ФИЗИКО-МАТЕМАТИЧЕСКИЕ НАУКИ

MODERN TECHNIQUES FOR DETERMINING THE SIZES OF GOLD NANOPARTICLES

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Аннотация

Золото при наноразмерах показывает необычные физические, химические и биологические свойства. В этой работе, для получения коллоидных наночастиц золота мы восстановили водный раствор золотохлороводородной кислоты ($HAuCl_4$) при помощи цитрата натрия, а также из того же раствора химическим способом осадили нанослой золота на Au-n-GaAs полупроводниковой наноструктуре. Для определения размеров и степени полидисперсности наночастиц мы воспользовались методом динамического рассеяния света. Поверхностную морфологию изготовленных наноструктур и размеры поверхностных наночастиц золота мы проанализировали с помощью атомно-силового и сканирующего электронного микроскопов. Также были определены преимущества и недостатки метода динамического рассеяния света, атомно-силового и сканирующего электронного микроскопов в определении размеров наночастиц.

Abstract

At nanoscale, gold exhibits unusual physical, chemical and biological properties. In this work, we reduced an aqueous solution of tetrachloroauric acid ($HAuCl_4$) with sodium citrate to obtain colloidal gold nanoparticles and we covered the Au-n-GaAs semiconductor structure with a gold nanolayer by chemical deposition from the same solution. To determine the size and the polydispersity of the nanoparticles we have used the dynamic light scattering method. The surface morphology of structures and the size values of the surface gold nanoparticles we analyzed with the atomic force and the scanning electron microscopes. The advantages as well as the disadvantages of the dynamic light scattering, the atomic force and the scanning electron microscopes in size determination of nanoparticles were also defined.

Ключевые слова: наночастицы золота, золотохлороводородная кислота, размер частицы, динамического рассеяния света, атомно-силового микроскоп, сканирующего электронного микроскоп.

Keywords: gold nanoparticles, tetrachloroauric acid, particle size, dynamic light scattering, atomic force microscope, scanning electron microscope.

1.INTRODUCTION

Research in nanotechnology is increasing and is prioritized in developed countries such as the United States, the United Kingdom and Japan. This technology exploits the unique properties of nanoparticles. These are particles ranging from 1 to 100 nm. Depending on the type of material, nanoparticles can be broadly divided into four classes: metallic, semiconductor, magnetic and others [1]. In this work, we focus on metal and, in particular, gold nanoparticles. Gold nanoparticles have attracted extensive attention due to their applications in various fields, such as medicine, biotechnology, catalysis, and nanoscale electronics, and are thus the most intensively studied nanoparticles [2-5]. Great interest in the study of structures of different chemical composition, structure and morphology is caused by extraordinary physicochemical, electromagnetic, optical, mechanical and other properties of nanomaterials that opens wide prospects of their practical applications [6-9,10]. The small size of nanoparticles in the range from 1 to 100 nm determine the uniqueness of their properties [11]. Certainly, the main impetus for this research is that nanoparticles exhibit size-dependent properties that are very different to the constituent bulk material. Implicit in this, is that actual dimensions of the nanoparticles are critical for their properties, and thus suitability for any application. Therefore, for any potential application, it is of extreme importance that suitable techniques are used to characterize the nanoparticles, in order to understand this structure-property relationship. Many different techniques have been applied to the study of nanoparticle dimensions during the past few decades of nanotechnology research [12,13]. Amongst these, microscopic techniques provide direct imaging of the dry particles. On the other hand, several techniques can be applied to particle solutions, such as dynamic light scattering, which measures the diffusion coefficient of particles in solution. At the present time, the following techniques are commonly used to determine the sizes of nanoparticles: dynamic light scattering, atomic force microscope and scanning electron microscope.

In this work, we determined sizes of gold nanoparticles, which prepared under different experimental conditions by three different modern techniques. They are dynamic light scattering, atomic force microscopy and scanning electron microscopy. The sizes of synthesized colloidal gold nanoparticles are determined by dynamic light scattering. We analyzed the surface morphology and the sizes of surface gold nanoparticles with an atomic force and scanning electron microscopes of Au-n-GaAs structure, which was prepared by the chemical deposition method at low temperature. Moreover, we have defined the advantages and disadvantages of the three techniques.

