











The Theoretical Description for the Electrochemical Synthesis of an Economic and Green CoO(OH)-based Hybrid Composite

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Abstract: In this work, the synthesis of a novel economic and green composite material, based on cobalt (III) oxyhydroxide and conducting polymer of an *Agaricus xanthodermus* mushroom dye, has been described theoretically. In this case, cobalt (III) oxyhydroxide acts as a reductant, yielding *in situ* cobalt dioxide, providing the 4-4'-dihydroxyazobenzene electropolymerization over it. The composite material formed may be thereby partly oxidized or overoxidized. The correspondent mathematical model analysis confirms the efficiency of the electrosynthesical process despite the high probability of the oscillatory behavior.

Keywords: *Agaricus Xanthodermus*; conducting polymer; cobalt(III) oxyhydroxide; electrochemical oscillations; stable steady-state.

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1. Introduction

Agaricus is one of Europe's most cultivated mushroom genus [1–4]. Two of them (*Agaricus bisporus* and *Agaricus campestris*), correspondent to button and field mushrooms, are edible and are known by the common name champignon. They are so popular that in some languages, the name champignon corresponds to the meaning “edible mushroom”.

Nevertheless, one *Agaricus* species is a toxic mushroom *Agaricus xanthodermus*, popularly known as a yellow stainer. It is toxic when consumed, and it may be readily grown among the edible *Agaricus* mushrooms sharing the same mycelium. Its toxicity and color are caused by the presence of phenolic compounds (Fig. 1), including 4-4'-dihydroxyazobenzene, a unique endogenous natural azo dye [5–10]. In the mushroom pulp, the phenols act as antioxidants.

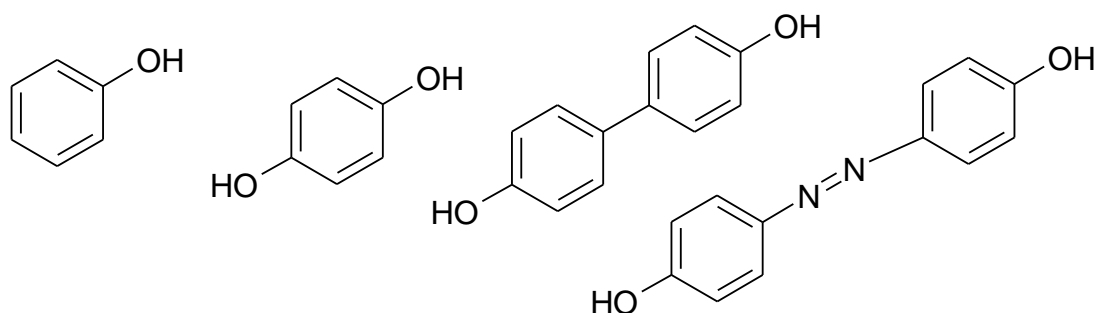


Figure 1. *Agaricus xanthodermus* phenols.

Considering the toxicity of the mushroom and its components, it cannot be eaten cooked. Nevertheless, the phenolic compounds from *Agaricus xanthodermus* may be interesting as monomers for conducting polymers and the proper mushroom – as an economical and green renewable natural source for the conducting materials [11–14], which needs a theoretical *a priori* investigation.

Generally, the conducting polymers are obtained from purely synthetic monomers, which may be environmentally unfriendly. Also, the synthetic monomer preparation and electropolymerization may be expensive for different reasons, and the mushroom solves both problems. The mushroom provides a rapidly renewed green source for the polyfunctional composite material, in which the organic phase is deposited over an inorganic oxide, augmenting its conductivity [15–21].

Therefore, the goal of this work is the theoretical description for 4-4'-dihydroxyazobenzene electrochemical polymerization over cobalt (III)-oxyhydroxide modified electrode. This leads to the economic and environmentally friendly composite, capable of being used in sensors, energy storage, and material science. Also, this synthesis is compared with similar systems [22–28].

