Acta Scientific Applied Physics

Volume 2 Issue 10 October 2022

Review Article

Gold Quantum Dots Based Thin Film Fabrication and Topographic Measurements

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Received: September 12, 2022

Published: September 26, 2022

Abstract

The project deals with the synthesis of gold quantum dots coated with didodecyldimethylammonium bromide (DDAB) and their electronic property study by fabricating thin film. Gold is a noble metal, and its quantum dots shows completely different electronic and optical properties than bulk. DDAB coating on gold quantum dots (QDs) gives a layer of positive charge on its surface. Hence, it can form a monolayer or multilayer thin film using the anionic inert polymer as counter layer due to the electrostatic attraction on different substrates. This electrostatic attraction only helps to grow the thin films without disturbing real QDs properties of gold. We prepared our gold QDs using chemical reduction synthesis. The optical property of the thin film has been characterized by UV vis and photoluminescence spectroscopy. The surface topography of the thin film has been characterized using Scanning Tunneling Microscopy. This work shows the successful formation of Gold QDs with a near uniform surface topography.

Keywords: Quantum Dots; STM; Spectroscopy; Gold Nano Particle

Introduction

Quantum dots of noble metals can be used as advanced materials as it possesses good electronic, optical, and thermal properties as well as catalytic properties and hence can be used in the fields of physics, chemistry, biology, medicine, and material science. Therefore, the synthesis and characterization of metal quantum dots has attracted a number of scientists to this field of research. Till date a variety of methods have been developed to prepare metal quantum dots. Modern scientific evaluation of colloidal gold was started by Michael Faraday in the 1850s. In 1856 basement laboratory of Royal Institution Faraday accidentally created a ruby red solution while mounting pieces of gold leaf onto microscope slides. As he was already interested in the properties of light and matter, Faraday further investigated the optical properties of the colloidal gold. His first prepared pure sample of colloidal gold was called 'activated gold', in 1857. In the Turkevich method of Au NP synthesis, citrate initially acts as the reducing agent and finally as the capping agent which stabilizes the Au NP through electrostatic interactions between the lone pair of electrons on the oxygen and the metal surface [1]. DDAB has also been used as a protective reagent for the formation of monolayer-protected gold quantum dots (Au QDs) in an organic medium in our group. In this study, we shall use a standard method for the preparation of very stable, DDAB lipid bilayer - protected Au QDs in an aqueous medium by in situ chemical reduction of $HAuCl_4$ with $NaBH_4$ in the presence of DDAB

[2,3]. The formation of DDAB-protected gold QDs was evidenced by UV-vis spectra and later its optical characteristics was determined by photoluminescence spectra. In addition after thin film synthesis of this Au QDs Scanning Tunneling Microscopy will be used to determine its electronic properties and device fabrication.

Experimental details

Raw materials

Aurochloric acid ($HAuCl_4$), freshly prepared sodium borohydride ($NaBH_4$), DDAB (didodecyldimethylammonium bromide), Deionised water.

Synthesis of DDAB lipid bilayer-protected gold quantum dots

We took 60 ml solution of 1.4 mM DDAB and deionised water in a beaker. We kept the beaker in magnetic stirrer at 850 rpm and then we added 375 µL of 0.048M $HAuCl_4$ to the solution. Further we added 200 µL of 0.4M freshly prepared $NaBH_4$ dropwise and the colour slowly changed to the wine red as shown in figure 1. The wine red colour indicates the formation of gold quantum dots. We stored the sample at room temperature for further analysis.

Figure 1: Photograph of as synthesized DDAB coated Au QDs solution.

Optical characterizations

UV-vis and Photoluminescence spectroscopy

We took 2ml of the prepared gold quantum dots solution and used it for UV-vis and photoluminescence spectroscopic analysis. The UV-vis spectroscopic analysis of DDAB coated gold quantum dots in aqueous solution was carried out by PerkinElmer LAMBDA 950 UV/vis/NIR Spectrophotometer and wavelength scanned from 380 to 850 nm to record the absorbance spectra. It has shown the peak absorbance peak at 521 nm due to surface plasmon resonance as shown in figure 2 b [4]. Theoretical formulations have been performed based on analytical formulation of Rayleigh approximation presented by Esumi., *et al*. [5] as shown in figure 2a. There is a good match between analytical and measured value.

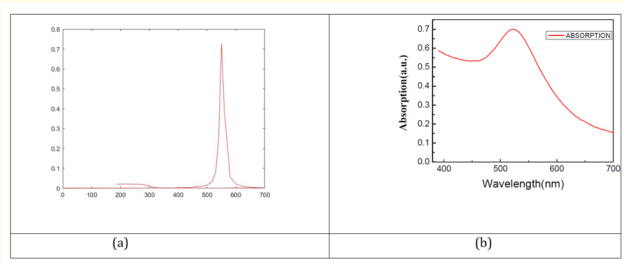

Figure 2: (a) Theoretical formulation showing absorption peak of Gold QDs, (b) UV-vis spectroscopy analysis of DDAB coated gold quantum dots dispersed in DI water.

