

Novel synthetic route for growth of gold nanorods via semiconductor procedure

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ABSTRACT

We represent here a novel facile synthesis type route based on semiconductor procedure for growth of gold nanorods GNRs using infinitesimal silicon nanoparticles USSiN. The reaction takes place immediately upon mixing monodispersed hydrogen terminated USSiN of 2.9 nm diameter with auric acid HAuCl₄ in presence and in absence of an emulsifier. The resulting colloids have been characterized via scanning electron microscope SEM, Energy dispersive spectrometry EDS and optical microscope OM. Photo-luminescence (PL) measurements have been also carried out. Our results show formation of gold nanorods GNRs, gold nanoplates GNPs, gold nanospheres GNSs and filaments. The formed GNRs have near uniform length of 1.5 μm and diameter of 300 nm (5 aspect ratio). The results are consistent with a seedless process in which the H-terminated silicon nanoparticles act as either the reducing as well as the directional growth agent, eliminating the need for toxic cetyl-trimethyl-ammonium bromide CTAB or, which is typically used as the directional growth agent.

Keywords: infinitesimal silicon nanoparticles; gold nanorods; directional growth agent

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1. Introduction

There has been a great interest in exploiting nanomaterials due to their countless uses in various applications such as energy storing systems, solar cells, chemical catalysis and innovative cancer therapies [1-4]. Gold nanoparticles GNPs are one of the most important class of nanomaterials due to its ease of preparation and functionalization [4]. In particular, gold nanorods (GNRs) which have a broad tunable aspect-ratio dependent longitudinal surface plasmon resonance (LSPR), are mainly interesting due to their unique optical properties [4-6]. Therefore, GNRDS have been used in various applications especially biomedical applications such as a bio-sensing or biomedical device [2,7-9] model systems for molecular imaging and targeted therapy [10] and drug delivery systems [11].

Up to now a number of studies for the preparation of gold nanorods have been reported involving a porous aluminum oxide membrane [12], an electrochemical method with surfactant molecules as directing agents [13], photochemical [14,15], sonochemical [16], and radiation-chemical [17,18] methods. The most used synthesis type route to obtain GNRs with a controlled size and shape is the seed-mediated growth method, which was initially developed by Obare *et al.* [19], and Sau and Murphy [20]. Seed-mediated growth occurs through two steps or several pots: the first step is to prepare gold seeds of definite particle size, and the other steps are growth steps of the seeds in presence of cetyltrimethylammonium bromide CTAB as a growth directional agent, ascorbic acid as reducing agent and AgNO₃ as size controlling agent. Recently, many modified seed-mediated growth methods have been reported by various researchers [6, 21-26].

However, there are two problems that limit the GNRs applications first, the presence of (CTAB) on the surface of GNRs which is highly toxic and second, the removal of CTAB may also result in uncontrollable aggregation of GNRs [27]. The mechanism of rod formation is still complex and not very clear. Also, using the same experimental conditions did not achieve exactly the same size and shape of GNRs [28].

In present work, we show for the first time that we can grow gold nanorods, plates, spheres and filaments from gold ions using USSiN seeds as both reducing and growth directional agent eliminating the use of toxic CTAB or metal-based reducers. A plausible mechanism for rod formation is also proposed.

2. Material and Methods

2.1 Materials

All chemicals used are products of Sigma-Aldrich, USA.

2.2 Silicon nanoparticles formation:

Silicon nanoparticles, 2.9 nm in diameter have been prepared by Nayfeh *et al.* [29] from Si wafers by chemical etching in hydrofluoric acid/ hydrogen peroxide HF/H₂O₂ solution using an electric current or hexa-chloroplatinic acid catalyst. The nanoparticles are H-terminated (Si-H) and have band gap of a 2.060 eV [30]. Nanoparticle suspensions are prepared in isopropyl alcohol (IPA). Monte Carlo simulation of the Si nanoparticle suggests a filled fullerene structure of Si₂₉H₂₄, in which a central core silicon atom and four other silicon atoms are arranged in a tetrahedral coordination and the 24 remaining silicon atoms undergo a H-terminated bulk-like (2 × 1) reconstruction of dimer pairs on (001) facets (6 reconstructed surface dimers) [31]. The structure of the silicon nanoparticle is represented in **Figure 1**.