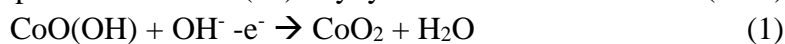
2. Materials and Methods

2.1. System and its modeling.

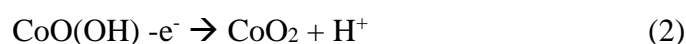
The electrochemical oxidation of 4-4'-dihydroxyazobenzene over CoO(OH)/CoO₂ redox pair is interesting from both electroanalytical and electrosynthetic point of view, and its electroanalytical function has already been investigated in [20,21].

The complete schematic description for this process, including the micro- and macromolecular monomer oxidation, like also quinone-hydroquinonic polymer oxidation, is depicted in Fig. 2. Taking into account that the quinone-hydroquinonic oxidation may be reversible, poly(4-4'-dihydroxyazobenzene) and its polyquinone may be proton and electron transfer mediators for either cathodic or anodic processes, which permits their wide use in electroanalytics and electrocatalysis. This polymer may also form a matrix for heavy metal ions recuperation and removal, like also for the MOF and other hybrid materials.

Both direct and indirect electropolymerization may be used to polymerize 4-4'-dihydroxyazobenzene. Indirect electropolymerization, in this case, is initiated by *in situ* formed cobalt dioxide, a product of cobalt (III) oxyhydroxide electrooxidation (1 - 2):



