

## Laser-induced nanoparticles in electroanalysis: Review

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Electroanalytical techniques have a broad application for chemical analysis of various samples because of their advantages such as versatility and high sensitivity. To improve the efficiency of the analytical setup, the electrodes for such measurements can be modified with nanoparticles. Laser synthesis is a promising candidate to fabricate suitable nanoparticles and has numerous advantages. The Review presents a description of laser techniques of synthesis of nanoparticles as well as achievements and prospects of usage of obtained nanoparticles in electroanalytical methods, which is important for its further application.

**Keywords:** laser synthesis, ablation, dewetting nanoparticles, electrode nanostructuration, electrochemical, electrochemiluminescence.

**Лазерно-індуковані наночастинки в електроаналізі: Огляд.** *В.С.Васильковський, М.І.Сліпченко, О.В.Сліпченко, К.М.Музыка, Ю.Т.Жолудов*

Електроаналітичні методи знаходять широке застосування для хімічного аналізу різноманітних об'єктів завдяки таким перевагам, як універсальність та висока чутливість. Для покращення ефективності аналітичної установки, електроди для таких вимірювань можуть бути модифіковані наночастинками. Лазерний синтез є перспективним методом для формування відповідних наночастинок і має безліч переваг. В огляді представлено перелік методів лазерного синтезу наночастинок, а також досягнення та перспективи використання отриманих наночастинок в електроаналітичних методах досліджень, що є важливим для його подальшого застосування.

Электроаналитические методы имеют широкое применение для химического анализа разнообразных объектов благодаря таким преимуществам, как универсальность и высокая чувствительность. Для повышения эффективности аналитической установки, электроды для таких измерений могут быть модифицированы наночастицами. Лазерный синтез является перспективным методом для формирования соответствующих наночастиц и имеет множество преимуществ. В обзоре представлен перечень методов лазерного синтеза наночастиц, а также достижения и перспективы использования полученных наночастиц в электроаналитических методах исследований, что является важным для их дальнейших применений.

## 1. Introduction

Electrochemistry is the branch of chemistry concerned with the interrelation of electrical and chemical effects. A large part of this field deals with the study of chemical changes caused by the passage of an electric current and the production of electrical or optical energy by chemical reactions. Namely, the measurement of electrical quantities, such as current, potential, or charge, as well as optical quantities and their relationship to chemical parameters [1, 2]. A variety of modern research areas and industrial techniques are part of electrochemical science — energy storage and conversion, corrosion studies and protection, chemical synthesis and surface modification, and electroanalysis [2].

Electroanalytical (Electrochemical, Photoelectrochemical, Electrochemiluminescent) techniques play a crucial role in modern analytical science due to their inherent advantages like simplicity, versatility, efficiency, sensitivity, rapidness, etc. To conduct electroanalytical measurements at least 2 electrodes and a sample solution are required. One of the electrodes, termed the reference electrode, is independent of the properties of the solution. The second one responds to the target analyte(s) and is thus termed the working electrode [1]. However, a single-electrode electrochemical system that requires using only one electrode with the gradient of an electric potential across it is also reported [3].

Modification of the working electrode surface is a way of creating electrochemical sensors — elements with new and interesting properties. Modified carbon and metal-based electrodes are widely applied as a working electrode for electrochemical detection of the analytes. The material for electrode modification is applied to the electrode surface in the form of electroactive thin films, monolayers, or thick coatings. Modification of the electrode surface can enhance the performance of an electrode as a sensor device suitable for biological and environmental samples in many ways [4].

The use of nanoparticles of different materials — a relatively new form of matter — for electrode modification can offer further enhancement of the performance of modified working electrodes for electroanalytical applications.

Nanoparticles (NPs) of different compositions and dimensions have become used as versatile and sensitive tracers [5]. The creation of NPs for enhanced sensitivity in elec-

troanalytical applications greatly benefits from their nanoscale size, where their properties are strongly influenced by increasing their surface area to volume ratio. Also, NPs are one of the most exciting areas in modern electroanalytical chemistry because they offer excellent prospects for creating highly sensitive and selective electrodes. Thus, the usage of NPs reduces the use of reagents and the required electroanalysis time. Many kinds of NPs, including metal, metal-oxide, semiconductor, and even composite-metal NPs, have been used for constructing electrochemical sensors [6].

