Chapter 1
Electrochemical Synthesis of Nanomaterials

D. M. Jeroh

Abstract This chapter discusses the process involved in synthesizing nanomaterials using electrochemical reactions. Nanomaterials and the various classes are introduced. Electrochemical synthesis is reported, some factors which influence the properties exhibited by nanomaterials are also discussed briefly. These factors which influence the properties of nanomaterials are current density, electrolyte temperature, pH of electrolyte, nature of substrate and voltage.

Highlights

This chapter addresses the following topics:

- Nanomaterials and the different categories
- Nanomaterials synthesis with emphasis on electrodeposition
- Parameters influencing electrodeposition.

1.1 Introduction

Nanomaterial's research is a vast and very significant field of study in the advancement of science and technology due to their abundant and essential applications in vast research fields including Physics, Chemistry, Material Science, Medicine, Engineering, etc. Nanomaterials are gaining attention and importance as a result of their many distinct properties which contradicts those of the traditional bulk counterparts [1]. Nanomaterials have at least a dimension in the nanometer scale range. This range is defined as 10^{-9} m.

To effectively understand the properties exhibited by nanomaterials, it is crucial to grow them using either physical or chemical means. A number of physical methods require very expensive equipment's to work with, hence the need to consider methods that will be less expensive and capable of bulk assembly of nanomaterials with good quality. Electrochemical preparation technique is among the possible

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options for nanomaterials fabrication with the advantage of having the possibility to deposit a large variety of materials in varying forms from different solutions and the opportunity to obtain nanomaterials in bulky amounts [2].

The major goal of this chapter is to report how nanomaterials are synthesized from electrochemical processes and also highlight and discuss the important parameters upon which nanomaterials synthesis from electrochemical reactions are relied upon.

1.2 Nanomaterials

Nanomaterials are considered the major building blocks of nanoscience and nanotechnology. Nanomaterials can be obtained from various dimensions: zero, one, two and three dimensions [3]. Nanomaterials garner interest because, at this scale, some distinctive magnetic, optical, electrical and other characteristics materialize and these evolving characteristics have the capability for immense impacts in medicine, electronics and other disciplines [4]. More recently, nanomaterials are considered more suitable as a result of their fascinating physicochemical properties, which are different from those displayed by their bulk equivalent [5].

Nano-sized materials are currently used in many industries. For example, carbon-black particles are exploited for manufacturing rubber tyres which render the rubber tyres wear resistant. Other examples include using nanofibers for insulation and reinforcement of composites, using iron oxides in fabricating the magnetic material employed in the manufacture of videotapes and disk drives (DDs). Some products currently relying on nanotechnology are: magnetic recording tapes; computer hard drives; bumpers on cars; solid-state compasses; automobile catalytic converters; metal-cutting tools; dental bonding agents; longer-lasting tennis ball; burn and wound dressing; ink; etc. [6]. Some examples of nanomaterials include quantum dots, carbon nanotubes, graphene and fullerenes.

1.2.1 Quantum Dots

A quantum dot (QD) is an extremely small semiconductor structure whose diameter is within the nanoscale range, say between 2 and 20 nm. However, their dimensions rely mainly on their preparative materials [7]. According to Pokropivny et al. [8], QDs are crystals that emit a single wavelength of light during electrons excitation. QDs could also be seen as a class of semiconductors which are composed of periodic groups of II-VI, III-V, or IV-VI materials (such as ZnO, CdSe, CdS, PbSe, InP) with size spanning between 1.5 and 20 nm (10–50 atoms) in diameter [9]. Quantum dots conform to quantum mechanical principle (quantum confinement) and they exhibit band gap that ascertains the necessary wavelength pertaining to the absorption and emission spectra [10]. It is believed that in the future QDs could serve as quantum bits and may possibly constitute the foundation of quantum computers [8].