1.1.Dynamic light scattering

Dynamic light scattering, a technique often referred to as photon correlation spectroscopy, is a

common technique for determining particle size in colloidal suspensions. Particles suspended in a liquid solvent undergo random Brownian motion. Light is scattered off the particles in suspension. Since the particles cause localized changes in the refractive index, intensity variations are produced by the particles and evaluated using the second order normalized autocorrelation function

$$g_2(\tau) = \frac{G_2(\tau)}{<I>^2} \quad (1)$$

where $< I >$ is the average intensity, τ is the correlation time, and $G_2(\tau)$ is the temporal correlation function. The second order normalized correlation function is then related to the first order correlation function $g_1(\tau)$ where $g_1(\tau)$ is expressed as

$$g_1(\tau) = e^{-q^2 D\tau} \quad (2)$$

for particles subject to Brownian diffusion where q is the magnitude of the scattering vector and D is the translational diffusion coefficient. The scattering vector q is expressed as

$$q = \frac{4\pi n}{\lambda_0} \sin(\frac{\theta}{2}) \quad (3)$$

where n is the refractive index of the solution, λ_0 is the wavelength of incident light in vacuum, and θ is the scattering angle of light. The sizes of particles in solution are determined using Stokes-Einstein equation

$$D = \frac{kT}{6\pi\eta R_h} \quad (4)$$

where D is the diffusion coefficient, k is Boltzmann's constant, T is the temperature, η is the solvent viscosity, and R_h is the hydrodynamic radius of the particles in solution [14-18].

1.2.Atomic force microscopy

The atomic force microscope, developed in 1986 by Binning et al. enables users to characterize nanoscale objects. The atomic force microscope utilizes piezoelectric ceramics to move a specimen in nanoscale increments in the X, Y, and Z directions. An atomic force microscope tip mounted on a cantilever is positioned above the specimen at a distance where the tip is repelled or attracted by the forces due to the interaction with the specimen surface. As the specimen is moved below the tip, the cantilever bends due to topography changes as the tip maintains a constant force from the surface. A laser reflects off the cantilever to a photo-detector. Detector electronics reads the deflection of the laser, processes it through the feedback loop, and the data acquisition software turns the measured deflections into a 3-dimensional image.

The ability of an atomic force microscope to characterize nanoscale objects makes it an ideal characterization tool for determining particle size distributions as well as image complex arrays of nanoparticles [19-21]. It has also been proposed that nanoparticles could function as a calibration standard for the atomic force microscope [22].

1.3.Scanning electron microscopy

In scanning electron microscope, a set of coils moves the electron beam across a sample in a two dimensional grid. When the electron beam across over the sample, different interactions occur. Some of the electrons from the surface material kick of their electrons by the beam thus producing secondary electrons. The secondary electron detector on a scanning electron microscope can then detect these secondary electrons. An image is then produced at the surface of the sample and is projected. Scanning electron microscope images can be magnified up to 100,000 times while maintaining a high resolution [23].

2.EXPERIMENTAL

2.1.Material and reagents

For the synthesis of colloidal gold nanoparticles, we used tetrachloroauric acid ($HAuCl_4$) as gold precursor and sodium citrate ($Na_3C_6H_5O_7$) as a reducing agent. The concentration of $HAuCl_4$ aqueous solution was 12 mM. We used freshly prepared sodium citrate. The glassware used was all cleaned in a bath of freshly prepared aqua regia solution, and then rinsed thoroughly with de-ionized water before use. We covered the Au-n-GaAs semiconductor structure with a gold nanolayer by chemical deposition from $HAuCl_4$ aqueous solution.