A wide variety of methods is available for nanoparticle synthesis, affording a broad spectrum of chemical and physical properties. Laser synthesis is one of the best candidates, as compared to other methods. This method allows the preparation of stable colloids in pure solvents without using either capping and stabilizing agents or reductants. Laser methods produce nanoparticles that can be more suitable for medical and food-related applications where it is important to use chemicals and materials non-toxic for humans. Besides, laser synthesis allows for achieving nanoparticles with different properties according to experimental laser parameters, in particular influencing their electrical and optical properties, size, antibacterial properties [7].

This work is dedicated to reviewing the promising future for the use of NPs that are generated using laser techniques for the development of new and efficient electrochemical methods, procedures, and devices for the analysis of liquids.

## 2. Laser fabrication of nanomaterials

The synthesis of nanoparticles has attracted considerable interest due to their potential applications in a variety of areas including medicine, energy, and environmental remediation [10]. Numerous methods and techniques were presented to synthesize nanoparticles including chemical, physical and biological techniques. However, the use of laser techniques for the synthesis of nanoparticles is of great interest due to a large number of advantages over other methods.

### 2.1. Pulsed laser ablation

Amongst the available techniques for synthesizing NPs, the pulsed laser ablation (PLA) route, either in liquid or solid phase, possesses several advantages over others [12]. PLA synthesis of nanoparticles is an

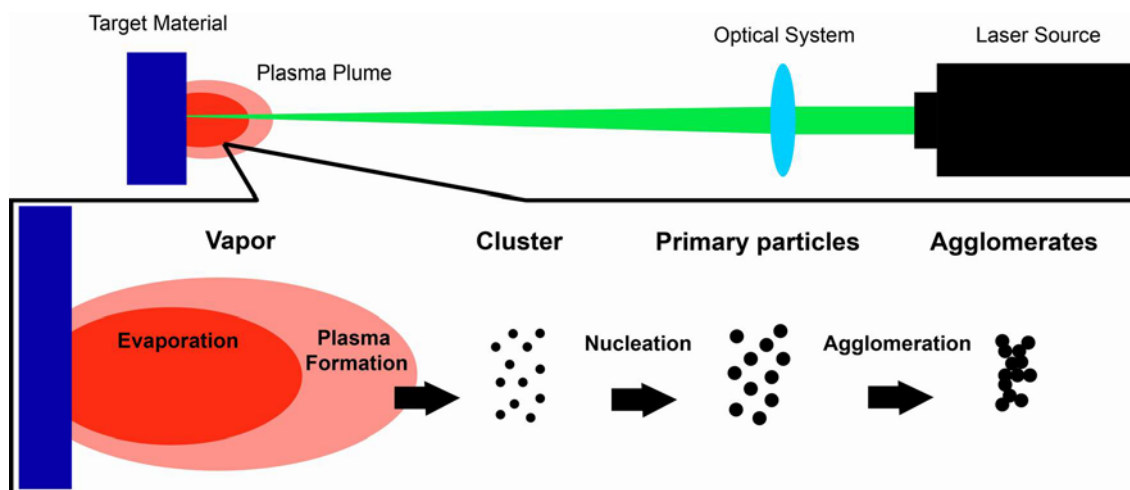


Fig. 1. Schematic of particle generation via laser ablation process [11].

interest in nanotechnology since pulsed laser synthesis is the fastest and green method to fabricate nanomaterials directly from bulk targets [8, 9].

Laser ablation is a method that utilizes laser as an energy source for ablating solid target materials. During this process, extremely high energy pulses are concentrated at a specific point for a few nanoseconds on a solid surface to evaporate light-absorbing material [11, 12]. The laser ablation process often utilizes wavelengths of commercial solid-state lasers and their 2<sup>nd</sup> and 3<sup>rd</sup> harmonics (e.g. 355, 532, and 1064 nm). Fig. 1 is a schematic of the nanoparticle formation by PLA. The laser systems for nanoparticle production consist of a pulsed laser, beam-handling optics, a target, and a substrate [8].

Targets required for the synthesis are less expensive than the metal salts and other chemicals required in the chemical routes, which makes this method cost-effective comparing to other methods [12]. Laser ablation can generate high-purity nanoparticles because the purity of the particles is determined by the purity of the target and ambient media (gas or liquid) without contamination by the precursor chemicals and other reagents [11]. In addition, laser synthesis techniques do not require special external conditions, such as high temperature or high pressure. The appropriate selection of significant parameters like ablation medium, as well as wavelength and laser intensity, is essential in minimizing unwanted by-products and increase the yield of the intended nanostructured materials [9, 10]. Most importantly, as-fabricated NPs are inherently surfactant-free; thus, their surface functionalization is simple if required [12]. PLA demonstrates excellent suitability for

the synthesis of a wide range of nanoparticles (semiconductor quantum dots (QDs), carbon nanotubes, nanowires, core-shell nanoparticles, ceramic and noble metal NPs, etc.). in terms of the yield and size homogeneity of the produced nanomaterials [10, 11, 13, 14]. Such nanomaterials can be effectively used for detection applications [12–26].

