Tin(IV) oxide-coated gold nanocomposite materials for solar thermal energy collection and harvesting

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Abstract

The synthesis of various stable metallic nanoparticles is increasingly becoming the source of interest to researchers, this is due to their key features such as surface plasmonic activity, catalytic activity, and stability, amongst others. These therefore indicate their potential uses in several promising applications. This study describes the synthesis of SnO_2-coated gold nanostructures, including nanospheres, nanoprisms, nano-octahedrals, and tip-blobbed nano-octahedrals (these are mono-metallic heteromorphic structures), with the aim to demonstrate the stabilizing effect of SnO_2 on the various gold nanostructures. While our understanding of the reaction mechanisms initiated at the metal-semiconductor interface is complicated by many of factors including spatial non-uniformities. Herein we also study the various resulting metal-semiconductor systems which might have general relevance in broadening our understanding of semiconductor stabilization and interaction at the surface of a metal. The wet chemistry approach used in this study has previously been successfully used to synthesize gold nanospheres stabilized with SiO_2, herein SnO_2 is investigated as an alternative to SiO_2. Additionally, the study demonstrates the potential uses of the stable colloids of gold-semiconductor nanocomposite materials as heat transfer fluid additives, owing to the outstanding heat storage capabilities of the coating semiconductor material and the impeccable surface plasmonic resonance activities of the core metal structures. The stabilities of the resulting colloids were determined and monitored using ultraviolet-visible (UV-Vis) spectroscopy. The UV-Vis spectra demonstrated a clear stabilization and absorption enhancement due the coating material. Furthermore, morphological analysis and elemental measurements of the metal nanomaterials before and after coating were carried out using transmission electron microscopy (TEM-EDS), confirmed the stabilization due to the metal-semiconductor interaction which aided in our description of the proposed reaction mechanisms.

1. Introduction

In recent years, the synthesis of various stable metallic nanostructures with controlled sizes, shapes, architecture, composition, and properties has increasingly become the source of interest to researcher seeking to develop materials suitable for such promising applications as solar thermal energy collection and transportation. The aim has been to acquire the nanostructures of gold, silver, gadolinium, and platinum. This is primarily because these structures, with key features such as **surface plasmonic activity, catalytic activity,** and **stability**, have proven to be the ideal building blocks in various applications including localized heat generation **[1]**, energy harvesting **[2]**, biosensing, optoelectronics, and catalysis **[3] [4].**

However, many of these metallic nanostructures, specifically Gold (Au), suffer significant drawbacks related to the agglomeration of particles or the formation of complex particle linkages, which tend to limit their applicability lifespan. From an applications perspective, the useful special properties of nanomaterials are those that stem from the single isolated particles, and these properties are in general negatively affected, or lost in the case of particle interactions **[5]**. As such, significant considerations concerning our ability to isolate these nanoparticles from each other is warranted, since two or more particle interactions may cause significant changes in the material properties. Nanocomposite materials of the shell/core architectural type offer a simple solution to this limitation. These are generally multi-phase materials, in which at least one primary phase has the desired properties of interest to be harnessed, and an additional distance-holder secondary phase to assist in stabilizing the initial primary phase. To improve the applicability of Gold (Au), Tin(IV) oxide is utilised as a secondary distance-holder phase in the synthesis of Tin(IV) oxide coated- Au nanocomposite materials (Au@SnO_2). Thus, this study describes the synthesis of Tin (IV) oxide (SnO_2) stabilized Gold (Au) nanostructures including nanospheres, nanoprisms, and nanorods. The resulting stable Au@SnO_2 nanocomposite materials were further evaluated as potential colloid additives for solar thermal energy collection and transportation **[6,7].** Additionally, important information about the (SnO_2) stabilization and interaction at the surfaces of the resulting various (Au - SnO_2) systems is noted.