2.2. Instruments

The preparation of colloidal gold nanoparticles was carried out by magnetic stirrer (AMTAST, MS-400). Size and size distribution of colloidal gold nanoparticles were analyzed by the dynamic light scattering method (PHOTOCOR Mini, 130130). To weigh chemicals and reagents, we used microscale (METTLER TOLEDO, MS204S). For the reactions, we used the chemical glassware (KLIN) and the pipette (Thermo Fisher Scientific) to transport a measured volume of liquids. Surface morphology and the sizes of surface gold nanoparticles of Au-n-GaAs structure were analyzed by scanning electron microscope (JEOL JSM-7500FA). Two-dimensional and three-dimensional images of surface morphology of Au-n-GaAs structure were taken by atomic force microscope (Nano Scan Technology 130081153).

2.3.Dynamic light scattering sample preparation

Colloidal gold nanoparticles were synthesized by the Turkevich method [24]. Briefly, tetrachloroauric acid (HAuCl4) was reduced with sodium citrate. C=0.5 mM and V=300 mL of the HAuCl4 aqueous solution was stirred vigorously and heated under reflux. C=38.8 mM and V=30 mL of the sodium citrate was added when the HAuCl4 aqueous solution was boiling ($T=100^0C$) and left to refluxing for an additional 30 minutes [25].

2.4.Atomic force microscopy sample preparation

Our sample is Au-n-GaAs structure. We covered the Au-n-GaAs semiconductor structure with a 120-150 Å gold nanolayer by chemical deposition from aqueous solution of $HAuCl_4$ at room temperature ($T=27^0C$) [26].

2.5.Scanning electron microscopy sample preparation

Our sample is Au-n-GaAs structure. We covered the Au-n-GaAs semiconductor structure with a 120-150

Å gold nanolayer by chemical deposition from aqueous solution of $HAuCl_4$ at room temperature (T=27^{0}C) [26].

3.RESULTS AND DISCUSSION

3.1.Dynamic Light scattering technique

Dynamic light scattering (DLS) provides a lot of possibilities to obtain information about such properties as size of nanoparticles and diffusion coefficient. The sizes of colloidal gold nanoparticles were measured using a PHOTOCOR Mini 130130 equipped with a 25 mW temperature stabilized diode laser (654 nm) and operating at an angle of 90^0 and a room temperature. A sample volume 2.5 ml was used in 10-mm-diameter cuvettes. All measurements were carried out at room temperature (T=23^0 C) with Photocor software package. Then we used DynaLS software package to analyze the data. The DLS intensity size distribution of synthesized colloidal gold nanoparticles are shown in Figure 1. The size (radius) and polydispersity of synthesized colloidal gold nanoparticles are 15.27 nm and 0.419.