1.2.2 Carbon Nanotubes

Carbon nanotubes are materials possessing a tube-like shape with diameters in the nanoscale range. CNTs are synonymous with cylinders made of sheets of graphites, having enclosures at both ends, with carbon atoms on the top of the hexagon [11]. CNTs are also known as "bulkytubes" and are depicted by a cylindrical nanostructure in the appearance of a tube [12]. CNTs exist as a single wall or multi-wall carbon nanotubes.

1.2.3 Graphenes and Fullerenes

Graphene consists of one atom thick planar sheet of carbon atoms closely spaced in a honeycomb crystal lattice which is the fundamental structural assembling block of CNTs and fullerenes [12].

Fullerenes are composed of allotropes of carbon wholly consisting of carbon and exist as hollow spheres (or buckyballs), ellipsoid (bucky tubes or carbon nanotubes) [13]. Fullerenes have 60 carbon atoms (C_{60}).

1.3 Nanomaterials Synthesis

Nanomaterials can be synthesized by "top-down" and "bottom-up" techniques.

The "top-down" technique involves getting the nanomaterials by disintegrating the bulk material bit by bit till the desired dimension is achieved. Figure 1.1 demonstrates the "top-down" approach.

Grinding and lithography are types of the "top-down" approach. Lithography involves depositing a computer-generated pattern on a substrate's surface. However, this technique is associated with some disadvantages such as the introduction of crystallographic defects to the generated patterns. Another disadvantage is the elevated cost of equipment and the inability to obtain a single nanostructure through this method. Moreover, despite the defects, the "top-down" approach plays a principal role in synthesizing and engineering nanomaterials in that the present state of nanoscience can be viewed as an amalgamation of bottom-up chemistry and top-down engineering techniques [14].

The "bottom-up" approach involves preparing bulk materials by assembling of a structure atom by atom till the desired thickness of the bulk structure is achieved. Bottom-up approaches include self-assembly, precipitation from chemical solutions and aerosol techniques. Figure 1.2 demonstrates the "bottom-up" approach.

Fig. 1.1 Demonstration of "top-down" approach

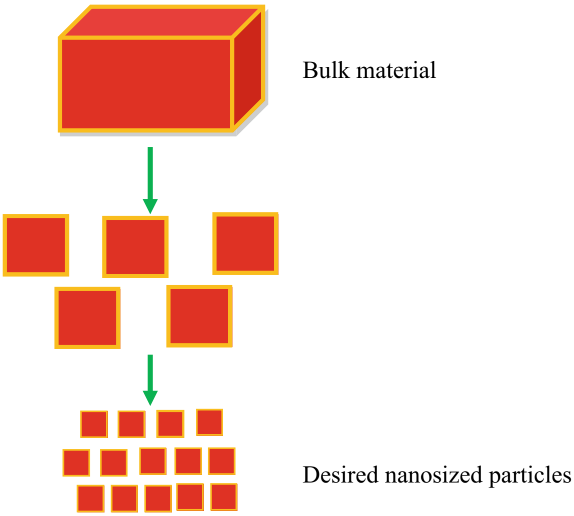
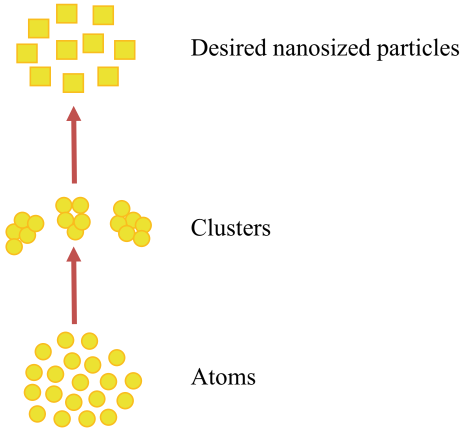


Fig. 1.2 Bottom-up approach of synthesizing nanomaterials



1.3.1 Electrochemical Synthesis

1.3.1.1 Electrodeposition Technique

Electrochemical deposition involves any type of electrochemical reactions which results in the deposition of a material [15]. According to [16], electrochemical deposition is defined as the production of a coating on a surface from an aqueous solution composed of several substances. Electrochemical deposition usually occurs inside an electrochemical cell. In this type of deposition technology, the film deposit can be formed on a substrate by allowing current to pass through an electrochemical cell with the aid of a power source connected externally. Alternatively, it can be grown by making a complex solution where chemical reactions take place continuously without any power source due to the sufficiently high potential between the surface and a solution [16].

