



# Electropolymerization: Applications of Electrochemically Hybrid Nanomaterials for Therapy and Diagnosis

Eltahtawy Oma\*

Department of Materials Science & Engineering, Faculty of Information Technology, Amman University, Jordan

## ABSTRACT

Hybrid nanoarchitectures where inorganic nanoparticles are added into a polymer matrix can present superior characteristics and unique synergetic effects. However, the homogeneously structured and monodispersed hybrid film has been a critical challenge because of the intrinsic incompatibility of hydrophobic nanoparticles and hydrophobic polymers. This review focuses on hierarchically hybrid nanoarchitectures of polymers and nanoparticles by electrochemical approaches. Of many methods, the use of electrochemically bottom-up in situ synthesis can prepare the controlled layered and hybrid formations of polymers and nanoparticles. The advantages are film-forming ability from very dilute solutions of nanoparticles and polymers, and covalently cross-linked structural stability. The electrochemical approach has provided highly predicted functions and performances for applications mostly studied including sensor, catalysis, and optoelectric relatives. With these in hand, electrochemically engineered hybrid nanoarchitectures of polymers and nanoparticles hold promise for the fabrication of hierarchically ordered materials on hardly or flexibly conductive substrates with rational scales and dimensions.

**Keywords:** Nanoarchitecture; Electrochemical sensor; Electro catalysis Conducting; polymers Nanoparticles; Electropolymerization

## INTRODUCTION

The hybrid nanoarchitectures that integrate polymers and inorganic nanoparticles at the molecular level or nanoscale can present superior characteristics and unique synergetic effects for applications including sensing catalytic, photoelectronic, and biomedical applications. In particular, the inorganic nanoparticles have specifically optical, electronic, magnetic, mechanical, and thermal functionalities, and highly tunable appearances including size, shape, morphology, and surface. The polymers can be structurally and functionally tailored and easily processed for the final materials with good biocompatibility, processability, and stimuli-responsibility to external light, heat, pH, etc. The polymers have long been used to stabilize metal nanoparticles and protect them from agglomeration [1].

It is well-known that the properties of hybrid composite depend not only on those of individual functional building blocks but also on their spatial organization at different length scales. However, the preparation of homogeneously structured and monodispersed hybrid film has been a critical challenge because the intrinsic incompatibility of hydrophobic nanoparticles and hydrophobic polymers often leads to agglomeration and inconsistency of

nanoparticles during and after solution-processed preparation. Of many methods including blending, sol-gel, and general polymerization, the use of electrochemically bottom-up in situ synthesis can prepare the controlled layered and hybrid formations of nanoparticles and polymers, having the advantage in film-forming ability from a very dilute solution of poor solubility nanoparticles or polymers [2]. Herein, in contrast to previous review articles this review focuses on the electrochemical engineering of polymers and inorganic nanoparticles for main applications including sensor, optoelectric function, and electrocatalysis.

## METHODOLOGY

### Electrochemically engineering methods

The general synthetic strategies for hybrid nanoarchitectures of polymers and nanoparticles can be divided into four main categories the simultaneous electrochemical synthesis of polymers and nanoparticles. There have been only a few papers published regarding the simultaneous electrochemical synthesis of polymers and nanoparticles. This method can simplify the multistep processes of hybrid materials. For example, Cunnane et al. prepared the polymertyramine and gold nanoparticle hybrid film by the

\*Correspondence to: Eltahtawy Omar, Department of Materials Science & Engineering, Faculty of Information Technology, Amman University, Jordan; E-mail: omarelta@edu.com

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simultaneous nucleation of gold nanoparticles and polymerization of tyramine at an immiscible electrolyte interface. Pringle et al. provided the hybrid nanoarchitecture of the conducting polymers polypyrrole and polythiophene containing incorporated gold or silver nanoparticles [3]. They used the metal salts as the oxidant for pyrrole and terthiophene allowing the hybrid formation to be formed in one step without the need for templates or capping agents.

