Photoluminescence Characteristics of Gold-decorated Zinc Oxide Nanostructures Synthesized by Pulsed-Laser Deposition

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Abstract
In this study, the effects of size and surface density of gold clusters on ZnO nanostructures were introduced. Photoluminescence characteristics revealed the formation of a Schottky junction and a distinct enhancement in emission efficiency with decreasing cluster dimensions. This work underscores the paramount importance of atomic-level cluster size control for fabricating functional nanomaterials with precise electronic behavior.

Keywords: Zinc oxide; Gold nanoparticles; Pulsed-laser deposition; Photoluminescence
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1. Introduction

The integration of precious metals, such as gold (Au), silver (Ag), and platinum (Pt), with nanostructured materials represents a cornerstone of modern nanotechnology. This strategy, often referred to as "decoration" or the formation of hybrid nanostructures, moves beyond simple mixing to create synergistic systems where the whole is significantly greater than the sum of its parts. By depositing nanoparticles of these noble metals onto the surface of other nanomaterials (such as metal oxides like TiO_2, ZnO, or carbon-based structures like graphene), scientists can engineer materials with tailored and enhanced properties. The advantages of this approach, the sophistication of the synthesis methods, and the breadth of applications span diverse fields from catalysis and medicine to sensing and renewable energy.

The decoration with precious metals confers several critical advantages that fundamentally alter the behavior of the host nanostructure. For semiconductor metal oxides like TiO_2, a major limitation is the rapid recombination of photogenerated electrons and holes, which reduces their efficiency in photocatalytic reactions. Decorating with metals like Pt, Au, or Ag creates a Schottky barrier at the metal-semiconductor interface. This barrier acts as an efficient electron trap, capturing photo-excited electrons from the semiconductor's conduction band. This process effectively separates the charge carriers, leaving more holes available to drive oxidation reactions. Consequently, the photocatalytic activity for processes like water splitting for hydrogen production or pollutant degradation is dramatically enhanced. Furthermore, Au and Ag nanoparticles exhibit a unique property known as localized surface plasmon resonance (LSPR). When illuminated with light of a specific wavelength, the conduction electrons in these metal nanoparticles collectively oscillate, leading to a strong absorption of light and the generation of highly energetic "hot" electrons. These electrons can be injected into the conduction band of a semiconductor, further boosting photocatalytic activity under visible light, which is a major advantage over wide-bandgap semiconductors that only absorb UV light.

Precious metal decoration drastically improves the performance of chemical and biological sensors. The LSPR of Au and Ag nanoparticles is exquisitely sensitive to changes in the local dielectric environment. When a target molecule adsorbs onto the surface of a decorated nanostructure, it alters the refractive index around the metal nanoparticle, causing a measurable shift in the LSPR absorption peak. This enables highly sensitive label-free detection. Similarly, in Surface-Enhanced Raman Spectroscopy (SERS), the intense electromagnetic fields generated by plasmonic nanoparticles (especially Ag and Au) at the interfaces with the host material can enhance the Raman scattering signals of analyte molecules by factors of up to 10^{10} to 10^{11}, allowing for the detection of single molecules. This makes decorated nanostructures powerful platforms for diagnosing diseases, detecting environmental pollutants, and identifying explosives.

A common challenge with nanoparticles is their tendency to agglomerate, which reduces their active surface area and effectiveness. Using a stable host nanostructure as a support for precious metal nanoparticles helps to anchor them, preventing aggregation and maintaining a high dispersion of active sites. This is crucial for catalysts that need long-term stability. The host material provides a robust scaffold, ensuring the durability and reusability of the hybrid system.

The method of decoration is critical, as it controls the size, distribution, density, and interaction of the precious metal nanoparticles with the host surface.

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Chemical reduction is a common and straightforward method. The host nanostructure is dispersed in a solution containing a precursor salt of the precious metal (e.g., $HAuCl_4$ for gold). A reducing agent, such as sodium borohydride ($NaBH_4$) or citrate, is then added to reduce the metal ions to their zero-valent state (Au^0), leading to nucleation and growth of nanoparticles on the host's surface. The choice of reducing agent and stabilizers (capping agents) allows for some control over nanoparticle size.