2. Experimental

General Considerations: Commercial samples of Hydrochloric acid (HCl) and Sodium hydroxide (NaOH), Sodium stannate trihydrate ($Na_2SnO_3 \cdot 3H_2O$), Chloroauric acid ($HAuCl_4 \cdot 3H_2O$), Cetyltrimethylammonium-bromide (CTAB), L-ascorbic acid, and Silver Nitrate ($AgNO_3$), and Sodium borohydride ($NaBH_4$) were used as received. All manipulations were performed in air. Deionized water was used in the synthetic preparations and stability studies. The synthetic methodologies for the CTAB-stabilized, and SnO_2-coated Au nanostructures were based on published procedures and are summarized below **[8-11].**

2.1. Synthetic preparations of Au nanostructures

Figure 2-1: Synthetic experimental setup for synthesis of Au@SnO_2 nanocomposite structures.

Figure 2-1 shows the experimental work undertaken in the synthesis and characterization of the nanocomposite materials of Au. Au@SnO_2 nanocomposite materials are synthesized via a three-step process. The initial Au seeds synthesis step involves the reduction reaction of the $HAuCl_4$ salt with $NaBH_4$ as the reducing agent in the presence of sodium citrate utilised as a capping agent. The resulting seeds are then used as prepared in the seed-mediated growth of the Au- nanospheres, nanorods, and nanoprisms in the second step. The third step is the hydrothermal spontaneous encapsulation process of the various Au structures with SnO_2 nanoparticles, and it is undertaken under basic reaction conditions using NaOH and $Na_2SnO_3 \cdot 3H_2O$, as the sources of OH^- and SnO_2 respectively. Particle re-concentration and removal of unreacted reagents, such as CTAB, was done through centrifuging (30 min at 3500 rpm) between the major steps above.

2.2. Characterization

The sizes and morphologies of the Au nanostructures before and after SnO_2 coating were determined using a JEOL FEGTEM-2100 FX transmission electron microscope (TEM) operated at a bias voltage of 200 kV. The samples for TEM analyses were prepared by dipping the carbon-coated copper TEM grids into the various colloidal sample solutions of Au@SnO_2 structures and then allowed to dry in air. This process was repeated (10 times or more) to obtain a quantity of sample suitable for analysis. UV−vis spectra were obtained in the range 300−1000 nm using a Cary 50 Scan UV−vis spectrometer. The samples for analyses were prepared by placing 1 ml of the as-prepared aqueous solutions into the quartz cuvettes and diluting to the mark with deionized water. The colloidal stabilities of these various Au@SnO_2 samples were determined from their UV−vis spectra collected for each solution over an extended period of three months and compared with the spectra of the parent solutions.

3. Results and Discussion

3.1. Synthesis results and discussion

As mentioned in section 2, SnO_2-coated Au nanocomposite materials can be prepared via three steps, and the synthetic procedures are adapted from the indicated literature references. Scheme 1 in figure 3-1 below, illustrates the synthetic procedures used in the synthesis of SnO_2-coated Au nanospheres, nanorods, and nanoprisms.

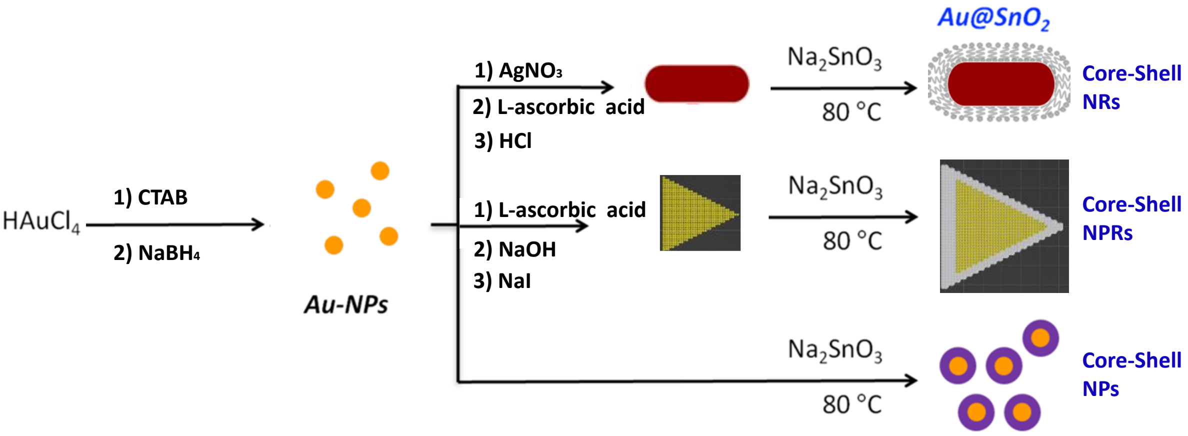

Figure 3-1: Scheme 1. Synthesis of SnO_2-coated Au nanospheres, nanorods, and nanoprisms.