### Electrochemical sensors

Hybrid nanoarchitectures of polymers and nanoparticles are extensively investigated for electrochemical sensors. The polymers are usually used as a good dispersing role for inorganic nanoparticles, and to improve their interfacial properties [4]. These nanoarchitectures facilitate the rate of electron transport between the current collector materials and the electrolyte. Therefore, they are employed in the construction of electrochemical sensors with enhanced performances such as rapid response, low detection limit, high repeatability, good selectivity, etc. This part aids the readers to analyze the electrochemical sensing species and performances, and provides a view that how to engineer the practical sensor by using a specific hybrid nanoarchitecture of polymers and nanoparticles [5].

### Optoelectric relatives

Tailoring two and three dimensional nanoarchitectures of polymers and nanoparticles attracted substantial research efforts on the fabrication of photoelectric materials and devices. The properties and performances of the nanoarchitectures depended on energy band matching, blend film morphology, composition ratio, semiconductor nanoparticle shape, etc [6]. Compared with the layered fabrication of polymers and nanoparticles, electropolymerization of polymerizable molecules capped on nanoparticles is a general method to prepare the monodispersed nanoparticles within the polymer matrix.

### Electrocatalysis

Hybrid polymer and nanoparticle nanoarchitectures are attractive by their electrocatalytic activities in the oxidation and reduction of various organic and small molecules. Conducting polymers are usually used for dispersing the nanoparticles to significantly enhance the performance by using their high surface areas and/or the synergistic effects [7]. In this case, surface immobilization of polymers and nanoparticles is a key process. In contrast to layered hybrid films of polymers and nanoparticles, the polymers grafted nanoparticles were the more promising type for the development of photo- and electro- catalysts.

## RESULTS

Both polymers and nanoparticles can be electrochemically engineered into the hybrid films. Xu et al. Studied polycarbazole as an efficient promoter for electrocatalytic oxidation of formic acid on the monometallic Pt and bimetallic Pt-Ru nanoparticles. The nanoparticles were electrochemically deposited and dispersed onto polycarbazole films obtained by electropolymerization [8]. This nanoarchitecture exhibited higher catalytic activity and stronger poisoning-tolerance ability towards the electrooxidation of formic acid. They showed that polycarbazole did depress the adsorption strength of CO on catalysts, making easier oxidation of CO under lower potential.

## DISCUSSION

Hybrid materials are an exciting class of carefully designed systems that can offer unusual performance improvement and new properties through novel combinations of nanoparticles and flexible polymers. This review has covered the most of research fields based on electrochemically engineered hybrid nanoarchitectures of polymer nanoparticles for applications including electrochemical sensors, electrocatalysis, and optoelectric relatives in the past decades [9]. The electrochemically engineered processes can be mainly divided into layer-by-layer electro polymerization and electro polymerization of electroactive molecules modified on inorganic nanoparticles, which are mostly formed ex-situ. Layer-by-layer electro polymerization is certainly mostly studied for the preparation of structure and function-controlled morphologies. Electrochemical fabrication can efficiently avoid the agglomeration of nanoparticles within the polymer matrix, the phase separation by covalently cross-linked Csingle bondC coupling bonding, and superior stability compared to non-covalent layer-by-layer approaches [10].

## CONCLUSION

Besides polymers and nanoparticles, other tremendous species including organic small molecules, fullerene, graphene, etc. are involved electrochemically in layered nanoarchitectures to meet the requirements of their final applications. The major challenges that limited their applications include: (1) how to engineer various non-metal nanoparticles with low conductivity; (2) design of novel functional polymers with unique features including high conductivity, high water-solubility, high biocompatibility, high stability, etc.; and (3) precise synthetic methodology and fabrication technique. Compared to metal nanoparticles, the number of non-metal nanoparticles will enrich the properties and functions of hybrid nanoarchitectures with further processing possibilities. By now, conventional polymers such as polythiophene, polyaniline, polypyrrole, etc. are mostly used, and novel conductive polymers with water-solubility, biocompatibility, and stability are always being pursued. Developing controlled electro polymerization along with developing new electrochemical reactions will facilitate precise synthesis.

## DECLARATION OF COMPETING INTEREST

The authors declare no conflict of interest

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