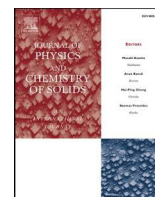




Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: <http://www.elsevier.com/locate/jpcs>

Molecular aspects of oligomer-coupled ultra-small Au nanoparticles

M. Boazbou Newmai, Nilesh Kumar Pathak, P. Senthil Kumar*

Department of Physics & Astrophysics, University of Delhi, Delhi, 110007, India

A B S T R A C T

In our quest for unlocking the growth mechanism of polymer stabilized metal nanostructures, we stumbled upon the solventless/templateless redox reaction between the monomer, N-vinyl pyrrolidone (NVP) and tetrachloroauric acid. This simple reaction results in the formation of oligomer-bridged ultra-small Au nanoparticles through an auto-catalyzed cluster aggregative nucleation process even under ambient conditions in the absence of any other external energy resources. Such intriguing, self-assembled nanostructures were beautifully illustrated through the TEM images, that are in strong correlation with the observed multiple optical absorption signatures. But, the sharp, intense peak at around 633 nm was quantified by quasi-static dipole model theoretical calculations as the predominantly coupled dimer peak, signifying the highly localized formation of small, cross-linked aggregates. Augmenting the same, the real time *in vitro* kinetic spectroscopic (such as FTIR, Raman, NMR etc.) measurements conveniently delineate, beyond doubt, the synergistic thermodynamic reaction mechanism as follows: the H⁺ ions from chloroauric acid react with NVP monomers and propagate *via* cross-linking, the diffusion rate of which kinetically diminish; the simultaneous square planar ligand substitution of the chloroaurate complexes with the carbonyl oxygen, not only annihilate the reaction sites, but also result in the disproportionate termination of cross-linked NVP oligomers, inter-dispersed with tiny metallic Au nanoparticles, stabilized through the aurophilic interactions. Further, the significance of NVP over other similar monomers were corroborated, thereby unleashing a molecular level understanding of the nanostructure-property functional relationship in a cohesive manner, for the development of unusual, unconventional methods of fabricating new smart materials with redefined application potentials.

1. Introduction

Ultra-small gold nanoparticles have attracted significant research interest in nanoscience due to their importance in fundamental science [1–3], technological applications such as optics [4], catalysis [5–7], chemical sensing [8] and biomedicine [9]. Ultra-small gold nanoparticles are a class of particles (≤ 2 nm) consisting of only few to tens of atoms with size comparable to Fermi wavelength of the conduction electrons, resulting in molecular like properties such as size tunable fluorescence and intra-band electronic transitions [10] due to the presence of discrete energy levels, unlike in nanoparticles with size > 5 nm. In general, ultra-small gold nanoparticles doesn't show bulk-like electronic properties and are considered not to support collective plasmon excitation [11,12], due to the fact that plasmon resonance absorption depends on the third power of the nanoparticle diameter. Thus, the plasmon absorption in ultra-small nanoparticles might simply be too weak to detect above the intra-band absorption [13].

Ultra-small gold nanoparticles are generally synthesized by a strong reducing agent (e.g. sodium borohydrate, NaBH₄) and then stabilized by specific surfactant such as thiol [14], which have unique interaction with Au surface via the thiolate-Au bonds. Due to the fast reaction kinetics, shape and size control of ultra-small Au NPs is very difficult and separation of different sizes requires complicated techniques such as size

exclusion chromatography (SEC), as strong ligands such as thiol may influence their physico-chemical properties to a large extent [15]. Several other stabilizers like phosphine [16–18] and macro-molecules such as protein [19], polymers [20,21] and dendrimers [22] were also used. In such a system, the macromolecules on which the ultra-small Au NPs are embedded are difficult to remove and so catalytic studies of single ultra-small Au NPs is a daunting task as the number of macromolecules or polymers (eg Poly vinyl pyrrolidone, PVP) interaction cannot be regulated experimentally. In recent years, there are extensive research works to synthesis atomically precise ultra-small Au NPs without chromatography or gel [23], but these methods require several complicated steps. Earlier reports on surfactant free synthesis of ultra-small Au NPs [24,25] involve harsh synthesis conditions and involve the use of NaBH₄ as reducing agent and thiol as the capping agent. The wide interest in structural analysis of ultra-small Au NPs is also driven by interest in their electronic properties. Several theoretical studies have been reported on the electronic structure of ultra-small Au NPs and the ligand effect on optical properties with various stabilizing agents [26] like thiol [27–29], PVP [30] and this reports have correlated well with the electronic properties in our case. There are several reports on optical properties of Au nanoparticles (> 10 nm) at near touching or overlaying distance [31,32], but to our knowledge our work is the first report on optical response due to interaction between ultra-small Au NPs

* Corresponding author.