The combination of advantages and tailored synthesis methods leads to impactful applications such as environmental remediation as plasmonic Au/TiO_2 or Ag/ZnO nanocomposites are used to degrade organic pollutants (dyes, pesticides) in water under solar light, making the process more energy-efficient. In renewable energy applications, the Pt/TiO_2 and Pt/CdS systems are leading catalysts for photocatalytic hydrogen production from water, a promising clean energy source. Plasmonic decorations also enhance the efficiency of solar cells. As mentioned, Au-decorated nanostructures are used for photothermal therapy, targeted drug delivery, and biosensing. Ag-decorated materials are applied in antibacterial coatings. In industrial catalysis applications, Pt and Pd-decorated oxides or carbons are vital as heterogeneous catalysts for chemical synthesis, petroleum refining, and automotive catalytic converters to reduce harmful emissions.

In this study, the effects of size and surface density of gold clusters on ZnO nanostructures are introduced. This work underscores the paramount importance of atomic-level cluster size control for fabricating functional nanomaterials with precise electronic behavior.

2. Experimental Work

ZnO-based nanostructures were synthesized via chemical bath deposition from a heated aqueous solution of zinc nitrate and hexamethylenetetramine, with ammonium fluoride added to form a composite material containing a zinc hydroxyfluoride phase. The resulting nanostructures were washed, decanted, dried, and dispersed in deionized water. Commercial graphene paper (GP) electrodes were cleaned and dried before the NS dispersion was drop-cast onto their surface and air-dried.

The gold clusters were produced using a DC magnetron-sputtering gas condensation source (Swansea University Nanocluster Source). Clusters were formed in a liquid nitrogen-cooled chamber, mass-selected with a time-of-flight selector, and soft-landed with low kinetic energy onto the ZnO NS-coated GP electrodes to ensure minimal structural damage and uniform coverage.

The amount of deposited gold was quantified using Rutherford backscattering spectrometry (RBS) with a 2.0 MeV He^+ beam. Photoluminescence (PL) spectra were obtained using a He-Cd laser (325 nm) as the excitation source.

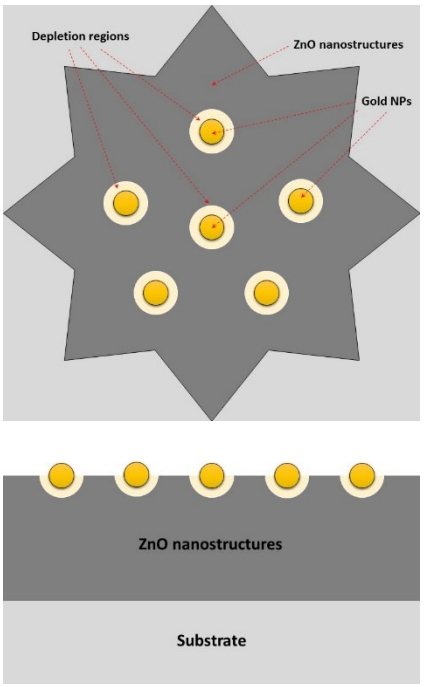

Fig. (1) Top view and front view of the Au-decorated ZnO nanostructures synthesized in this work