A typical electrochemical cell comprises a reaction vessel (a beaker in most cases) and maybe two or three electrodes. The two-electrode cell comprises a working electrode (substrate) and a counter-electrode. The reactions can be controlled in the two-electrode cell by the application of current between the working electrode and the counter-electrode. In the three-electrode cell, deposition of the required film on a substrate can be achieved either by controlling the potential or the current and the corresponding potential or current is measured.

Figure 1.3 illustrates a simple electrochemical cell for synthesizing nanomaterials.

In electrochemical synthesis, when a potential different (PD) is applied across the system, a direct current (DC) source supplies current which flows in one direction through the external circuit. The DC source could be either a motor, generator or a rectifier. Electrons are the main carriers of current in the external conductors. Electricity is transferred in the solution through electrically charged particles (ions). When a PD is applied, the positive ions referred to as cations move towards the negative electrode (cathode), while the negative ions known as anions move towards the positive electrode (anode). As this mechanism takes place, deposition of materials

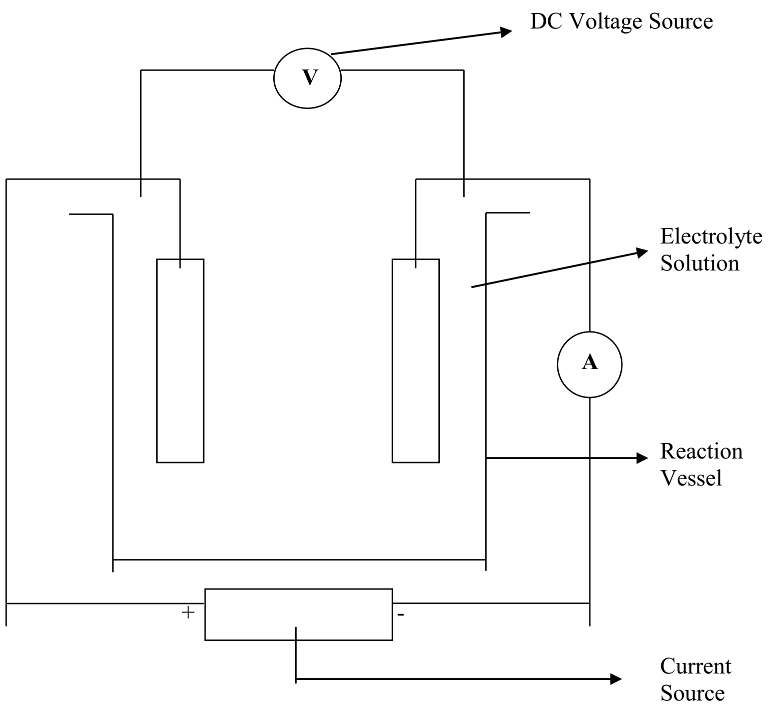


Fig. 1.3 Schematics of a simple electrochemical cell

occurs on the substrate from the aqueous solution. Electrochemical deposition is an interesting method for preparing materials in large quantities because it relies on inexpensive equipment, enables large area deposition and offers eased control of growth factors through applied current, PD, bath temperature and pH [17].

1.4 Parameters Influencing Electrodeposition of Nanomaterials

Some factors have been identified to have some notable influence on electrodeposition of nanomaterials. Some of these include temperature, current density, substrate nature, applied voltage and solution pH.