First, gold nanospheres (40 nm average particle diameter) were synthesised using a common CTAB stabilised $NaBH_4$ reduction reaction method. These nanospheres served as seeds in the subsequent steps for the synthesises of nanorods and nanoprisms. The seed-mediated growth of these structures required a careful selection of reagents to assist in controlling the sizes and the shapes of these nanostructures. The aspect-ratio of the gold nanorods was controlled by the addition of $AgNO_3$, whilst their growth rate was lowered by the addition of HCl. For gold nanoprisms, the necessary reagents proved to be NaOH and NaI, which respectively assisted in controlling the directionality of the depositing atoms and in improving the flat-anisotropic (planar) growth of the prisms. In each case, it was necessary to control the sizes of the depositing atoms since depositing atoms of the same size as the seed particles would result in complex structures. And this was accomplished using L-ascorbic acid. The as-prepared structures consisted of bare-Au nanorods of average lengths of 125 nm and bare-Au nanoprisms of average lengths 129 nm, with average diameters similar to their seed particles (40 nm).

The preparation of the SnO_2-coated Au nanospheres, nanorods, and nanoprisms involved the spontaneous encapsulation of these Au nanostructures within the tin(IV) oxide shell upon the addition of sodium stannate trihydrate ($Na_2SnO_3 \cdot 3H_2O$) via a simple hydrothermal process in the presence of NaOH. Tin(IV) oxide is an inorganic semiconductor compound (Band gap of 3.6 eV at room temperature **[12]**) with high chemical and thermal stability. And a nanostructured layer of SnO_2 nanoparticles around the Au nanostructures occurs following the hydrolysis of stannate at a temperature of above 60ºC via the reaction equations in figure 3-2.

$$Na_2SnO_3 + 2H_2O \rightarrow H_2SnO_3\downarrow + 2NaOH \qquad (1$$

$$SnO_3^{2-} + 3H_2O \rightarrow Sn(OH)_4\downarrow + 2OH^- \qquad (2$$

$$Sn(OH)_4 + 2OH^- \rightarrow Sn(OH)_6^{2-} \qquad (3$$

$$Sn(OH)_6^{2-} \rightarrow \boxed{SnO_2\downarrow} + 2OH^- + 2H_2O \qquad (4$$

Figure 3-2: Stannate hydrolysis process [13].

The SnO_2 nanoparticles resulting from equation 4 in figure 3-2 spontaneously encapsulate themselves around the Au-nanostructures in a non-uniform fashion resulting in a meso-porous layer. As expected, after coating the Au nanostructures with SnO_2, their sizes (diameters and lengths) increased this is due to the formation of the Au@SnO_2 nanocomposite materials. The Au@SnO_2 composite materials of the nanospheres increased to an average particle diameter of 65 nm. And the average particle lengths of the Au@SnO_2 nanocomposite materials of the nanorods and nanoprisms increased to 132 and 300 nm, respectively.

3.2. Morphological analysis

Figure 3-3 shows TEM images of the Au nanospheres. From the TEM images these structures can be classified as zero-dimensional nanomaterials, having sizes that are <100 nm in all dimensions. Sample measurements were collected over a period of three months to monitor and evaluate their colloidal stability. The Au nanospheres had an average particle diameter of about 60 nm. This particle size was maintained throughout the assessment period, however a degree of particle agglomeration of the uncoated Au nanospheres started emerging. After imparting a SnO_2 coating of thickness of approximately 150 nm, the composite particle sizes increased to average particle diameters of ~208 nm. And these coated Au nanospheres remained kernelled inside the SnO_2 coatings, which afforded them the colloidal stability that was maintained for a period of three months. The TEM images also show that the nano-spherical core/shell particles have excellent uniformity.