or



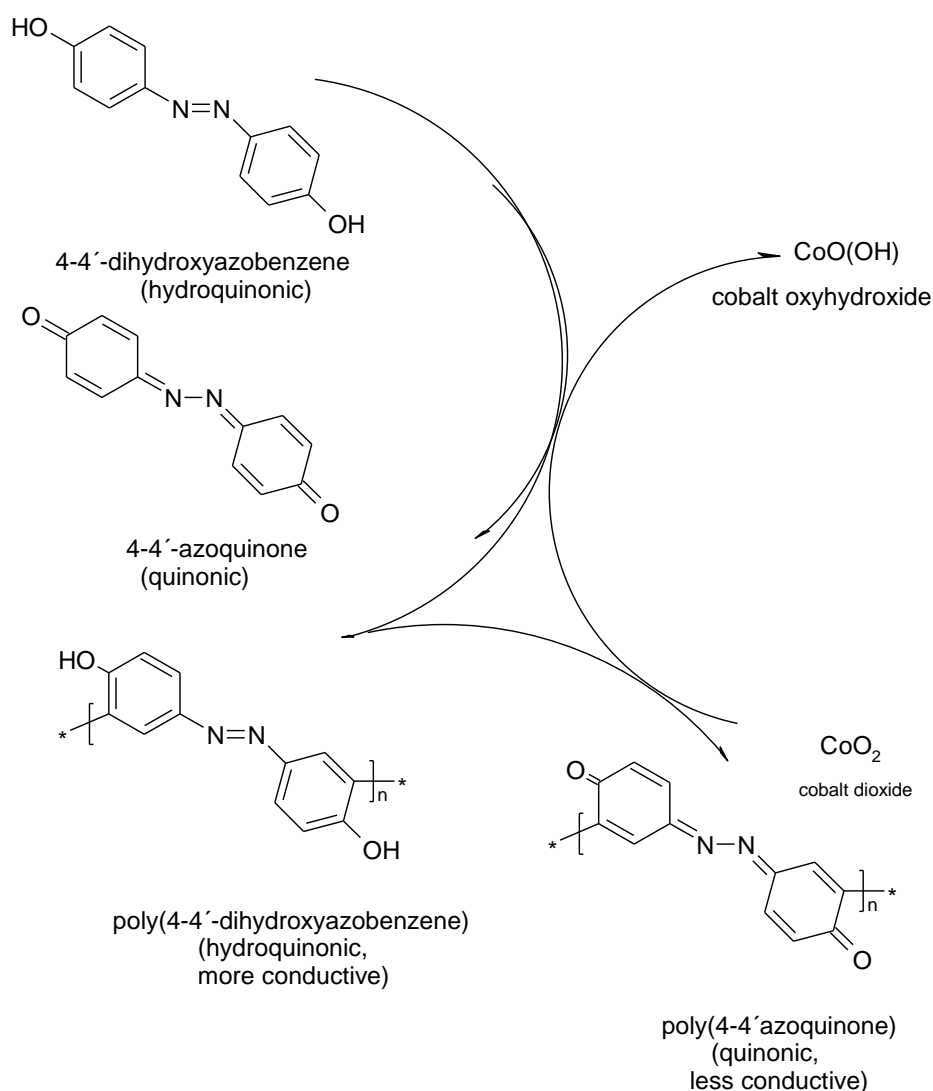


Figure 2. Schematical description for CoO(OH)/CoO₂ – assisted 4-4'-dihydroxyazobenzene and its polymer electrooxidation.

The resulting material will be CoO(OH)-based hybrid polymer composite, which may tend to either reversible (quinone-hydroquinone) or irreversible (overoxidation) electrochemical oxidation, depending on the potential, reason why in the present model, the resulting composite material will be considered.

Therefore, to describe the behavior of this system, considering some assumptions taken in [15–21], we investigate the bivariate equation-set (3):

$$\begin{cases} \frac{dp}{dt} = \frac{2}{\delta} \left(\frac{P}{\delta} (p_0 - p) - r_1 - r_p \right) \\ \frac{dc}{dt} = \frac{1}{c} (r_p - r_{O1} - r_{O2}) \end{cases} \quad (3)$$

In which p is the phenolic compound concentration in the pre-surface layer; p_0 is its bulk concentration, P is its diffusion coefficient, δ the pre-surface layer thickness, c is the composite material surface coverage degree, C is the composite maximal surface concentration and the parameters r are the correspondent reaction rates, capable of being calculated as (4 – 7):

$$r_1 = k_1 p (1 - c)^2 \exp(-ap) \quad (4)$$

$$r_p = k_p p^x (1 - c)^y \exp(-ap) \quad (5)$$

$$r_{O1} = k_{O1} c \exp \frac{2nF\phi_0}{RT} \quad (6)$$

$$r_{O_2} = k_{O_2}c \exp \frac{wF\varphi_0}{RT} \tag{7}$$

Herein, the parameters k are the correspondent reaction rate constants, x, and y are polymerization reaction orders, n is the polymer average chain length, w is the number of electrons transferred during the composite overoxidation, F is the Faraday number, φ_0 is the zero-charge-related potential slope in the double electric layer (DEL), R is the universal gas constant, and T is the absolute temperature.

Considering that all four reactions composing the process affect the DEL, the oscillatory and monotonic instability will be highly probable. Nevertheless, the electrosynthetic system will be efficient, as shown below.

3. Results and Discussion

We describe the electrochemical synthesis of poly(4-4'-dihydroxyazobenzene)/CoO(OH) composite, applying the linear stability theory to the equation set (4). The steady-state Jacobian matrix may be described as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \tag{8}$$

In which:

$$a_{11} = \frac{2}{\delta} \left(-\frac{P}{\delta} - k_1(1-c)^2 \exp(-ap) + ak_1p(1-c)^2 \exp(-ap) - xk_p p^{x-1}(1-c)^y \exp(-ap) + ak_p p^x(1-c)^y \exp(-ap) \right) \tag{9}$$

$$a_{12} = \frac{2}{\delta} (2k_1p(1-c) \exp(-ap) + yk_p p^x(1-c)^{y-1} \exp(-ap)) \tag{10}$$

$$a_{21} = \frac{1}{c} (xk_p p^{x-1}(1-c)^y \exp(-ap) - ak_p p^x(1-c)^y \exp(-ap)) \tag{11}$$

$$a_{22} = \frac{1}{c} \left(-yk_p p^x(1-c)^{y-1} \exp(-ap) - k_{O_1} \exp \frac{2nF\varphi_0}{RT} - k_{O_2} \exp \frac{wF\varphi_0}{RT} + j \left(k_{O_2}c \exp \frac{wF\varphi_0}{RT} + k_{O_1}c \exp \frac{2nF\varphi_0}{RT} \right) \right) \tag{12}$$

The main singular point conditions for the bivariate systems may be joined in Table 1:

Table 1. The main singular point conditions for bivariate equation sets.

