third layer or from below the cluster to away from the cluster. Most strikingly, we found that for all the doping concentrations and configurations considered by us, the planar arrangement P is significantly favored over the tetrahedral arrangement T. The difference in energy between T and P shows a linear dependence on the Al concentration, as can be seen in Figure 1a. The smallest concentration of Al required to flip the stability of the cluster from the tetrahedral geometry to the planar geometry is around 0.4%. The stability of P over T is not very sensitive to the position of the Al atom. We note that the use of different exchange and correlation functionals may change the precise value[17,18] for the relative stability of the P and T clusters, but we expect the general trend to be maintained.

In Figure 2, we have plotted isosurfaces of the charge transfer that occurs when the P and T Au_{20} clusters are placed upon the substrate, for the particular case where the Al concentration is 2.78% (i.e., 4 of the 36 Mg atoms in the second layer of the substrate have been replaced by Al). We draw particular attention to the dipolar electronic charge that is accumulated between the cluster and the substrate; this shows up clearly in the charge-transfer plots and arises from the pillow effect.[19] This is also visible in parts c and f of Figure 2, where we have plotted the planar integral of the charge transfer vs *z*, the coordinate normal to the surface. The integral of the charge accumulated from the interface between the cluster and the substrate (defined as the plane of zero charge variation) up to the vacuum gives the total charge acquired by the cluster from the substrate.[9] These charge transfer values are plotted in Figure 1b, where we see a monotonic dependence of the charge transfer upon the dopant concentration. Note that this particular way of defining charge transfer gives a finite value also in the undoped case because of the contribution from the negative lobe of the interface dipole. For the T case, there is a depletion of charge from the substrate and an accumulation within the cluster, while in the P case, there is a larger depletion of charge from the substrate and a larger accumulation of charge both within the Au layer and between the Au and the substrate. We also wish to point out that the sites of charge accumulation on the cluster are believed to be the active sites for oxidation reactions, where the oxygen molecules preferentially adsorb. Comparing the regions of charge accumulation on both the clusters (the three vertices for T and the peripheral atoms for P), we can say that the P cluster may have more active sites than T and may therefore prove to be more catalytically active for oxidation reactions.

In summary, we have shown that doping an MgO substrate with Al atoms stabilizes a planar Au_{20} isomer over the tetrahedral form. The stabilization energy as well as the charge transferred from the substrate depend monotonically on the dopant concentration and are otherwise rather insensitive to the precise position of the impurities. We believe we have theoretically demonstrated a simple and feasible way to control the morphology of Au_{20} clusters, which is of interest for applications in catalysis. We hope our work will stimulate experimental investigations which will support our conclusions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Figures giving charge transfer isosurface plots of Au_{20}(P/T) supported on different concentrations of Al-doped MgO (Al in second layer) and pure MgO and text giving the complete author listing for ref 14. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We acknowledge funding from the Indo-Italian Programme Of Cooperation in Science and Technology, administered by the Department of Science and Technology, Government of India, and the Italian Ministry of External Affairs. We especially thank Lydia Szpyrkowicz for her assistance. Computational facilities were provided by CINECA.

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