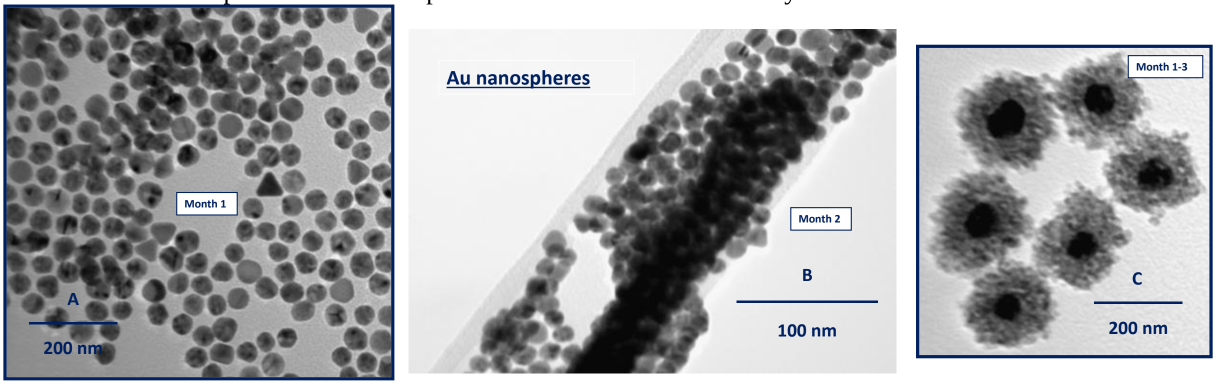

Figure 3-3: TEM micrographs of Au nanospheres before and after SnO_2 coating, images are taken over a period of 3 months.

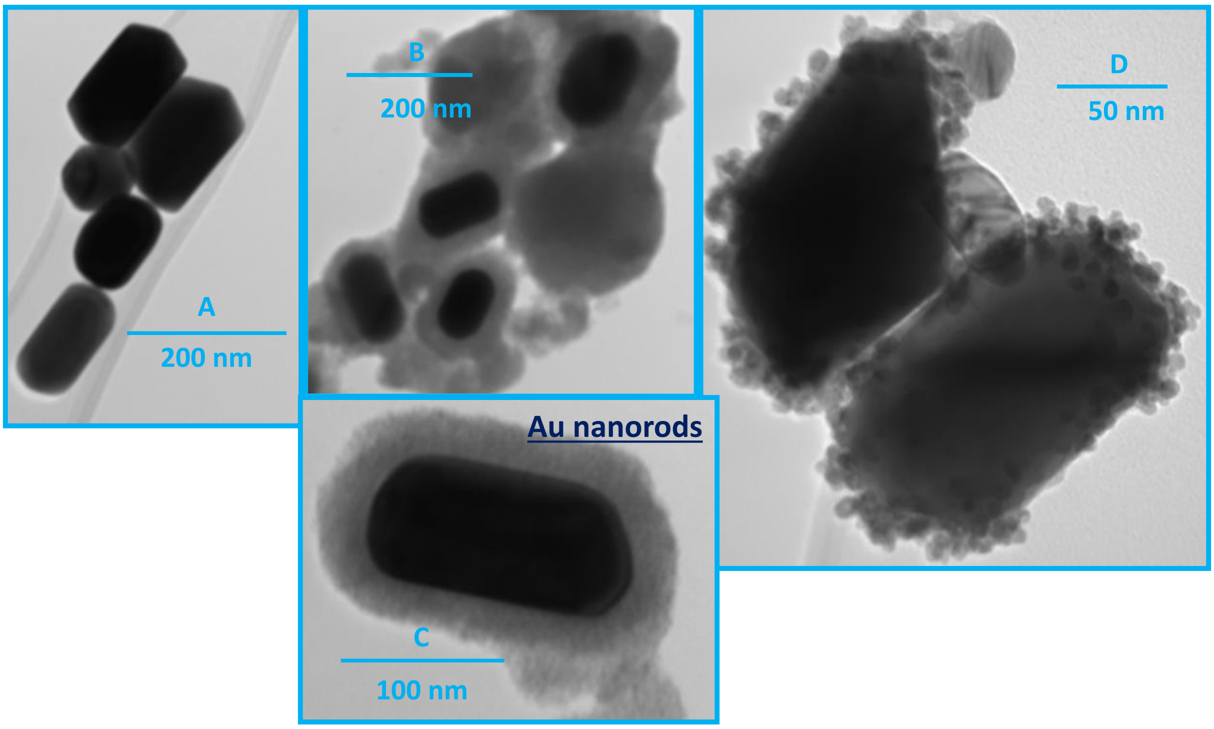

Figure 3-4: TEM micrographs of Au nanorods before and after SnO_2 coating.