E-mail address: duplasmonics@gmail.com (P. Senthil Kumar).<https://doi.org/10.1016/j.jpcs.2020.109378>

Received 21 May 2019; Received in revised form 2 January 2020; Accepted 25 January 2020

Available online 27 January 2020

0022-3697/© 2020 Elsevier Ltd. All rights reserved.



Plasmonic Nanostructures for Energy Application

Nilesh Kumar Pathak*

Department of Physics, Maharaja Agrasen College, University of Delhi, New Delhi, India

The present work furnishes the optical properties of metal nanostructures and their application in energy. Metal supports plasmonic resonances that can be tuned in the desired range of the solar spectrum by changing its size, shape, and surrounding environment. Two different systems, isolated and coupled gold metal nanospheres, are taken into account to study optical properties. These optical properties of the chosen nanostructure are analyzed in terms of surface plasmon resonances using the Boundary Element Method (BEM). The tuning of surface plasmon resonances under different parameter domains and their applications in energy are the main thrusts of this work. The simulated extinction spectrum and corresponding spectral width of metallic nanogeometries could be used in several applications like solar stills, solar collectors, and solar cells.

OPEN ACCESS

Keywords: plasmon, nanostructure, SPR, BEM, extinction

Edited by:

Mariana Amorim Fraga,
Federal University of São Paulo, Brazil

Reviewed by:

Diego Alexandre Duarte,
Federal University of Santa
Catarina, Brazil
Daniel Neves Micha,
Federal Center for Technological
Education Celso Suckow da
Fonseca, Brazil

*Correspondence:

Nilesh Kumar Pathak
nileshpiitd@gmail.com

Specialty section:

This article was submitted to
Micro- and Nanoelectromechanical
Systems,
a section of the journal
Frontiers in Mechanical Engineering

Received: 11 April 2020

Accepted: 09 June 2020

Published: 21 August 2020

Citation:

Pathak NK (2020) Plasmonic
Nanostructures for Energy
Application. *Front. Mech. Eng.* 6:53.
doi: 10.3389/fmech.2020.00053

INTRODUCTION

Solar energy is the utmost abundantly available, clean, pollution-free, and economically viable energy source on the Earth, and the sun is the ultimate source of this solar energy. The sun will supply an unlimited amount of energy to the Earth for an unlimited time due to the abundance of hydrogen in its core. This abundance of hydrogen inside the sun's core fuses together to produce energy known as solar energy. The sun is continuously supplying solar energy without any expectation therefore, everyone who is working in this field wants to use this freely available energy (Aybar, 2006; Govorov and Richardson, 2007; Modi and Nayi, 2020). Solar energy attracts the scientific community because it is economically viable, free from pollution, and available throughout the year. Due to its inherent features, it is believed that solar energy is an alternative source of energy (Atwater and Polman, 2010; Liu et al., 2011; Pathak et al., 2014). There are a variety of technologies available throughout the globe that are being used to harness sunlight. These technologies include solar photovoltaics, solar stills, solar cookers, and solar heat collectors. In solar photovoltaics, solar energy is converted into electrical energy by using a solar cell device. A solar still is a kind of technology that is used to obtain fresh water from seawater/brackish water (Duffie and Beckman, 1991; Shukla and Modi, 2017). A solar cooker is used for cooking food by solar radiation, and a solar heat collector is used to collect the sun's radiation for distilling and heating water for kitchen and general home purposes (Riffat and Cuce, 2011; Cuce and Cuce, 2013; Modi and Modi, 2019). Several efforts have been made in the last three to four decades to design, simulate, and fabricate a variety of technologies to harness sunlight. Researchers are still working on these technologies to optimize the various parameters for better output efficiency (Park, 2015; Pathak et al., 2017).

There have been several upgrades to optimize the parameters of the said technologies for better output. The upgrades have been in terms of the miniaturization of technologies. Miniaturization means shifting the technologies from a larger scale to the nanoscale domain. In the nanoscale