1.4.1 Temperature

Temperature is vital in influencing the end properties exhibited by nanomaterials. An increase or decrease in the electrolyte temperature may result in significant modification of the properties of the nanomaterials being synthesized. An increased temperature of the electrolyte results in an increase in solubility, catalysis of reactions, increase in transport number and energizing of ions leading to higher deposition density and the rate of deposition [18]. The general trend is that increased bath temperature reduces internal stress of the material [19]. A substantial grain size reduction is witnessed at increased bath temperature implying that the growth rate of the grains reduces at higher temperatures due to lower concentration of oxygen [20].

1.4.2 Current Density

An important factor that plays a major role in influencing the characteristics of electrodeposited nanomaterials is "current density." There is a correlation between the rate of deposition and current density. This can be best explained by Faraday's law of electrolysis. Faraday's law states that the level to which an electrochemical reaction takes place is proportional to the electrical charge that passes through the electrolyte [21].

In a mathematical notation, Faraday's law as reported by Bijoy [22] may be expressed as:

$$m = \left\{\frac{Q}{F}\right\}\left\{\frac{M}{Z}\right\} \tag{1.1}$$

In 1.1, *m* represents the altered mass of the substance at the electrode, *Q* represents the electric charge in the system, *M* equals the material's molar mass, *F* is Faraday's constant given as 96.485 $Cmol^{-1}$ and *Z* is transferred electrons per ion [22].

At low current density, the speed of nucleation centers creation is much lower compared to crystal growth of the existing seeds, while for high current density, a decrease of ions concentration near the deposited surface is observed, or hydrogen evolution takes place and the obtained layers become non-continuous, spongy and porous [2]. In the electrochemical synthesis of Ni/SiCw nanocomposite coatings, [23] reported that electrodeposits acquired at low current density resulted in smooth surface morphology and fine grains in comparison to electrodeposits acquired at elevated current density. However, in the experiment conducted by Zaki et al. [24], limitation of nucleation and growth of deposits of copper on Ni-zincates Al surface was witnessed at low current density (0.5 mA/cm^2), while improved nucleation was recorded at elevated current density (6.0 mA/cm^2).

1.4.3 Nature of Substrate

Synthesizing nanomaterials using electrochemical synthesis technique requires a conducting substrate. Substrates commonly employed for electrodeposition are Fluorine-doped tin oxide (FTO) and Indium-doped tin oxide (ITO) conducting substrates. Synthesis cannot occur using a non-conducting substrate.

1.4.4 Electrolyte pH

The constituent bath (electrolyte) pH is another important parameter that affects the growth of nanomaterials electrochemically. An electrolyte is said to be acidic having pH value less than seven, while it is considered alkaline with a pH value greater than seven. Increase in electrolyte pH results in increased deposition rate [25], which obviously resulted in improved characteristics displayed by nanomaterials. Low pH results in the evolution of hydrogen, which breaks through the layer, resulting in the deposited material being hard and in turn result in a lot of stress to the layer [2]. Hence, in fabricating nanomaterials from electrochemical processes, a suitable pH is essential to develop a good quality material as the final product.

1.4.5 Voltage

Applied voltage also has a significant effect on deposition of nanomaterials using electrochemical deposition technique. The applied voltage has a linear relationship to the current that is passed within the electrolyte. In electrochemical synthesis, a higher voltage implies the availability of more energy at the cathode which will eventually result in reduction while the anode will record more energy leading to oxidation. In the growth of zinc selenide nanofilms, an improved crystallinity of the films at increased potential (voltage) [26] is reported.

1.5 Conclusion

Electrochemical synthesis of nanomaterials has been discussed. Some parameters which influence nanomaterials properties obtained by electrochemical synthesis were identified and discussed. It is emphasized that temperature, current density, voltage and nature of substrate play vital roles in influencing the end properties of nanomaterials. To obtain good quality nanomaterials using electrochemical process, it is pertinent to optimize all synthesizing conditions.

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