Singular point	Condition	Effect
Hopf bifurcation	Tr J = 0, Det J > 0	Oscillatory behavior
Saddle-node bifurcation	Tr J < 0, Det J = 0	Steady-state stability margin
Steady-state stability	Tr J < 0, Det J > 0	Rapid steady-state formation

To simplify the determinant, we introduce new variables, rewriting the determinant as (13):

$$\frac{2}{\delta c} \begin{vmatrix} -\kappa - E & P \\ E & -P - \Omega \end{vmatrix} \tag{13}$$

Observing the main-diagonal elements (9) and (12), we may confirm that the *oscillatory behavior* in this system is possible. Moreover, it is of high probability.

It's known that the Hopf bifurcation may be realized if the main diagonal contains the positive addendums corresponding to the positive callback. These addendums are $ak_1p(1-c)^2 \exp(-ap) > 0$, $ak_p p^x(1-c)^y \exp(-ap) > 0$, if $a > 0$ and $j \left(k_{O_2}c \exp \frac{wF\varphi_0}{RT} + k_{O_1}c \exp \frac{2nF\varphi_0}{RT} \right) > 0$, if $j > 0$ corresponds to DEL capacitance and conductivity influences of chemical and electrochemical reactions. The oscillation amplitude depends on the background electrolyte composition, including pH. Mathematically, the oscillatory behavior conditions will be described as (14):

$$\begin{cases} -\frac{2}{\delta}(\kappa + \Xi) - \frac{1}{c}(P + \Omega) = 0 \\ \frac{2}{\delta c}(\kappa P + \kappa\Omega + \Xi\Omega) > 0 \end{cases} \quad (14)$$

To obtain the *steady-state stability* requirement, we apply the general condition $\text{Tr } J < 0$, $\text{Det } J > 0$. For this system, it will be exposed as (15):

$$\begin{cases} -\frac{2}{\delta}(\kappa + \Xi) - \frac{1}{c}(P + \Omega) < 0 \\ \frac{2}{\delta c}(\kappa P + \kappa\Omega + \Xi\Omega) > 0 \end{cases} \quad (15)$$

As the parameters κ and P may only have positive values, the condition (15) is readily satisfied if the parameters Ξ and Ω are also positive. It occurs if the DEL capacitance impacts aren't strong enough to destabilize the system.

Really, if $\Xi > 0$ and $\Omega > 0$, the left side of the first inequity will be shifted to more negative values, and the second expression will remain more positive, describing a diffusion-controlled electroanalytical system with a vast parameter region, correspondent to the easy formation and maintenance of the steady-state, providing the well-developed polymer composite surface formation. The resulting polymer composite may be an efficient electrode modifier for electroanalytical and electrosynthetic processes.

The *monotonic instability*, correspondent to the N-shaped part of the voltammogram, delimits the margin between the stable steady-states and unstable states. Its condition for the bivariate systems is $\text{Tr } J < 0$, $\text{Det } J = 0$.

$$\begin{cases} -\frac{2}{\delta}(\kappa + \Xi) - \frac{1}{c}(P + \Omega) < 0 \\ \frac{2}{\delta c}(\kappa P + \kappa\Omega + \Xi\Omega) > 0 \end{cases} \quad (16)$$

As for the composite synthesis in *galvanostatic and potentiodynamic modes*, it foresees a somehow more dynamic behavior. In this case, the trivariate equation set, including the electrode charge balance, has to be analyzed. This set will be described in one of our next works.

4. Conclusions

From the theoretical analysis of CoO(OH)/CoO₂-assisted 4-4'-dihydroxyazobenzene electrochemical polymerization, it was possible to conclude that either the polymerization or the resulting polymer reversible and irreversible oxidation may be responsible for the oscillatory behavior in this system. The oscillation frequency and amplitude depend strongly on the background electrolyte composition, including pH. Nevertheless, the polymer synthesis may be efficient, yielding a well-developed composite material used in electroanalysis and electrocatalytic processes and in heavy metal removal.

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Conflicts of Interest

The authors declare no conflict of interest.

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