



# Chemical vapor deposition - based synthesis of conductive polydopamine thin-films



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## ABSTRACT

Polydopamine (PDA) represents a family of synthetic bio-inspired pigments offering high functional activity combined with semiconducting properties. To date, it represents one of the main synthetic biopolymers used mainly because of its simple synthesis in aqueous solutions. Thereby dopamine polymerizes in the presence of ambient oxygen to polydopamine. However, its structure renders a sophisticated backbone relating to variations of ambient growth parameters such as temperature, local pH and partial oxygen pressure; preponderant repeating units found in aqueous polydopamine are 5,6-hydroxyl-indole derivatives. However, hydrogen-bonded aggregation competes with the polymerization leading to complex systems. In order to reduce the aggregation we hypothesized that acidic oxidants will direct the polymerization towards C–C coupling and hence create synthetic biopolymers.

In this work we demonstrate oxidative chemical vapor deposition (o-CVD) for PDA, where we obtain the desired consistent biopolymer thin-films as shown by structural analysis. Furthermore, as-gained polydopamine is conductive and renders fingerprint signatures of free charge carriers. Concomitantly it preserves its functionality – imperative for potential applications in catalysis or as bio-linker.

## 1. Introduction

Natural molecular units, such as hydrogen-bonded pigment molecules, represent an emerging class of conjugated semiconductors proposed for manifold bio-compatible optoelectronic linkers. Bio-compatible semiconductors can be implemented in living tissue and mutually address biologic-electronic signals. In addition, decomposable, non-toxic semiconductors can decrease electronic littering [1–7].

Among other bio-related conjugated systems polydopamines (PDAs) are commonly used conjugated biopolymers. PDAs adopt indole-based conjugated - functional repeating units reminiscent to eumelanins – a group of natural pigments built from 5,6-dihydroxy-indoles and derivatives thereof (Fig. 1). Unlike eumelanins, PDAs assemble to 1 - dimensional structures. Originally, they have been derived from 3,4-dihydroxy-L-phenylalanine – a protein existing in mussels responsible for the high binding strength. Consequently, early research has focused bio-mechanical applications [8–15]. Meanwhile the synthesis procedures have eased and PDAs are used in manifold coatings, template layers and catalyst carriers [15]. The dominant synthesis to date uses

oxidative polymerization of dopamine in aqueous solutions [7,15–18]. Thereby, ambient oxygen serves as C–C coupling agent making the synthesis straightforward (*i.e.* self-polymerization in a glass beaker). However, the downside of aqueous synthesis is resulting complex structures such as disrupted conjugation. Studies have shown that entire building blocks of hydrogen bond networks (H-aggregates) are formed within PDA and inhibit covalent coupling among the monomers. Hence, aqueous PDAs are often not processable and show limited electronic properties [7,8,15]. In addition, the establishment of consistent growth parameters (*i.e.* temperature, pressure, local pH) is difficult, as minor changes in ambient conditions significantly alter the final molecular structure [8,9,15,19]. In order to promote covalent polymerization, monomer intermediate formation has to occur under controlled oxidative conditions. Discretely, these are the oxidation of dopamine (DA) to dopamine-quinone (DAQ), the intramolecular cyclization to leucodopaminechrome (LDC) and thereafter the formation and polymerization of indole and its derivatives (Fig.1) [15].

To suppress PDA's affinity to build up H-aggregates, we pursue a synthesis strategy that adopts insights from classic conductive polymers

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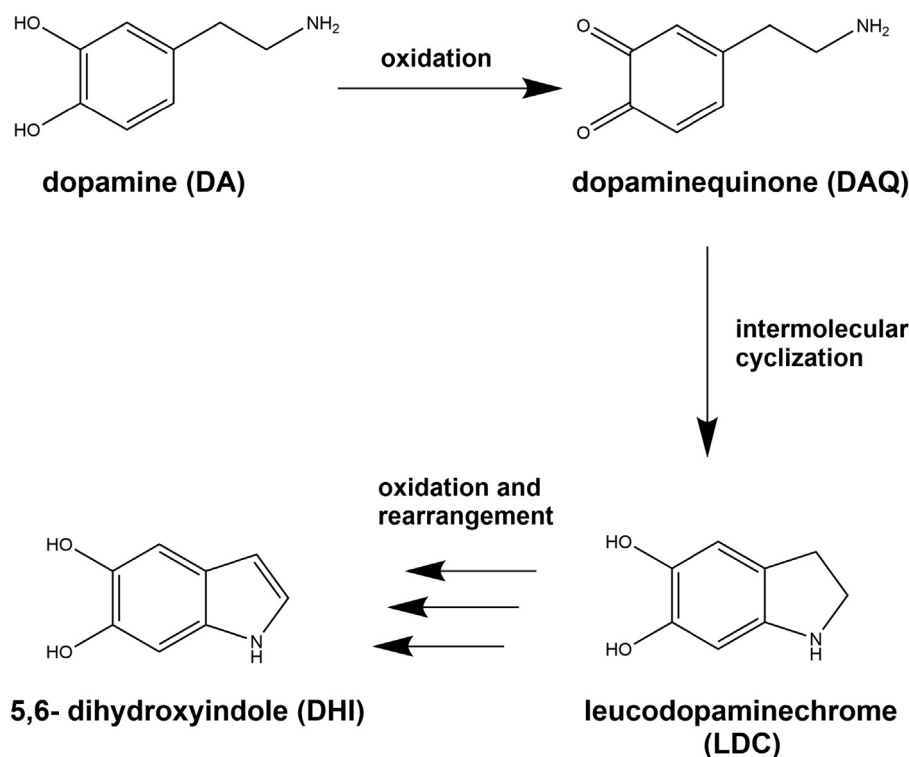


Fig. 1. Chemical structures of the polydopamine (PDA) intermediate steps undergoing numerous oxidation and rearrangement reactions.