Figure 3-4 shows the TEM images of the Au nanorods. From the TEM images these structures can be classified as one-dimensional nanomaterials, having sizes that are <100 nm in exactly two dimensions. The Au nanorods had an average particle diameter of about 70 nm. And an average length of about 130 nm before SnO_2 coating was imparted. After imparting a SnO_2 coating of thickness of approximately 40 nm, the composite particle lengths increased to an average of ~202 nm. The TEM images of the coated nanorods also show the distribution of SnO_2 nanoparticles around the Au nanorods, which indicates a degree of non-uniform distribution typically observed in meso-porous layers of nanomaterials. The Au nanorod core/shell particles also have excellent uniformity.

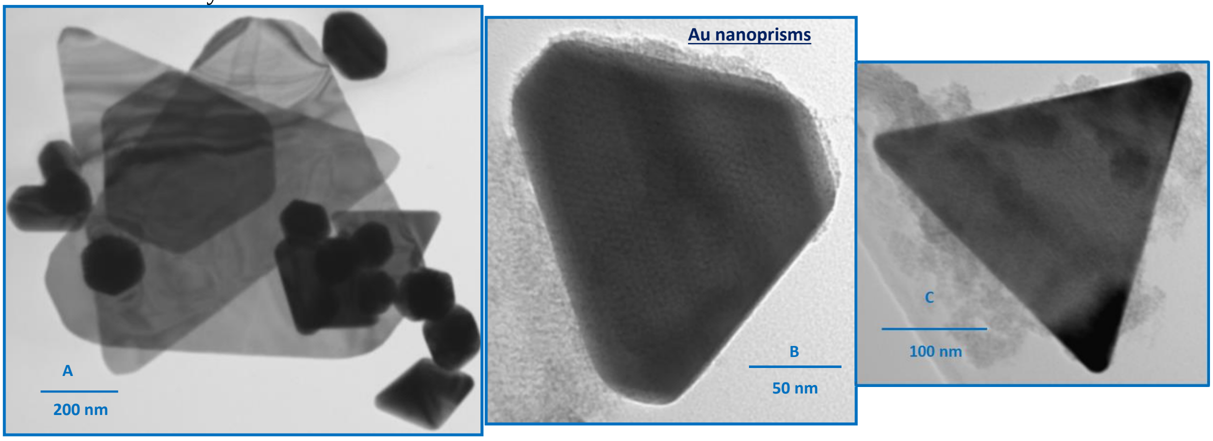

Figure 3-5: TEM micrographs of Au nanoprisms before and after SnO_2 coating.

Figure 3-5 shows the TEM images of the Au nanoprisms. From the TEM images these structures can be classified as two-dimensional nanomaterials, having sizes that are >100 nm in exactly two dimensions. These are therefore referred to as thin film nanomaterials characterized by having thicknesses of a few atoms. The Au nanoprisms had average areas of about 15574 nm^2 and 18199 nm^2, before and after imparting a SnO_2 coating of approximately 10 nm. The TEM images of the coated nanoprisms also show the distribution of SnO_2

nanoparticles around the Au nanoprisms, which indicates a degree of non-uniform distribution similar to that observed in the coated nanorods, which implies that a meso-porous layer of SnO_2 nanomaterials has encapsulated the Au core structures.

3.3. Spectroscopic analysis

Figure 3-6 shows the absorption spectra of the colloidal sample solutions of the uncoated and coated Au nanostructures. The surface plasmon resonance (SPR) bands observed for the uncoated and SnO_2-stabilized/coated Au nanospheres had maxima at 522, and 552, respectively, which are consistent with previously reported values **[14]**. As mentioned, the stability of the Au nanospheres was monitored over a period of three months, and from the UV-Vis spectra it can be observed that the coated Au nanospheres were excellently stabilized by the coating materials as opposed to their uncoated counterparts.