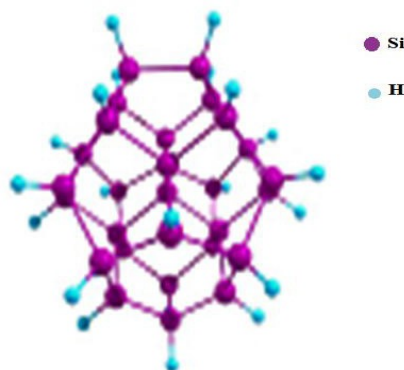


Figure 1. Ultrasomal silicon nanoparticle USSiN [31].

2.3 Formation of gold nanorods GNRs in absence of an emulsifier:

We use a solution of 10 mM of auric acid (HAuCl₄) as a source of gold ions. In the procedure, 0.5 ml of 1.65 mM auric acid solution is added to Si nanoparticles dispersed in IPA solution. A fast reaction occurs leading to change in color from yellow to pale pink color characteristic for gold nanoparticles.

2.4 Formation of gold nanorods GNRs in presence of an emulsifier:

0.05 μL dodecyl benzene sulfonic acid DBSA as an emulsifier has been added to silicon nanoparticles dispersion in isopropyl alcohol IPA, followed by adding 0.5 ml of 1.65 mM auric acid HAuCl₄ solution under continuous vigorous stirring using high shearing effect homogenizer. The reaction takes place immediately giving rise to fast color change from yellow to pale pink color characteristic for gold nanoparticles.

2.5 Characterization of GNRs

2.5.1 Scanning electron microscope (SEM):

Samples have been measured using SEM JOEL 6060 LV, Japan at the MRL Lab, University of Illinois – Urbana Champaign (UIUC).

2.5.2 Light microscope (LM):

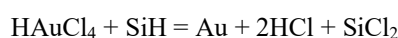
The samples have been examined by Mitutoyo Micro-scope, MRL fabrication facility, University of Illinois at Urbana Champaign (UIUC), USA.

2.5.3 Photoluminescence spectroscopy

A fiber-optic spectrometer (ocean optics, USB4000, USA) with excitation in the UV region is used to record the luminescence spectra of the prepared samples.

3. Results and discussion

GNRDs have great potential for applications in display technologies because the reflectivity of the rods can be changed by changing their orientation with an applied electric field for; as well as in microelectromechanical systems (MEMS). Moreover, nanorods may find application in biomedical imaging, drug delivery and photothermal therapy due to unique surface plasmon resonance (SPR) ranging from visible to near infrared (NIR) region. The mechanism of formation of GNRDs has received concentrated activity in recent years yet it is not completely understood. However, it has now been demonstrated that the necessary ingredients for forming GNRs [20] are (i) the presence of gold ions in solutions, (ii) a mild reducing agent, (iii) a shape-control or directing surfactant, which forms a rod shaped template that is filled with gold atoms (CTAB for example), otherwise, only spheres would form, and finally (iv) a protecting agent to prevent aggregation (such as polyvinyl alcohol PVA and CTAB (plays this role) for example). In this paper, we report on a new facile synthesis type route in which we use monodispersed H-terminated USSiN of 2.9 nm diameter as both reducing as well as directional growth agent, eliminating the need for CTAB as a directional growth agent. Forming metal gold structures from gold ions requires a reducing agent. It is plausible that the silicon nanoparticles act as a reducer. Once gold ions are attracted to the silicon nanoparticles, they get reduced spontaneously. The overall neutral reduction reaction is as follows:



After gold ions got reduced, the formed gold atoms diffuse in the particle, making an amorphous agglomerate of Au-Si, which act as a gold seed. More and more ions get reduced and diffuse to the gold seed, while pushing the silicon material outward in a near floating condition. This action is assembling into a gold nano structure, most likely a wire or rod configuration. The mechanism of Formation of GNRs is represented in **Figure 2**.