[8,15,20]. The aim is to generate conjugated *and* conductive PDA from dopamine by using oxidative chemical vapor deposition (o-CVD). This technique allows us to use stronger oxidation reagent (as compared to ambient  $O_2$ ) in combination with acidic surrounding to enforce oxidative C–C coupling. The goal is to arrive at the desired functionalized polyparaphenylene (PPP) type of backbone.

In this work we adapt o-CVD for PDA *i.e.* we contact gaseous dopamine free base with sulphuric acid. The latter serves as acidic oxidation agent and directs the synthesis to deposit conjugated and conductive PDA thin films; we can define film thickness and deposition on various substrates such as glass, sapphire or carbon-materials for potential (catalytic) applications [21]. We are in particular interested in the consequent structural changes induced by o-CVD (as compared to the aqueous PDA). Therefore, we employ spectroscopic tools such as Fourier Transform Infrared Spectroscopy (FTIR), Raman and variable angle spectroscopic ellipsometry (VASE) on par with structural investigations (atomic force microscopy - AFM). We find evidence of covalent polymerization and high structural consistency in o-CVD PDA on par with a preservation of its functionalization. O-CVD PDA offers higher processability and yields consistent structural conformity leading to electronic activations such as electrical conductivity.

## 2. Experimental detail

### 2.1. Materials and methods

The oxidative chemical vapor deposition (o-CVD) is conducted on glass substrates (20 mm × 20 mm) and sapphire (10 mm × 10 mm × 0.5 mm) purchased from CrysTecKristall technology with Cr/Au electrodes used for the characterization of the polymer films. For the conductivity measurements on sapphire, the metal contacts are deposited by PVD through a 4-in-line contact mask. First, the substrates are cleaned using ultra-sonic bath 15 min each in acetone, isopropyl alcohol, Hellmanex-detergent (Hellma, 70 °C) and deionized water. Before starting the synthesis, dopamine hydrochloride (Sigma Aldrich) is dried in an oven at 150 °C overnight in presence of  $CaH_2$  (95%, Sigma Aldrich) to remove any water residual. The reaction

is carried out in a tube furnace (Carbolite company; glass tube length: 45 cm; tube diameter: 2.4 cm; reaction temperature: 300 °C) under nitrogen atmosphere with a carrier gas-flow of 3 L/min. Sulphuric acid (95–97%, J.T. Baker) and sodium sulphate ( $\geq 99.0\%$ , Sigma Aldrich) are utilized as oxidation agent and corresponding salt in the synthesis, respectively, in order to shift the balance towards  $SO_3^-$  and  $SO_4^{2-}$  in the gas phase. The reaction times are varied to reach the desired film thickness. For electrical characterization the samples are stored under inert conditions to avoid humidity and are sealed by drop casting a polymethyl methacrylate (PMMA) film on top of the active area. The simplified structure of vapor phase polydopamine during the one-step polymerization in the tube furnace is presented in Fig. 2.

### 2.2. Film characterization

The FTIR measurements are done using a Bruker Vertex 80 (8000  $cm^{-1}$  to 600  $cm^{-1}$ ; resolution 4  $cm^{-1}$ ). The Raman spectra are recorded at room temperature with a WITec Alpha 300 R-Raman-System (WITec GmbH, Ulm, Germany) instrument. Nd:YAG laser (532 nm) is used for the excitation and thermoelectrically cooled CCD (DU970N-BV) detector is applied for all measurements. A grating of 600  $mm^{-1}$  is used with a resolution of 4  $cm^{-1}$ . For all three molecules 20 × Zeiss EC Epiplan (Carl Zeiss Jena GmbH, Germany) objective lens is used, while the laser intensity, integration time and accumulations are varied for the monomer (10 mW, 15 s., 10), aqueous PDA (5 mW, 2 s., 3), and o-CVD PDA (5 mW, 3 s., 20), respectively.

Variable angle spectroscopic ellipsometry (VASE) measurements are conducted using a Wollam M-2000 spectrometer at 6 incident angles. The dielectric model has been derived using VASE program with film thickness used as an input parameter. For electrical characterization PMMA-sealed PDA films are contacted using indium solder and loaded to the cryosystem for electrical probing (Physical Property Measurement System, DynaCool, Quantum Design). The electrical conductivity is characterized as a function of temperature and time (at 300 K). The surface imaging of polydopamine films is taken by MFP 3D-Stand Alone atomic force microscopy (AFM) from Asylum Research with the cantilever OMCL-AC240TS of Olympus. It is operated in the

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