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REVIEW

Effects of Stern components on electronic structures and spectroscopic properties in gold superatom models*

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5f-elements encaged in a gold superatomic cluster are capable of giving rise to unique optical properties due to their hyperactive valence electrons and great radial components of 5f/6d orbitals. Herein, we review our first-principles studies on electronic structures and spectroscopic properties of a series of actinide-embedded gold superatomic clusters with different dimensions. The three-dimensional (3D) and two-dimensional (2D) superatom clusters possess the 18-electron configuration of $1S^2 1P^6 1D^{10}$ and 10-electron configuration of $1S^2 1P^4 1D^4$, respectively. Importantly, their electronic absorption spectra can also be effectively explained by the superatom orbitals. Specifically, the charge transfer (CT) transitions involved in surface-enhance Raman spectroscopy (SERS) spectra for 3D and 2D structures are both from the filled 1D orbitals, providing the enhancement factors of the order of $\sim 10^4$ at 488 nm and $\sim 10^5$ at 456 nm, respectively. This work implies that the superatomic orbital transitions involved in 5f-elements can not only lead to a remarkable spectroscopic performance, but also a new direction for optical design in the future.

Keywords: 5f-electrons, ds-electrons, superatom, first-principles

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1. Introduction

Gold nanoparticles exhibit strong d–s hybridization and relativistic effects which results in a wide variety of optical phenomena. These properties have attracted a huge interest in the optical studies of bimetallic nanoparticles.[1–4] On the other hand, the spectroscopic properties of actinide also play a remarkable role in the regular arrays of metals.[5–10] The absorption and/or emission lines of 5f valence shell electrons are narrow and sharp in the visible range,[10–12] and these spectra lines could be hardly influenced by the external coordination environment.[5,9] Consequently, the superatom model comprised of f-block and ds-block elements could be envisioned to very likely carry a revolutionary spectroscopic performance.

One of the first superatomic experiments was the seminal work of Knight *et al.* in 1984.[13] They observed conspicuous peaks in the mass spectra of Na clusters containing 2, 8, 20, 40, ... atoms. The electrons in Na $[3s^1]$ clusters are confined in quantized orbitals $1S^2$, $1S^2\ 1P^6$, $1S^2\ 1P^6\ 1D^{10}\ 2S^2$ $1S^2\ 1P^6\ 1D^{10}\ 2S^2\ 1F^{14}\ 2P^6$, ..., respectively, and successive electronic shell closure accounts for the enhanced stability of the magic clusters. Subsequent mass spectra of other simple homo- as well as heteroatomic metal clusters have confirmed the relationship between electronic shell closure and enhanced stability.[14] Currently, the electronic structures and derived properties of stable bimetallic gold-based clusters can also be modeled via the superatom models.[14–18] The first predicted superatomic cluster was the icosahedral $W@Au_{12}$ based on density functional theory (DFT) involving the 18-electron count ($1S^2 1P^6 1D^{10}$),[19] which was later confirmed via photoelectron spectroscopy (PES).[20] Soon after that, a series of bimetallic gold superatom models ($M@Au_n$), where M is a d-block atom, have been proposed theoretically.[21–25] Among them, these superatomic clusters all possess a great advantage compared with the pure gold clusters in tuning the excitation light,[26–36] which has been identified on the experimental study.[37–40] Besides, also such as one- and two-photon optical absorption,[41,42] circular dichroism,[43–45] electron paramagnetic resonance spectra,[46] etc. All these optical phenomena can be effectively explained by superatom models.

As is well known the f-block elements have a high density of electronic states, because of their hyperactive valence electrons. This particular attribute has led to an intense interest in optics and magnetic fields in applications of f-element-embedded gold clusters, such as $Ac@Au_7$,[7] $Sg@Au_{12}$,[47] $An@Au_{14}$ (An = Ac, Th, Pa, U),[8,48] $Gd@Au_{15}$,[49] etc. Specific optical characteristics of these superatom models were obtained through their structural and compositional modifications.[26–34] The relevant modification produces spectral shifting in a very wide range that is even as important as the morphological modification in one-component nanoparticles.[50] As reflections of electronic structures, spec-

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Carbon-coated $Na_3V_2(PO_4)_2F_3$ nanoparticles embedded in a porous carbon matrix as a potential cathode material for sodium-ion batteries with superior high-rate and long-term cycle life

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A carbon-coated $Na_3V_2(PO_4)_2F_3$ nanocomposite (NVPF@C) is successfully realized by a facile sol–gel method. Carbon-coated NVPF nanoparticles are dispersed inside the mesoporous carbon matrix, which can not only improve the electron/ion transfer among different nanoparticles, but also benefit the electrolyte wetting during cycling. As a result, the NVPF@C cathode demonstrates remarkable Na^+ storage performance: a high reversible capacity of nearly 130 mA h g^{-1} over 50 cycles between 4.3 and 2.0 V; superior rate capability with specific capacities of nearly 74 and 57 mA h g^{-1} at high current densities of 15C (1.92 A g^{-1}) and 30C (3.84 A g^{-1}), respectively; long-term cycle life with capacity retentions of 70% and 50% over 1000 and 3000 cycles at 10C and 30C rates. Thanks to the manifested high energy and power densities, the NVPF@C nanocomposite is suggested as a promising cathode material for grid energy storage.