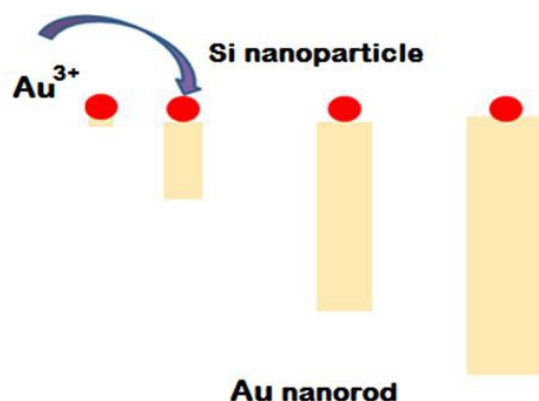


Figure 2. Gold nanorod GNRs formation

3.1. Characterization of GNRs

3.1.1 Scanning electron microscope SEM

The resulting colloids have been characterized by SEM. A thin film was made by dispensing a certain volume of the formed colloid on device quality silicon wafer. **Figure 3** gives a scanning electron microscope image of the colloid formed in presence of DBSA. Our results show formation of gold nanorods with near uniform length of 1.5 μm and diameter of 300 nm (5 aspect ratio). One can see also some non-cylindrical GNRs. The figure also shows examples of close up of monodispersed GNRDs and GNSs. The sizes of GNSs are in the range from 200-300 nm. The GNRDs lengths are in the range from 1.5 to 5 μm . The rods of length 1.5 μm and diameter 300 nm (aspect ratio of 4–5) are more frequent.

Figure 4 shows SEM image for the colloidal dispersion prepared in absence of an emulsifier. The figure shows formation of massive assembly of gold filaments.

Figure 5 displays other nano structures that this procedure in absence of an emulsifier can yield, including gold nanoplates GNPs (squares).

The gold-silicon (Au-Si) binary system belongs to the eutectic-alloy compounds, which exhibits lower melting temperatures and transform directly between solid and liquid [32]. This enables wafer-bonding, device connection and growth of Si nanowires using nanogold seeds.

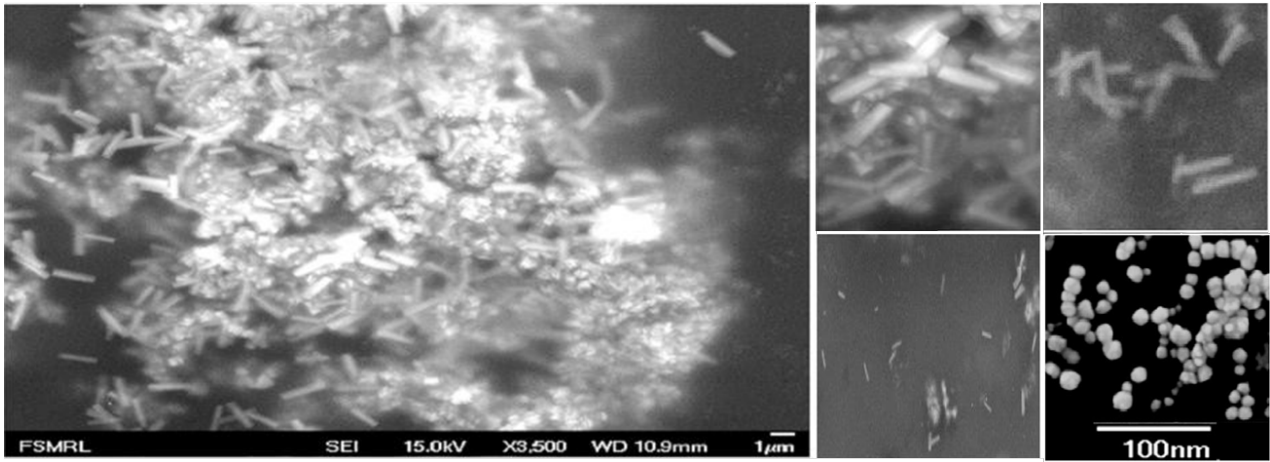


Figure 3. SEM images of GNRs and spherical particles (in presence of an emulsifier)