Many researchers perform the PLA process under different environments like vacuum, buffer, and gas [8]. That is why, there are different experimental setups for the synthesis of nanostructures using lasers, which depend on the precursor materials, the laser parameters, and the ambient conditions [10].

## 2.2. Laser dewetting method

The construction of metallic NPs of controlled size, spacing, and ordered distribution is essential for the modification of electrodes for electroanalytical purposes. However, it is very challenging to precisely and efficiently arrange individual nanostructures into desired patterns with controlled periodicity, particularly over large areas. NPs can form on solid surfaces by the spontaneous dewetting of thin metastable metal films on various substrates [31]. Self-assembly via laser dewetting of the heated thin film is a cost-effective and environmentally-friendly approach for nanostructures fabrication. Moreover, this method can be applied for dielectric, semiconductor, and multilayer substrates, allowing them to precisely control their microscopic properties [33]. Hence, dewetting can be an effective method to form nanoparticle arrays for electroanalytical applications [25–28].

Table. Existing electrochemical nanomaterials-based sensors

Synthesis method	Type of Nanoparticles	Solution	Type of the electrode	Detectable substance	References
Laser dewetting	Au NPs	H <sub>2</sub> SO <sub>4</sub> , NaOH	ITO	Ascorbic acid, glucose	[25], [26]
	Au NPs	Phosphate buffer	Graphene	Fructose, glucose, Furazolidone, Flutamide	[27], [28], [29]
Laser ablation	Au NPs	N <sub>2</sub> , NaOH, H <sub>2</sub> SO <sub>4</sub>	Carbon	Glucose, Ascorbic acid, Cd <sup>2+</sup> , Pb <sup>2+</sup> , Cu <sup>2+</sup> , Hg <sup>2+</sup>	[16], [17], [18]
	Ni NPs	NaOH	Carbon	Hydroquinone, glucose	[17], [24]
	Ni NPs	Fe(CN <sub>6</sub> )	ITO	Aflatoxin B1	[23]
	Pd NPs	H <sub>2</sub> SO <sub>4</sub>	Carbon	Dopamine, ascorbic acid	[17]
	Cu NPs	H <sub>2</sub> SO <sub>4</sub>	Carbon	Ascorbic acid	[17]

Dewetting is a spontaneous phenomenon that refers to the decomposition of a film into droplets or other structures on an inert substrate. Its driving force is the minimization of the total energy of the free surfaces of the film and substrate, and of the film-substrate interface [15]. The dewetting is known to occur either through heterogeneous nucleation, which emanates from surface particles and impurities that grow into circular patches, or spinodal dewetting, where there is an amplification of thermal fluctuations on the surface of the film [30].

A method of dewetting of gold formed in an ordered array of NPs by femtosecond laser without the need for lithography has been proposed by Makarov et al. A single element is cut to a patch with a dimension greater than the edge uncertainty of the groove. The cut patch is thermally isolated since the thermal conductivities of the silica substrate and air are two and four orders of magnitude smaller than gold, respectively. Therefore, the isolated patch can be easier heated up to the temperatures where the film undergoes the dewetting process [33].

### 3. Applications of laser-fabricated nanomaterials in electroanalytical methods

Modified electrodes (carbon-based, graphene-based, and ITO) are often used as a working electrode for electrochemical detection of many biomaterials (ascorbate, glucose, fructose, dopamine, etc.), toxins,

drugs, antibiotics, pollutants, heavy metals, and other substances in liquids [34].

The most common materials of electrode surfaces for electrochemical detection are Indium tin oxide (ITO), carbon (glassy carbon, carbon fiber), graphene (graphene paper, graphene substrate), and silicon. ITO, graphene, and carbon electrodes are some of the most widely used for electrochemical sensing of liquids. It is due to their high electrical conductivity, high chemical resistance, stable physical and electrochemical properties, low electrochemical activity over a wide potential range, and the possibility of a variety of chemical functionalization [26, 28, 38]. Recently, several works have demonstrated that hybrid structures that include nanoparticles can offer unique physicochemical properties that are desirable for sensing applications by enhancing achievable sensitivity.

