A LOW-COST ALTERNATIVE TO SILVER AND GOLD NANOPARTICLES BY ALKALI METAL DOPING FOR PLASMONIC APPLICATIONS

An Experimental Approach Utilizing BIOVIA® Materials Studio® Software

A collaborative work with the Electrical Engineering Department of University of Malaya was performed on a systematic study of the electronic and optical properties of the Li and Na doped Al-X and Cu-X (X=Li, Na) nanoalloys in the framework of density functional theory in order to evaluate their potential as low-cost plasmonic materials as alternatives to silver and gold[1]. In particular, the surface-doped $Al_{12}X$ clusters exhibit a remarkably large bandgap extending from 3eV to 11eV. Due to their electronic and optical properties, the Al-X and Cu-X doped clusters may be considered as an excellent low-cost alternative to silver and gold, which will be useful in catalytic, opto-electronic and UV-absorption applications.

INTRODUCTION

Plasmonic metamaterials can be described as the metallic nanoparticles that exploit surface plasmons, which are produced from the interaction of light with metal-dielectric materials and which originate from the collective oscillations of the free charges in the material due to an applied electromagnetic field. Nowadays, these plasmonic systems are finding applications in various fields such as super lensing,[2] medical therapeutics[3] and diagnostic equipment,[4] solar cells[5] and catalysis[6].

FOUNDATION

Among the conventional plasmonic materials, silver and gold are the most used materials to date. In terms of optical losses, silver possesses the lowest loss in the visible and NIR region. However, where nano-fabrication is concerned, silver degrades comparatively quickly and the thickness threshold for uniform continuous films is around 12-13 nm, which is a major barrier for transformation optic (TO) and several other micro and nano-devices. In the quest for alternative plasmonic materials, Al and Cu appear promising for their low cost and abundance and have demonstrated surface plasmon resonance in the ultra-violet and visible regions respectively. However, the high optical and plasmonic losses of these two metals compared to silver and gold have restricted their usage in many practical applications. On the other hand, amongst the nanometals reported to date for their plasmonic potential, lithium, sodium and potassium have been shown to possess the highest absorption efficiency (Qabs), coupled with very low inter-band transition losses at optical frequencies. Of particular merit, these transition losses have been noted to be comparable to or surpass those of silver and gold. This is coupled with the additional advantage of exhibiting the strongest free-electron-like-behavior, which results in very prominent surface plasmon resonance (SPR) in the visible-UV range.

Therefore, the introduction of elemental free electron metals (alkali metals) into the Al and Cu nanoparticles may be considered for potential improvement of the optical properties of the Al and Cu nanoparticles.

AIM

A systematic investigation of electronic and optical properties of doped neutral clusters of $Al_{12}X$ and $Cu_{12}X$ were explored with regard to their potential for plasmonic applications. For this purpose, a single Al/Cu atom has been replaced by an alkali metal atom (X=Li, Na) to form the $Al_{12}X$ and $Cu_{12}X$ bimetallic clusters as shown in Figure 1, respectively. Using these geometrically optimized structures, calculations of binding energy, HOMO-LUMO gap, vertical ionization potential (VIP) and vertical electron affinity (VEA) are carried out in the framework of the Density Functional Theory (DFT) to characterize the stability and chemical inertness of the doped bimetallic clusters. TDDFT (Time-Dependent DFT) calculations have been carried out to predict the optical spectra of the clusters.

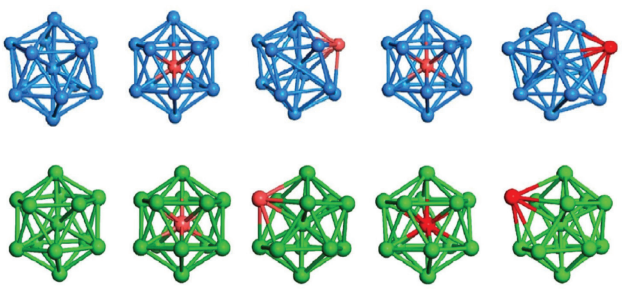

Figure 1. Geometry optimized cluster model for $Al_{12}X$ and $Cu_{12}X$ clusters

CALCULATION METHOD

Geometrical characteristics, energetics and optical properties of $Al_{12}X$ and $Cu_{12}X$ bimetallic structures were investigated using the density functional spin-polarized calculations using DMol3 code of BIOVIA Materials Studio modeling and simulation software.[7-10] All geometrical structures of the neutral clusters are optimized without imposing any symmetry. Calculations have been performed using the Perdew-Burke- Ernzerhof (PBE) exchange correlation functional.

Compound	BE	VIP	VEA	HOMO-LUMO Gap
Al$_{13}$	33.44	6.82	3.01	1.16
c-doped Al$_{12}$Li	30.89	6.59	2.82	1.29
s-doped Al$_{12}$Li	32.23	6.25	1.84	1.08
c-doped Al$_{12}$Na	27.94	6.09	2.47	1.22
s-doped Al$_{12}$Na	31.68	6.03	2.39	1.06

Table 1: Binding energy (BE), Vertical ionization potential (VIP), Vertical electron affinity (VEA) and HOMO-LUMO gaps of Al_{13} and $Al_{12}X$ clusters. All values are in eV.