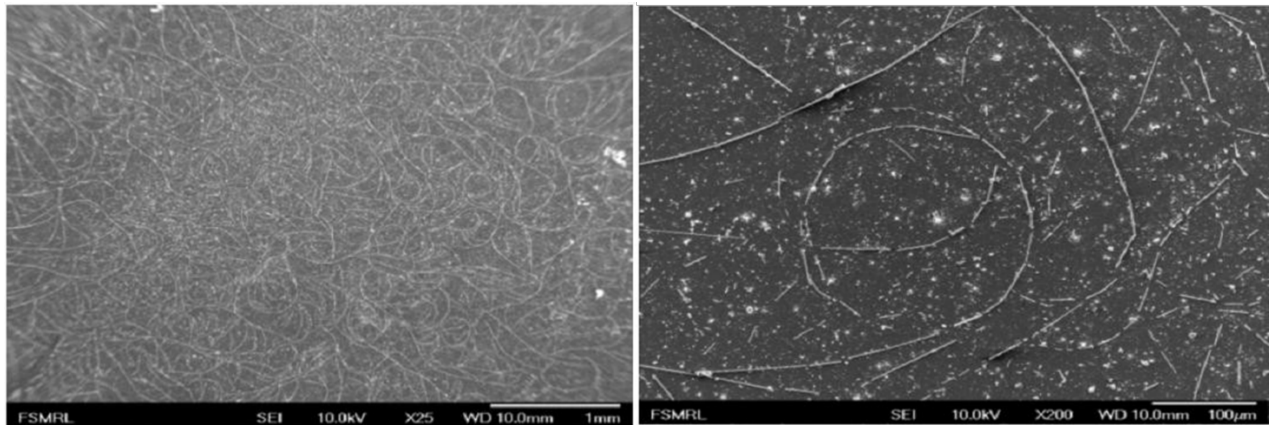


Figure 4. SEM images of gold nanofilaments in (absence of emulsifier)

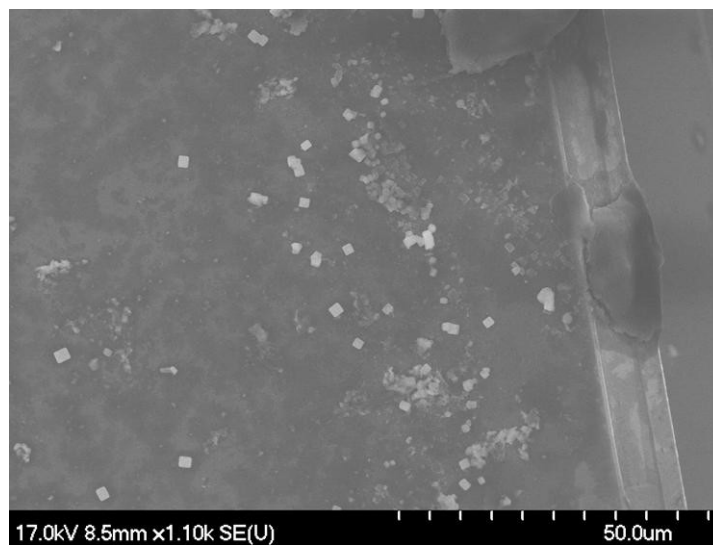


Figure 5. Gold nano plates in absence of emulsifier

Figure 6A shows that nanocomponents beneath some of the plates/sheets are observable with SEM imaging (electronically visible) indicating that those sheets are ultrathin. To get a measurable signal from beneath, incident electrons must suffer absorption due to two passes through the top plate and a backscattering from the structure under. Using the relation $I = I_0 e^{-x/\lambda}$ where I_0 is the primary electron current, I is the transmitted current without deflections, x is the film thickness, and λ is the mean free path. For a free mean path of $\lambda = 1$ nm, and backscattering efficiency of 0.5 at 30 KeV [33], we get 0.07 for I/I_0 which is measurable.

Figure 6B shows several images of 2-D plates or sheets of gold in the act of side-to side (lateral) coalescence. The process is characterized by a growing neck. Observing coalescence at room temperature is consistent with the sheets being ultrathin (~ 1 nm thick). In detailed simulations using a number of mechanisms models, it was found that coalescence between two identical particles accelerates for smaller particles since the melting temperature drops considerably for the infinitesimal particles (~ 300 °C for 2.5-nm nanoparticles, compared to 1064 °C for bulk) [34].

Figure 6C shows several examples of when sheets are stacked on top of each other. In a complete contact configuration, vertical coalescence over the entire sheet takes place simultaneously. In this case sheets dissolve and fade away.