#### 3.1. Laser-fabricated nanomaterials in electrochemical assay

Currently, numerous papers are reporting on the applications of nanomaterials in the method of electrochemical (EC) analysis. Electrochemical sensors use an immobilized receptor (chemical recognition system) on the electrode surface for reacting with the analyte selectively. The recognition is detected by a change in currents and/or voltages at the localized surface. Based on their operating principle, the electrochemical sensors can employ potentiometric, amperometric, impedimetric, and conductometric techniques to convert the chemical information into a measurable signal [35].

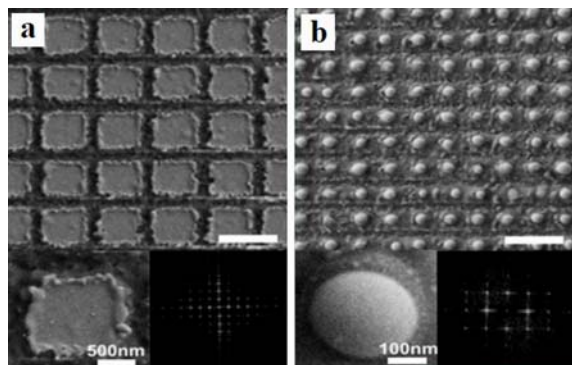


Fig. 2. Metal nanoparticles fabricated by laser dewetting a) SEM image before laser dewetting b) SEM image of an Au nanoparticle array made of a 30 nm film on a  $\text{SiO}_2$  substrate at a fluence of  $40 \text{ mJ/cm}^2$  [32].

Recent works on the usage of laser-fabricated nanoparticles in the method of electrochemical analysis show the versatility of this method in the detection of various substances in Table [16–18, 23–29].

### 3.1.1. Applications of laser-fabricated gold NPs in EC

Gold nanoparticles are one of the most studied materials in nanotechnology comparing to the other metal-based nanoparticles. Au nanoparticles (Au NPs) have also drawn much attention in electrochemical fields because of their favorable properties which include: unique optical and electronic properties, high chemical stability, biocompatibility, and ability to facilitate electron transfer between biomolecules and electrodes [23, 39, 40]. According to the analyzed articles, laser-fabricated Au NPs have been successfully used for the signal amplification for detection of glucose, ascorbic acid, fructose as well as heavy metal ions ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ) and medicinal agents (Furazolidone, Flutamide) [16–18, 25–29].

In [18] have used laser-ablated Au NPs as sensors for the detection of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ . The laser for PLA was first harmonic 1064 nm Nd:YAG, with a pulse duration of 1 ns and a frequency of 10 Hz and was focused on the gold target with a 2 mm spot size. Obtained Au NPs were negatively charged and the bare Glassy carbon electrode's working surface (diameter 2.0 mm) was successfully modified by the electrophoretic deposition method. The simultaneous detection via differential pulse anodic stripping voltammetric (DPASV) method of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  have been successfully performed under the following experimental conditions: potential

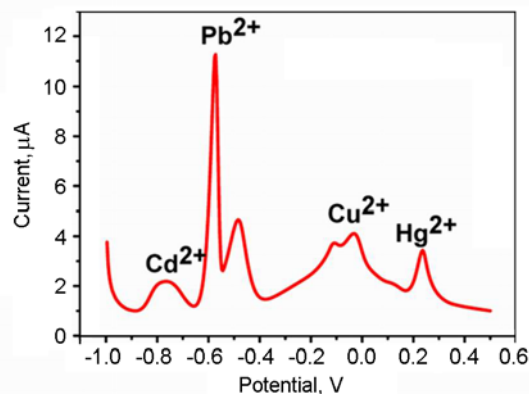


Fig. 3. DPASVs for  $0.8 \mu\text{M}$  each of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  on Au nanoparticle modified GC electrode in  $0.1 \text{ M}$  acetate buffer [18].

range of  $-1.0$  to  $0.5 \text{ V}$ ; increment potential =  $4 \text{ mV}$ ; amplitude =  $50 \text{ mV}$ ; pulse width =  $0.06 \text{ s}$ , test solution —  $0.1 \text{ M NaAc-HAc}$  ( $\text{pH } 5.0$ ) [18].

Laser-fabricated AuNPs in combination with ITO electrodes, carbon fiber microelectrodes as well as graphene paper showed good results in the detection of glucose. The size-range of nanoparticles in observed works varies in the range of  $20\text{--}150 \text{ nm}$  [16, 26, 28, 29].