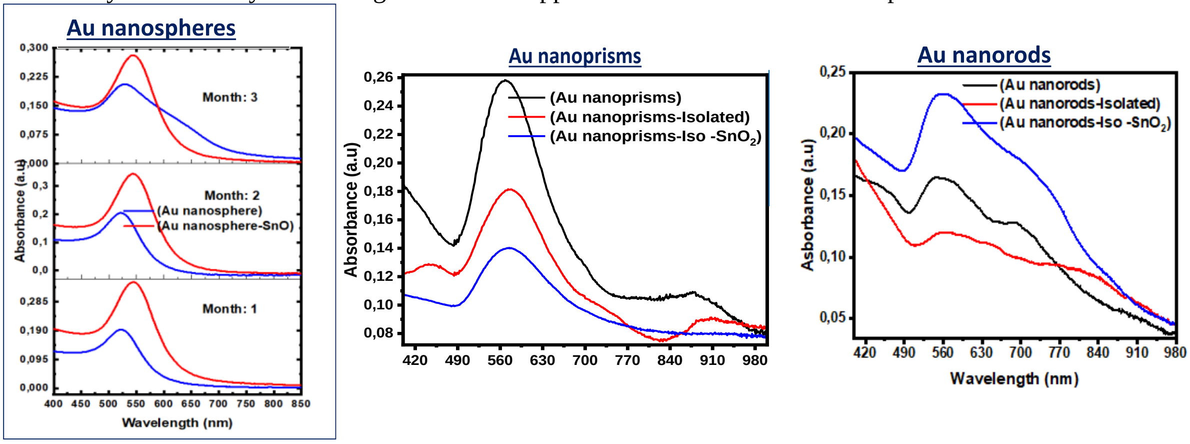

Figure 3-6: UV-VIS spectra of the Au-nanospheres, nanoprisms, and nanorods.

Figure 3-6 (b): Au nanorods shows the SPR bands (Transverse and Longitudinal) for the uncoated and SnO_2-stabilized/coated Au nanorods which had maxima (560 and 702 nm), and (562 and 710 nm), respectively. which are consistent with previously reported values [17,28]. Figure 3-6 (c): Au nanoprisms shows the SPR bands (only Transverse, since their longitudinal bands were out of range of the UV-Vis instrument) for the uncoated and SnO_2-stabilized/coated Au nanoprisms which had maxima at 562 and 564 nm, respectively.

The red shifts of the SPR bands for the SnO_2-stabilized/coated Au nanostructures (nanospheres, nanorods, and nanoprisms) are due to the high refractive indexes of 2.2 due to the SnO_2 **[15]** coatings. Notably, the SPR band of the SnO_2-coated particles was observed to undergo a red shift with increasing thickness of the SnO_2 layer.

4. Conclusion

In summary, three different Au@SnO_2 nanocomposite material systems of the core-shell architectural type were synthesised. These systems consisted of Au nanospheres, nanoprisms, and nanorods as the primary phases taking the core/kernel positions and with SnO_2 as the secondary distance-holder phase taking the shell position. The stabilities of these nanocomposite materials were investigated. The morphological analysis of these materials demonstrated strong evidence of structural stability. That is, the kernelled Au structures remained perfectly and uniformly dispersed from each other, thus preserving the colloidal stability. The SnO_2 -coated Au nanospheres, proved to be more durable as opposed to their counterparts. Furthermore, TEM micrographs of the Au nanoprisms revealed the nature/arrangement of the SnO_2 nanoparticles around the Au metal surfaces, this proved to be a mesoporous structural layer. As such, any future application that might seek to utilise the metal surface can do so through the partial pores on the coating material. In addition to improving the stability of the Au nanostructures, SnO_2 has also demonstrated an enhancing capability to the optical properties of these Au structures. That is, enhanced absorption as well as band shift were observed for the nanocomposite materials. This enhancement proved to be due to the refractive index of SnO_2.

5. References

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