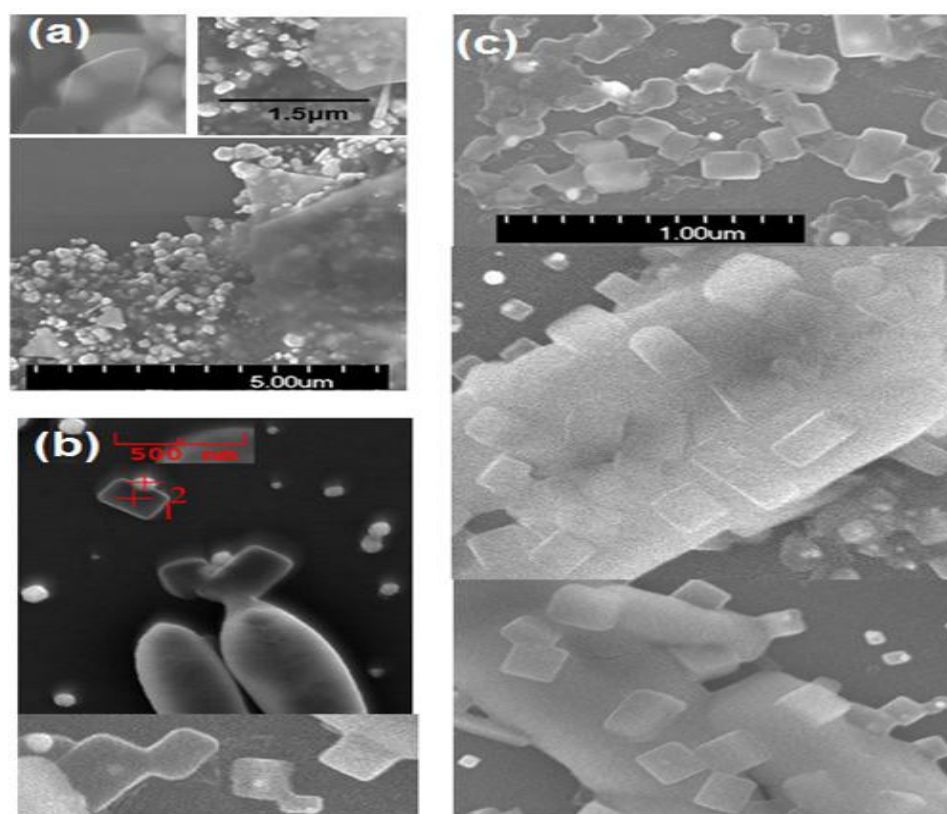


Figure 6. Vertical and lateral coalescence and melting of 2-D plates into each other (in the absence of emulsifier)

Figure 7 shows the elemental analysis by energy-dispersive spectrometry (EDS) taken with incident 30 KV X-ray. It shows 2 characteristic peaks for gold at 2.13 eV which given off as electrons return to the inner electron Ma shells of gold and a smaller peak at 9.7 eV which confirms the presence of gold nanoparticles.

3.1.2 Optical Microscope

We used an optical microscope (magnification is $10\times$) to observe the optical characteristics of the formations observed by SEM. **Figure 8** gives two images of the sample and the left one is a close-up view for orange spots. **Figure 8** shows the large assemblies of the gold filaments as dark brown. We also observe orange-green spots which are surrounded by light brown and dark brown spots. For regions where the green to yellow color is most dominant, we believe it is scattering from gold nanospheres [35], corresponding to the surface plasmonic enhancement of scattering light in the

visible region. This could also emanate from the plasmonic transverse mode of nanorods. On the other hand, the dark and light brown areas are due to gold nanorods, corresponding to the surface plasmonic enhancement of the longitudinal oscillation.