### 3.1.2. Applications of laser-fabricated nickel NPs in EC

Nickel nanoparticles attract much interest for biosensing application due to their biocompatibility, strong absorption ability, ability to promote fast electron transfer resulting in enhanced sensitivity, selectivity, shelf-life, and large detection range.

Kalita et al. have shown the possibility of usage of the self-assembled ring-like nickel nanoparticles (size  $\approx 10\text{--}20 \text{ nm}$ ) prepared by laser ablation method deposited onto iridium-tin-oxide functionalized by dimethyl sulfoxide for electrochemical detection of aflatoxin. Produced electrodes have shown the affinity towards aflatoxin, the detection limit of  $32.7 \text{ ng}\cdot\text{dL}^{-1}$ , and sensitivity of  $0.59 \mu\text{A}/\text{ng}\cdot\text{dL}^{-1}$  [23].

The other research of Kaneko et al. shown that Ni nanoparticles (size  $\approx 3 \text{ nm}$ ) prepared by pulsed laser deposition (using a Nd:YAG laser) on glassy carbon electrodes can be used in electrochemical nonenzymatic glucose detection [25].

### 3.2. Application of laser-fabricated nanomaterials in photoelectrochemical assay

Photoelectrochemistry evolved from electrochemistry is a vigorous discipline explor-

ing the effect of light on photoactive materials, which involves the transformation of light into electricity and interconversion of electric energy and chemical energy. It is accepted that the photoactive materials absorb photons with enough energy to produce electron-hole pairs [37].

The applications of laser-fabricated nanomaterials in the detection of substances via the photoelectrochemical method has not been studied. The research of Hajjaji et al. showed that TiO<sub>2</sub> nanotubes decorated by laser-fabricated PbS nanoparticles have a photocatalytic efficiency and good photoelectrochemical properties. A pulsed KrF excimer laser ( $\lambda = 248$  nm; repetition rate = 20 Hz) was used to ablate the PbS enabling the growth of PbS NPs on the Ti/TiO<sub>2</sub> [20].

### 3.3. Application of laser-fabricated nanomaterials in electrochemiluminescent assay

Electrogenerated chemiluminescence or electrochemiluminescence (ECL) is a phenomenon where light-emitting species are produced in a course of energetic electron transfer reaction. The luminescent signal originates from the excited states of an electrochemiluminescent luminophore generated at the electrode surface during the electrochemical reaction. [42, 43] Electrochemiluminescence is an analytical method that combines both electrical and luminescent characteristics. In the electrochemiluminescent technique the electrochemical reaction taking place on the surface of the working electrode causes a specific chemiluminescence reaction. A light-emitting excited state of luminophore species is formed by a highly energetic electron transfer reaction in the solution near the surface of the electrode from the electrochemically generated precursors. Luminescent transitions occur during relaxation from an excited intermediate level to a lower energy level state. ECL detection consists of monitoring the production of photons and, thus, the light intensity produced during the electrochemical reaction in solution. Therefore, the light intensity is related to the concentration of one or all the reactants involved in the electrochemical reaction and is applicable for the creation of efficient and highly sensitive analytical techniques and sensors possessing unique properties [35, 36, 44, 45].

ECL assay can also benefit from electrode modification with various functional structures and films [46–49] that has great potential for the development of cheap, reli-

able and reusable analytical ECL devices — ECL sensors. The use of various nanoparticles of fluorescent and conductive materials for functionalization of ECL sensors' electrodes is widely exploited to enhance their analytical performance [50, 51].

In our previous research, we have also shown that fluorescent CdSe NPs can be successfully generated using the PLA approach and that CdSe QDs deposited onto the ITO electrodes can exhibit ECL emission. This allows believing that such laser-fragmented fluorescent semiconductor nanoparticles are suitable for application in ECL experiments and the development of ECL assay procedures [14, 52, 40].

## 4. Conclusions

Observed research works indicate that the utilization of the nanoparticles obtained by laser methods and the modification of electrodes by these modifiers are promising for electrochemical, electrochemiluminescent, and photoelectrochemical assays. Also, it has been shown the effectiveness of the detection of organic substances, toxins, and heavy metal ions in liquids by the use of these electrodes in electroanalytical methods. At the same time, it is worthy to point out that an overall number of research related to the usage of laser-induced NPs for electroanalytical applications is rather scarce and further work and collaboration of research groups in this multidisciplinary field is required and has great potential for success.

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