All calculations were performed using a double numeric quality basis set (DNP) with polarization functions. To consider the relativistic effect, the DFT Semi-core Pseudo-potentials are used for the treatment of the core electrons of the doped clusters. The orbital cut-off range and Fermi smearing were selected as 5.0 Angstrom and 0.001 Ha respectively. The self-consistent-field (SCF) procedures were performed with the aim of obtaining well converged geometrical and electronic structures with a convergence criterion of 10-6a.u. The energy, maximum force and maximum displacement convergence were set as 10-6 Ha, 0.002 Ha/A0 and 0.005 A0 respectively. While calculating the IP and EA, it was assumed that the lowest-energy structure for a charged cluster is the same as their neutral clusters; hence, the calculated IP and EA are actually vertical IP (VIP) and vertical EA (VEA). Regarding the optical properties, the adiabatic local density approximated (ALDA) exchange-correlation kernel is employed in the TDDFT calculations for simulating the optical absorption spectra.

The absorption spectra of doped clusters are shown in Figures 2 and 3. The oscillator strength is provided as a function of the excitation energy. In each case, Lorentzian broadening (with a full width at half-height of 0.1 eV) is applied to provide a result more comparable to the experimental results. The resulting spectra include the calculated excitation energies of up to 6 eV and 11 eV for Cu clusters and Al clusters respectively. The spectrum of Cu_{13} is characterized by an intense and narrow band centered at 3.55 eV, and several weak transitions above 5 eV. The substitution of a Cu atom by an alkali atom, either in surface or in the core, leads to a broadening of the main band. More specifically, the doping in surface with Li and Na leads to an increase of the optical response in the entire energy domain above 2.2 eV, with new peaks well scattered in the total range of energies evaluated. The scattering is particularly manifested in the UV range and is also of significant magnitude in the visible range. Similarly, core substitution results in an increase in the optical scattering with particular strength in UV region, whilst the increase is stronger in the UV domain than in the visible one.

CONCLUSION

A key indication of the potential of these nanoalloys is the observation of a large energy gap between the HOMO and LUMO along with very low electron affinity of the $Al_{12}X$ and $Cu_{12}X$ clusters, which results in high reactivity of their anions. As such, these doped clusters are suggested to be excellent low cost alternatives to Ag and Au nanoparticles for catalytic applications. The outcome from the optical absorption calculations of the doped clusters is even more interesting. Li and Na doping into the Al and Cu clusters has been shown to yield a significant increase in the absorption bandgap in both of the $Al_{12}X$ and $Cu_{12}X$ clusters. In particular, the s-doped $Al_{12}X$ clusters have exhibited a remarkably large bandgap from 3 to 11 eV. Of particular mention, these nanoalloys have shown a strategic advantage over conventional Ag and Au nanoparticles, not only in terms of cost but also elimination of destructive interference in the visible light spectrum. Practical development of these bimetallic clusters in plasmonic solar cell applications will have a significant impact on the efficiency of these devices. Hence, this work can be the first step towards material engineering of low-cost nanoalloys with promising applications in catalysis and photovoltaic applications. In addition, s-doped $Al_{12}X$ clusters offer excellent potential as the UV absorber and emitter for applications in the textile and food processing industries and UV light therapy in cancer treatments.

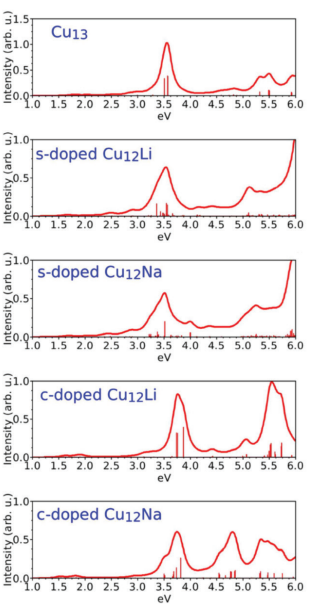

Figure 2. Absorption spectra of Cu13 and Cu12X (X=Li, Na) clusters

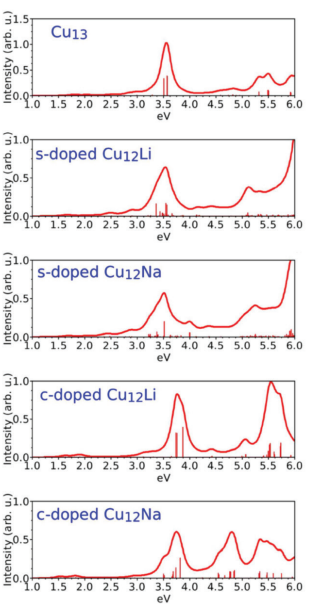

Figure 3a. Absorption spectra of Al_{13} and $Al_{12}X$ (X=Li, Na) clusters up to 6 eV

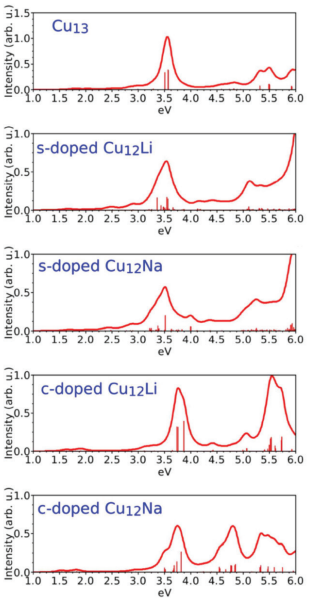

Figure 3b. Absorption spectra of Al13 and Al12 X, (X=Li, Na) clusters up to 11 eV

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