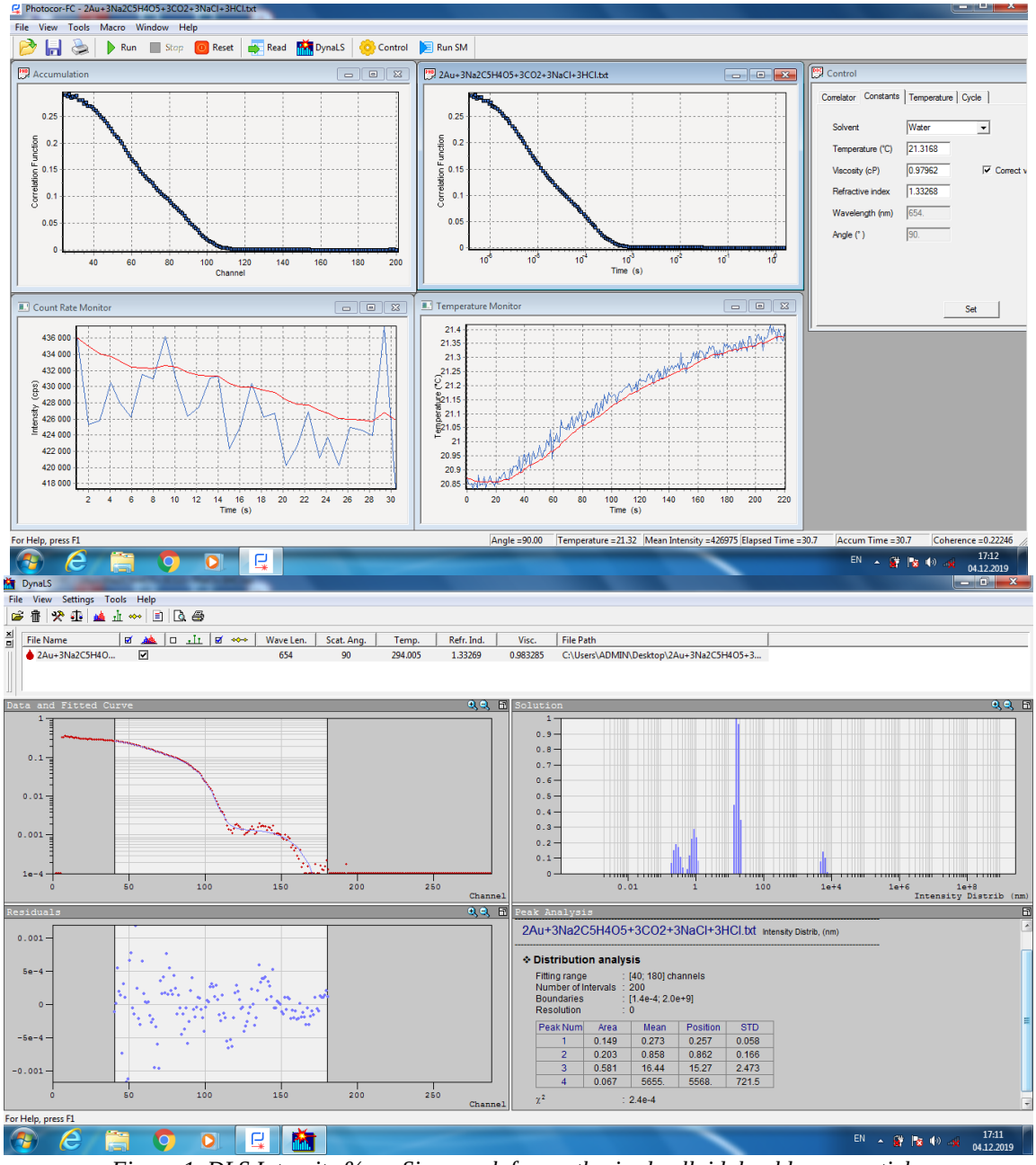

Figure 1. DLS Intensity % vs. Size graph for synthesized colloidal gold nanoparticles

3.2.Atomic force microscopy technique

The Atomic force microscope data is considerably different to the other two techniques because it contains information in three spatial dimensions. The image of surface of Au-n-GaAs structure was taken at room temperature (T=23^0 C). Then the size of surface gold nanoparticles of Au-n-GaAs structure was determined using atomic force microscope Nano Scan Technology 130081153. The image size was varied so that 200-400 particles were detected in image. Most of particles are spherical. Two and three-dimensional morphology of surface of Au-n-GaAs structure are shown in Figure 1 and Figure 2.

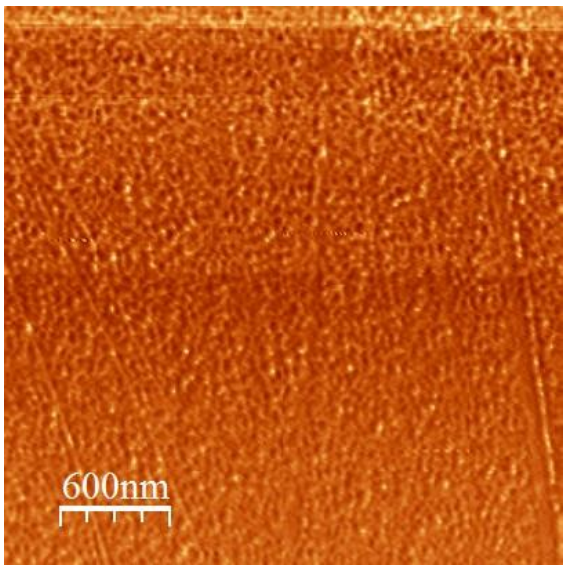

Figure 2. The image of Au-n-GaAs structure that was taken from Au side using atomic force microscope. Two-dimensional morphology of surface

Analysis of two-dimensional surface morphology of surface of Au-n-GaAs structure shows size (radius) of most of surface gold nanoparticles is 10 nm.