Introduction

Recently, sodium-ion batteries (SIBs), as a promising candidate for grid energy storage, have attracted worldwide interest owing to the natural abundance and low cost of sodium.[1–4] In particular, SIBs share the identical intercalation chemistry with lithium-ion batteries (LIBs), which triggers extensive studies on electrode materials analogous to those of LIBs.[5–10] Among various cathode materials, compounds with a NASICON-type (Na super-ionic conductor) structure have received particular attention because the three-dimensional open framework gives rise to plenty of interstices, capable of allowing fast Na^+ insertion and extraction with little lattice strain.[11] $Na_3V_2(PO_4)_3$ (NVP), as a widely studied cathode material with a NASICON-type structure, has been found to demonstrate attractive Na^+ storage properties both at high and low working potentials.[12–17] However, its low electronic conductivity still hinders the rate capability and long-term cycle life, which are considered as two crucial characteristics of SIBs. To improve the Na^+ storage performance, preparing nanocomposites with carbon-related materials, such as one-dimensional carbon sheaths,[18,19] porous carbon,[20] CMK-3,[21] nanofibers[22–24] and core–shell structures,[25] is employed as an effective strategy. In particular, Mai *et al.*[15] studied the effect of carbon matrix dimensions on the properties of NVP nanograins and found that the NVP/acetylene carbon composite demonstrated the best promising performance in comparison with NVP/graphite and NVP/carbon samples, because the 3D carbon framework not only greatly increased the electronic conductivity but also provided the robustness for the structure during cycling.

Fluorophosphate, $Na_3V_2(PO_4)_2F_3$ (NVPF), is known as another appealing NASICON-type material, exhibiting motivating intercalation chemistry for both Na and Li ions.[26–30] Basically, NVPF can be considered as using three F^{1-} to replace one $(PO_4)^{3-}$ polyanion of NVP to maintain the charge neutrality. However, NVPF crystallizes in tetragonal symmetry with a space group of $P4_2/mnm$,[31] in sharp contrast to the rhombohedral symmetry of NVP (space group: $R\bar{3}c$).[32] NVPF is built up with $[V_2O_8F_3]$ bioctahedral units alternatively bridged by $[PO_4]$ tetrahedral units, which forms an extended three-dimensional framework with large tunnels along [110] and [1−10] directions beneficial to both Na^+ and Li^+ migration. Besides the difference in the crystal structure, the ion configuration related to the ion occupation and the number of diverse Na sites would vary after F^{1-} is introduced.[11] Also, the inductive effects of the $(PO_4)^{3-}$ polyanion might be enhanced due to the strong ionicity of the

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Actinide embedded gold superatom models: Electronic structure, spectroscopic properties, and applications in surface enhanced Raman scattering

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actinide element, DFT calculation, gold nanoparticle, superatomic orbital, surface-enhanced Raman scattering

ABSTRACT

Actinide elements encaged in a superatomic cluster can exhibit unique properties due to their hyperactive valence electrons. Herein, the electronic and spectroscopic properties of $Th@Au_{14}$ are predicted and compared with that of the isoelectronic entities $[Ac@Au_{14}]^-$ and $[Pa@Au_{14}]^+$ using density functional theory. The calculation results indicate that these clusters all adopt a closed-shell superatomic 18-electron configuration of the $1S^21P^61D^{10}$ Jellium state. The absorption spectrum of $Th@Au_{14}$ can be interpreted by the Jelliumatic orbital model. In addition, calculated spectra of pyridine-$Th@Au_{14}$ complexes in the blue laser band exhibit strong peaks attributable to charge transfer (CT) from the metal to the pyridine molecule. These charge-transfer bands lead to a resonant surface-enhanced Raman scattering (SERS) enhancement of ~10^4. This work suggests a basis for designing and synthesizing SERS substrate materials based on actinide-embedded gold superatom models.

1 Introduction

Hollow gold clusters have received substantial attention in recent years in studies of metallic clusters [1–3] because of their ability to house foreign guest atoms and molecules. Encapsulated atoms can affect the formation of gold clusters and their agglomerates. The optical, electronic, and magnetic properties of these encapsulated atoms can also be modified in order to satisfy specific requirements in the design and fabrication of cluster-based functional nanomaterials [4–9]. Interestingly, many stable endohedral gold clusters have been characterized by specific "magic numbers" of valence electrons consistent with atom-like electronic

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