3. Results and Discussion

The field-emission scanning electron microscopy (FE-SEM) images in Fig. (2) illustrate the morphological features of ZnO nanostructures before and after surface decoration with gold (Au) nanoparticles. In Fig. (2a), the pristine ZnO nanostructures exhibit a dense and vertically aligned arrangement of nanorods with uniform dimensions. The nanorods appear to have smooth surfaces and well-defined hexagonal cross-sections, typical of wurtzite ZnO growth. Their high density and ordered orientation indicate a successful synthesis process, which is favorable for optoelectronic and sensing applications due to the large surface-to-volume ratio and efficient charge transport pathways. In contrast, figure (2b) shows the ZnO nanorods after being decorated with Au nanoparticles. It is evident that the smooth surfaces of the pristine ZnO rods are now coated with discrete clusters of Au nanoparticles, which appear as bright, granular features distributed mainly on the tips and sidewalls of the nanorods. The Au decoration not only increases the surface roughness but also introduces plasmonic active sites, which can enhance optical absorption and catalytic performance. Such hybrid ZnO–Au nanostructures are highly advantageous for applications in photocatalysis, surface-enhanced Raman spectroscopy (SERS), and photodetectors, owing to synergistic effects between the semiconductor and metallic nanoparticles.

A comparative photoluminescence (PL) analysis was conducted on both the center and border of each sample to evaluate the impact of Au cluster decoration across different sizes and densities. Figure (4) displays a Jacobian-transformed PL spectrum for the gold sample, facilitating visualization of the

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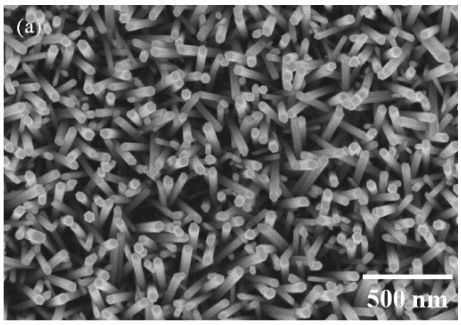
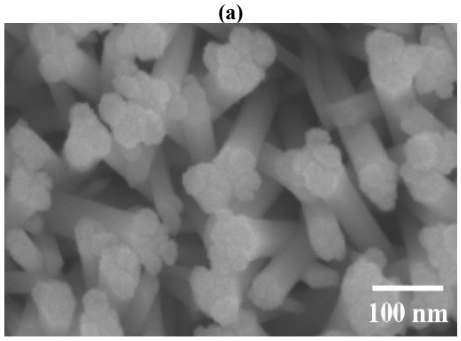
photon energy dispersion. The data reveal that Au decoration leaves the UV peak intensity unchanged but significantly enhances the visible band maximum. This enhancement is quantified by the parameter η, defined as the ratio $Max_{visible}/Max_{UV}$, representing photons emitted in the visible range per UV photon. Table (1) demonstrates that η values are stable for bare ZnO but exhibit a systematic increase upon Au functionalization. Crucially, the magnitude of this increase is strongly correlated with the surface density of the deposited clusters.



(a)



(b)

Fig. (2) FE-SEM images of ZnO nanostructures (a) before and (b) after decoration with Au NPs

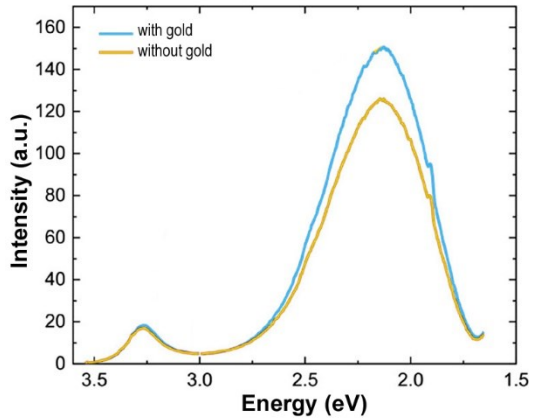


Fig. (2) Effect of gold clusters on PL spectra of ZnO nanostructures sample (excitation wavelength is 410nm)

4. Conclusions

The photoluminescence (PL) intensity of ZnO nanostars in the visible spectrum increased when decorated with gold clusters, an effect that depended on the clusters' size and density. This enhancement is due to the formation of a Schottky junction at the metal-semiconductor interface, which improves charge separation and the material's photoresponse. These findings demonstrate that using size-selected clusters is a powerful method for precisely tuning the electronic properties of hybrid nanomaterials for tailored applications.

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