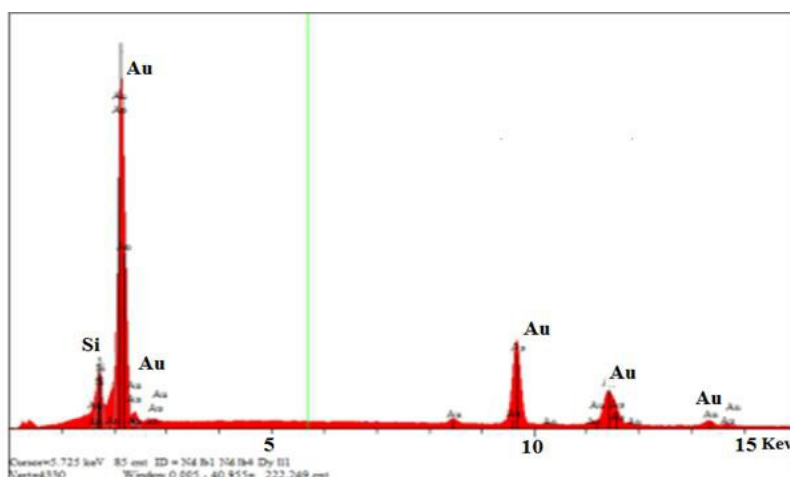


Figure 7. Energy dispersive spectrum for GNRs



Figure 8. Light microscope images for GNRs and GNSs

3.1.3 Photoluminescence measurements

We have conducted the absorption measurements of the colloidal dispersion of the formed GNRs as well as Si nanoparticles dispersion in IPA under the UV-excitation at 365 using UV lamp. **Figure 9a, b** shows the luminescence spectra of SiNPs and GNRs respectively. As shown from figure 9a upon irradiation by UV radiation at 365 nm the SiNPs emit orange red light in the range from 580 to 620 nm ^[36]. **Figure 9B** shows that the red luminescence of the SiNPs disappeared as the gold nanostructure formed.

4. Conclusion

The present procedure represents the first demonstration of the use of semiconductor silicon nanoparticles seed to grow gold nano-rods without metal-based reducers or organic dimensional growth agents. It can also produce gold nanoplates and spheres. We recorded also millimeter-long filaments that exhibit anticrossing, as well as disordered end-to-end and end-to-side networks of gold nanorods. The resulting colloid was characterized. Our results show formation of gold nanorods with near uniform length of 1.5 μm and diameter of 300 nm (5 aspect ratio). The gold-silicon (Au-Si) binary system belongs to the eutectic-alloy compounds, which exhibits lower melting temperatures and transform directly between solid and liquid. Our results showed that the formed sheets are stacked on top of each other and in this case the sheets dissolve and fade away. This will enable wafer-bonding, device connection and growth of gold nanorods and filaments using Si nanoparticles seeds.

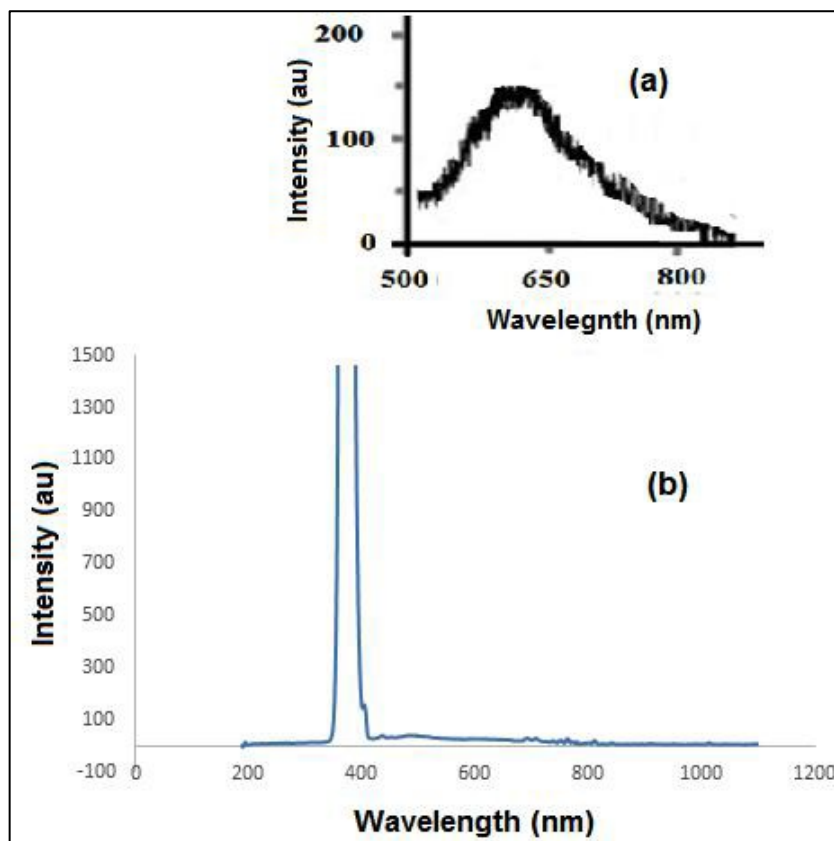


Figure 9. Photoluminescence spectra of (a) SiNPs and (b) GNRs.

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