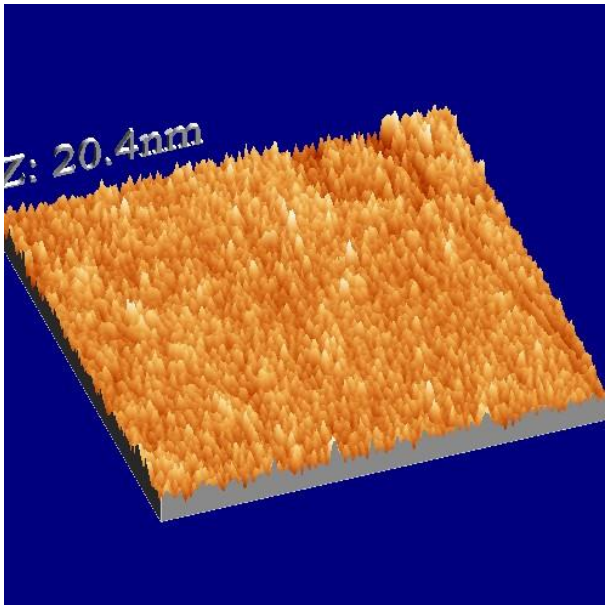

Figure 3. The image of Au-n-GaAs structure that was taken from Au side using atomic force microscope. Three-dimensional morphology of surface

In fact, in Atomic force microscope images the height dimension (z-axis data) is typically used to determine the diameter of spherical particles [27], and this method was used in this work. Figure 3 shows z-axis data is 20.4 nm and this means the size (radius) of most surface gold nanoparticles is 10.2 nm.

3.3.Scanning electron microscopy technique

Scanning electron microscope presented the most difficulties in obtaining images, and for every sample, several different imaging and sample preparation conditions were tested before optimal conditions were found. Two-dimensional morphology of surface of Au-n-GaAs structure is shown in Figure 4. 300 particles was detected in image. The most of detected particles are spherical. The image magnified 75000 times using scanning electron microscope JEOL JSM-7500FA. Image of sample was taken at 5 kV in vacuum. Analysis of two-dimensional surface morphology of surface of Au-n-GaAs structure shows size (radius) of surface gold nanoparticles varies 10-15 nm.

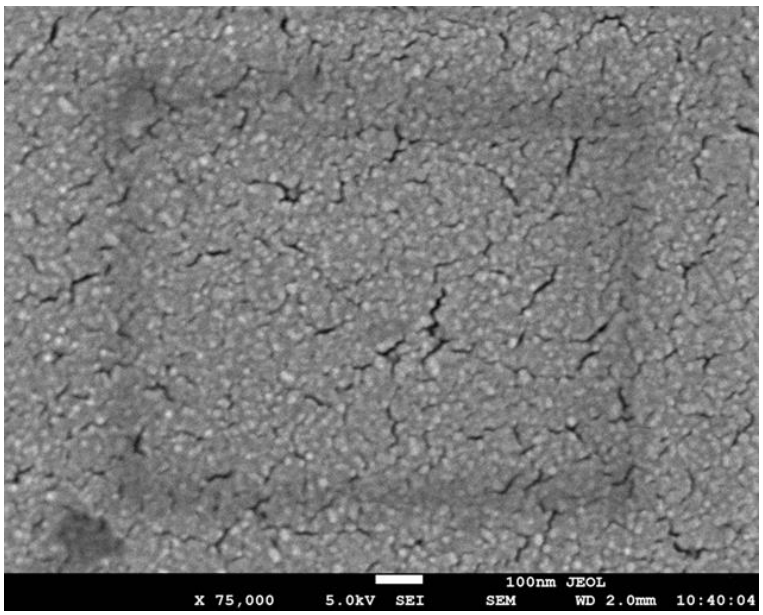

Figure 4. The image of Au-n-GaAs structure that was taken from Au side using scanning electron microscope. Two-dimensional morphology of surface

