

# Effects of Substituents on the Electrocatalytic Activity of Cobalt Phthalocyanines when Conjugated to Graphene Quantum Dots

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**Abstract:** We report on the  $\pi$ - $\pi$  interactions between graphene quantum dots (GQDs) and the following cobalt phthalocyanine derivatives: cobalt monocarboxyphenoxy phthalocyanine (complex **1**), cobalt tetracarboxyphenoxy phthalocyanine (complex **2**), and cobalt tetraaminophenoxy phthalocyanine (complex **3**). The conjugates (conj) with GQDs are represented as **1**@GQDs(conj), **2**@GQDs(conj) and **3**@GQDs(conj), respectively. The resulting phthalocyanine/GQDs conjugates were adsorbed on con-

taining a glassy carbon electrode (GCE) using the drop and dry method. We explore the electrochemical properties of phthalocyanines functionalized with both electron withdrawing groups and electron donating groups when non-covalently linked to the  $\pi$ -electron rich graphene quantum dots. GCE/**3**, GCE/**2**@GQDs(conj) and GCE/**1**@GQDs(conj) had the lowest limits of detection (LOD). Sequentially modified electrodes showed less favourable detection limits compared to the conjugates.

**Keywords:** cobalt phthalocyanines • graphene quantum dots • hydrazine • electrocatalysis

## 1 Introduction

Graphene quantum dots (GQDs) are in the latest frontiers of research on carbon based nanomaterials [1–4]. GQDs have earned scientific attention due to their fluorescent properties and their excitation wavelength dependant emission [5]. Owing to their low toxicity, good photo-stability and chemical inertness, carbon based quantum dots have found applications in various fields such as *in-vivo* and *in-vitro* bio-imaging [6,7], electrochemical sensing, bio-sensing [8–10], photocatalysis [11] and in light emitting diodes [12]. Carbon based materials have properties that are desirable in electrochemistry such as wide potential windows, fairly inert electrochemistry and good electrocatalytic activity for many reactions [13–15]. GQDs have been used to modify electrode surfaces for electrochemical sensing [16,17].

On the other hand, metallophthalocyanines (MPcs) are well known as electrocatalysts [18]. Electrode modification using MPcs enhances electron transfer reaction [18,19]. The electrochemical behaviour of MPcs is governed by their metal centres, the number, type and position of substituents. Owing to their planar structure, MPcs can undergo redox processes without losing their stability thus allowing reversible redox reactions [19]. In this work we combine the two electrocatalysts: MPcs and GQDs for enhanced electrocatalysis by synergistic effect.

We have previously reported on the conjugates of GQDs with MPcs for optical sensing [20–22], this work present the first study of the electrocatalytic behaviour of these conjugates. CoPc derivatives are employed since MPcs containing Co central metal are known to exhibit high catalytic activity for various reactions including the electro-oxidation of hydrazine [18,19,23]. The CoPc derivatives

employed are: cobalt monocarboxyphenoxy phthalocyanine (complex **1**), cobalt tetracarboxyphenoxy phthalocyanine (complex **2**), and cobalt tetraaminophenoxy phthalocyanine (complex **3**), Figure 1. We study the effect of nature of substituent by comparing complexes **2** and **3**, and the number of substituents by comparing **1** and **2** towards the electrocatalytic detection of hydrazine. Hydrazine is employed as a test analyte. All the CoPc derivatives are adsorbed onto GQDs via  $\pi$  $\pi$  stacking, followed by drop dry adsorption onto a glassy carbon electrode.

## 2 Experimental

### 2.1 Materials

N, N dimethyl formamide (DMF) was purchased from Merck. Potassium hexacyanoferrate (II) ( $K_4[Fe(CN)_6]$ ), potassium hexacyanoferrate (III) ( $K_3[Fe(CN)_6]$ ), dialysis tubing (MWCO 1.5kDa), and citric acid were from Sigma-Aldrich. Millipore water was obtained from Milli-Q Water Systems (Millipore Corp. Bedford, MA, USA). Stock solution (1 mM) hydrazine was prepared in 0.1 M sodium hydroxide. GQDs were synthesized as reported in literature [24]. Complexes **1** to **3** were synthesized as reported in literature [25–27].

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/elan.201700252>