The formation of gold quantum dots is evidenced by UV-vis spectra of the colloidal gold solution thus formed, as shown in figure 2b. The peak of the plasmon resonance band is located at 521 nm, which indicates the formation of gold quantum dots. DDAB coated gold quantum dots are very stable and do not get agglomerated or precipitated. Excitation and Emission spectra of this solution were recorded with Horiba Nanolog photoluminescence tool. Emission spectra is recorded for the wavelength range 500 to 850 nm and we used 490 nm as the excitation wavelength which is higher than the resonance band gap wavelength 521 nm. The emission spectra showed the peak at 736 nm as shown in figure 3. For recording excitation spectra, the scanning wavelength range was 300 to 700 nm and emission peak was fixed at 736 nm. The excitation spectra showed the peak position at 499 nm as shown in figure 3 which is showing blue shift compared to UV-vis peak position.

The formation of gold quantum dots was confirmed by photoluminescence analysis of the colloidal solution as shown in figure 3 above. The emission spectra showed the peak at 736 nm and the excitation peak at 499 nm. The difference of wavelength from UV-vis and excitation spectra is due to blue shift of gold quantum dots.

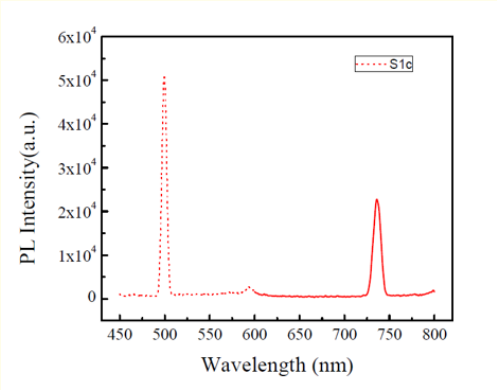

Figure 3: Photoluminescence analysis of DDAB coated gold quantum dots dispersed in deionized water the dotted graph shows excitation and the solid graph shows the emission spectra.

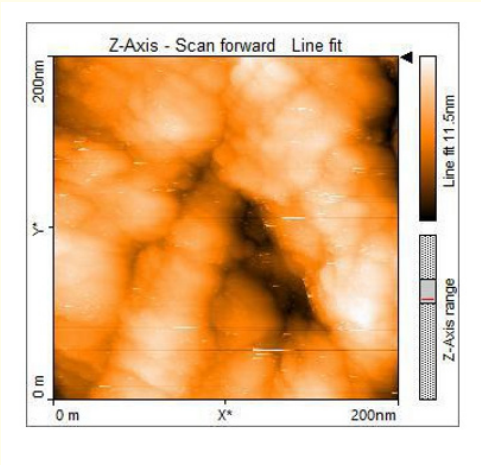

Figure 4: Measured STM topographic image of gold thin film using a mechanically cut STM tip.

Scanning tunneling microscopy (STM) analysis

Standardization of the probe

The instrument to be used is scanning tunneling microscope. The tip is made of platinum iridium wire (Pt/Ir)0.8/0.2. The tip is cut using mechanical techniques. This tip will be used to analyse the topography of gold quantum dots based thin films and doing electronic measurements. A good tip is one which will have single atom at the end. Mechanical cutting cannot provide such a high accuracy. Hence to check whether the tip is suitable for measuring my sample the step followed is analysis of standard samples like HOPG and Gold thin film to observe its topography and perform spectroscopic analysis. If the image observed with the standardized samples bear close resemblance to the standard structure, then the tip can be used for the actual experimental sample analysis. Figure 4 shows that our deposited gold thin film topography is nearly uniform and matches with standard published data by previous authors. Thus, confirming successful thin film preparation.

Conclusions

We worked on chemical synthesis of gold quantum dots (Au-QDs) and checked the optical properties of prepared sample using UV-vis and photoluminescence spectroscopy. The tip standardization of the mechanically cut STM tip was done first with a standard gold thin film, followed by our thin film characterization. The measured topographic images bear close resemblance to standard topographic images. Hence the tip is good and can be used for STM and STS analysis of DDAB coated monolayer thin film. Thin film preparation is successfully completed, and its electronic measurement is the scope of our future work.

Acknowledgements and Fundings

The author would like to acknowledge Dr Bikas C. Das and Mr Anubhab Dey of IISER Trivandrum for helping in successful completion of the project. The project has been funded by IISER Trivandrum, Department of Physics summer 2016 visiting student research funding.

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