4.CONCLUSION

At nanoscale, gold exhibits remarkably unusual physical, chemical and biological properties. In this research we have applied the citrate reduction of tetrachloroauric acid in an aqueous medium to obtain colloidal gold nanoparticles. We covered the Au-n-GaAs semiconductor structure with a 120-150 Å gold nanolayer by chemical deposition from $HAuCl_4$ aqueous solution at room temperature ($T=27^0C$) [26]. To determine the size and the polydispersity of the nanoparticles we have used dynamic light scattering technique, while to analyze the surface morphology and the sizes of surface gold nanoparticles of Au-n-GaAs structure, which was prepared by the chemical deposition method at low temperature we have used atomic force and scanning electron microscopy techniques. Moreover, this paper also discusses the advantages and disadvantages of the three techniques. Atomic force and scanning electron microscopy techniques were used on dried samples, and dynamic light scattering technique used on solution sample. The main advantages of atomic force and scanning electron microscopy techniques are to give information on size, size distribution, and shape of particles and surface morphology of sample. The disadvantage of dynamic light scattering technique is to give information only on size and size distribution of particles. One serious disadvantage of atomic force and scanning electron microscopy techniques is the risk of changes in particle properties during drying and contrasting of the sample. Moreover, atomic force and scanning electron microscopes are the relatively expensive of apparatus and complex to use. The main advantages of dynamic light scattering technique are the short time required to perform the measurements and the relatively low cost of the apparatus. Dynamic light scattering, therefore, has become the preferred technique for nanoparticle sizing. It can be very powerful if used carefully. All of the techniques used here have considerable value as methods to determine dimensions of nanoparticle samples. However, the most appropriate technique depends on sample type, as well as the type of information, which is required. Overall, before choosing a technique to characterize a nanoparticle sample, it is recommended that researchers consider the type of information required and the appropriateness of the techniques to particular samples, in particular considerations such as the size of the nanoparticle, and the material of which it is composed. A combination of methods, with careful interpretation of the data is usually the best option.

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ИНЖЕНЕРНЫЙ ВЗГЛЯД НА ПРОЦЕССЫ ВЗАИМОДЕЙСТВИЯ ЭЛЕКТРОМАГНИТНОГО ИЗЛУЧЕНИЯ С ПРОТОНАМИ, НЕЙТРОНАМИ И АТОМНЫМИ ЯДРАМИ

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Аннотация

В данной статье рассматривается взаимодействие электромагнитного излучения с ядрами атомов на основе теории приёмных и передающих антенн, а также линейных, апертурных антенн и антенных решёток, применяющихся в устройствах радиоэлектронных средств. Предлагается альтернативный взгляд на опыт Комптона в части не смещенного излучения на атоме в целом. На основе предложенных фактов сделаны выводы о некоторых свойствах кварков.

Ключевые слова: Атом, кварк, антенна, электромагнитное излучение, свойства кварка

Как известно фотоны рентгеновского излучения имеют энергию от 100 эВ до 250 кэВ, что соответствует излучению с частотой от $3 \cdot 10^{16}$ до $6 \cdot 10^{19}$ Гц и длиной волны 0,005—10 нм т. е. от 10^{-14} до 10^{-8} м, что согласуется с линейными размерами атомов: их радиусы составляют от 0,3 до 2,6 ангстрема (1 ангстрем = 10^{-10} м). Радиус ядра около 10^{-5} ангстрема, то есть 10^{-15} м. Т.е. ядро атома работает как антенна поглощающая ЭМИ. А как известно чтобы антенна хорошо ловила ЭМ её длина должна быть сопоставима с длиной волны ЭМИ а наилучшие результаты дают четвертьволновые (для штыревых) или 2 четвертьволновых отрезков (для дипольной) .

Кроме того самые энергичные гамма-кванты (т.е с наименьшей длиной волны - $\mathbf{10^{-14}}$) даже внедряются в структуру элементарных частиц, таких как протоны и нейтроны. Сопоставим их линейные размеры - $0{,}8 \cdot 10^{-15}$ протона что опять таки согласуется с приёмом ЭМИ антенной, особенно если учитывать что протон в современных представлениях состоит из 3 кварков