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Electrocatalytic hydrogen evolution reaction on reduced graphene oxide electrode decorated with cobaltphthalocyanine

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ABSTRACT

Electrocatalytic hydrogen evolution reaction (*HER*) on azido graphene oxide (GO-N_3) and reduced azido graphene oxide (RGO-N_3) electrodes decorated with the cobaltphthalocyanine complex bearing terminal alkyne moieties (***TA-CoPc***) was investigated. GCE/**RGO-N_3** electrode was constructed with the electrochemical reduction of GO-N_3 coated on a glassy carbon electrode. Decoration of GCE/**RGO-N_3** and GCE/**GO-N_3** electrodes were performed with a new electrode modification technique, "click electrochemistry (CEC)", with which ***TA-CoPc*** complex was bonded to azido functional groups of GO-N_3 and RGO-N_3 on the electrodes. The modified GCE/**RGO-N_3**/***TA-CoPc*** and GCE/**GO-N_3**/***TA-CoPc*** electrodes were characterized with square wave voltammetry and electrochemical impedance spectroscopy (EIS), and then tested as heterogeneous electrocatalysts for *HER*. GCE/**RGO-N_3**/***TA-CoPc*** electrode illustrates well electrocatalytic activity by decreasing the over-potential of the bare electrode about 340 mV and increasing the current density of the electrode about 15 fold at low pHs with absolutely high stability and reproducibility.

1. Introduction

Due to the world serious energy problems, the development and realization of alternative energy options become increasingly important. Among the possible options, solar-hydrogen energy systems are among a number of encouraging technologies. Hydrogen is one of the most preferable renewable energy carrier and ideal energy storage, since it has high energy density, and could be easy converted into various available energy forms. One of effective solar-hydrogen conversion approaches is indirect usage of solar energy in electrocatalytic water electrolysis reactions. Highly purified hydrogen can be produced from water electrolysis, but the biggest disadvantage is high-energy consumption of this method [1,2]. In order to reduce the production costs by lowering the overpotential (potential differences between the reversible reduction potential and practical discharge potential) of hydrogen evolution reaction (*HER*), various electrocatalytic materials have been frequently tested as the best solutions [3–6]. A wide variety of functional materials; such as, nickel and cobalt based alloys, MoSx, cobalt clathrochelates, iron hydrogenase, glyoxime and tetraimine complexes [7–10].

Graphene Oxide, strictly two-dimensional material, exhibits exceptionally high crystal and electronic quality, and, despite its short history, has already revealed new potential applications. Within a short time of being available in bulk quantities, graphene oxide, have become highly versatile, inexpensive building blocks for the development of several advanced carbonaceous materials. For example, it is not difficult to imagine the incorporation of a variety of additives into composites of graphene oxide to create novel material compositions [11]. In these novel composites, it is also evident that graphene not only promotes the effective electron transfer [12,13] but also increases the specific surface area through increased dispersion of functional materials. Due to these versatile properties 2-D graphene based functional hybrid nanomaterials have been used for many fields such as, sensors [14,15], transparent conductors [16], purification [17,18], and dye-sensitized solar cells [19,20]. Now a days, GO based materials have been tested as active photocatalysts and photoelectrocatalyst for water splitting reactions [21–24].

GO is an electrically insulating material due to their disrupted sp^2 bonding networks. As-synthesized GO is insulating but controlled deoxidation leads to an electrically and optically active material that is transparent and conducting. Because electrical con-

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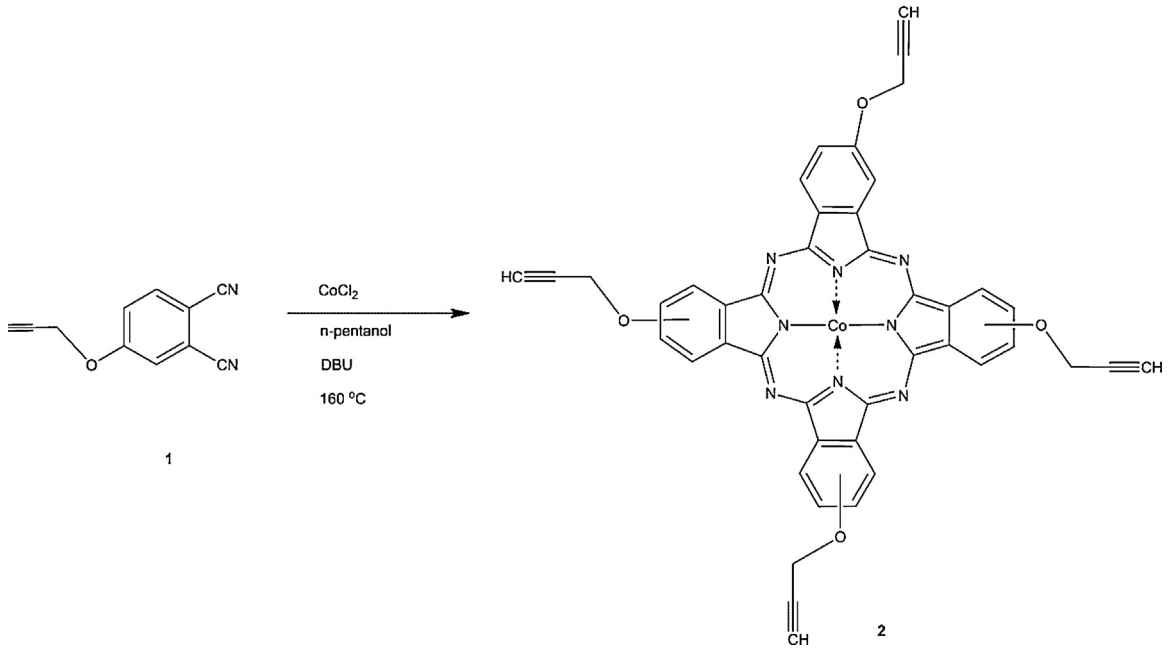
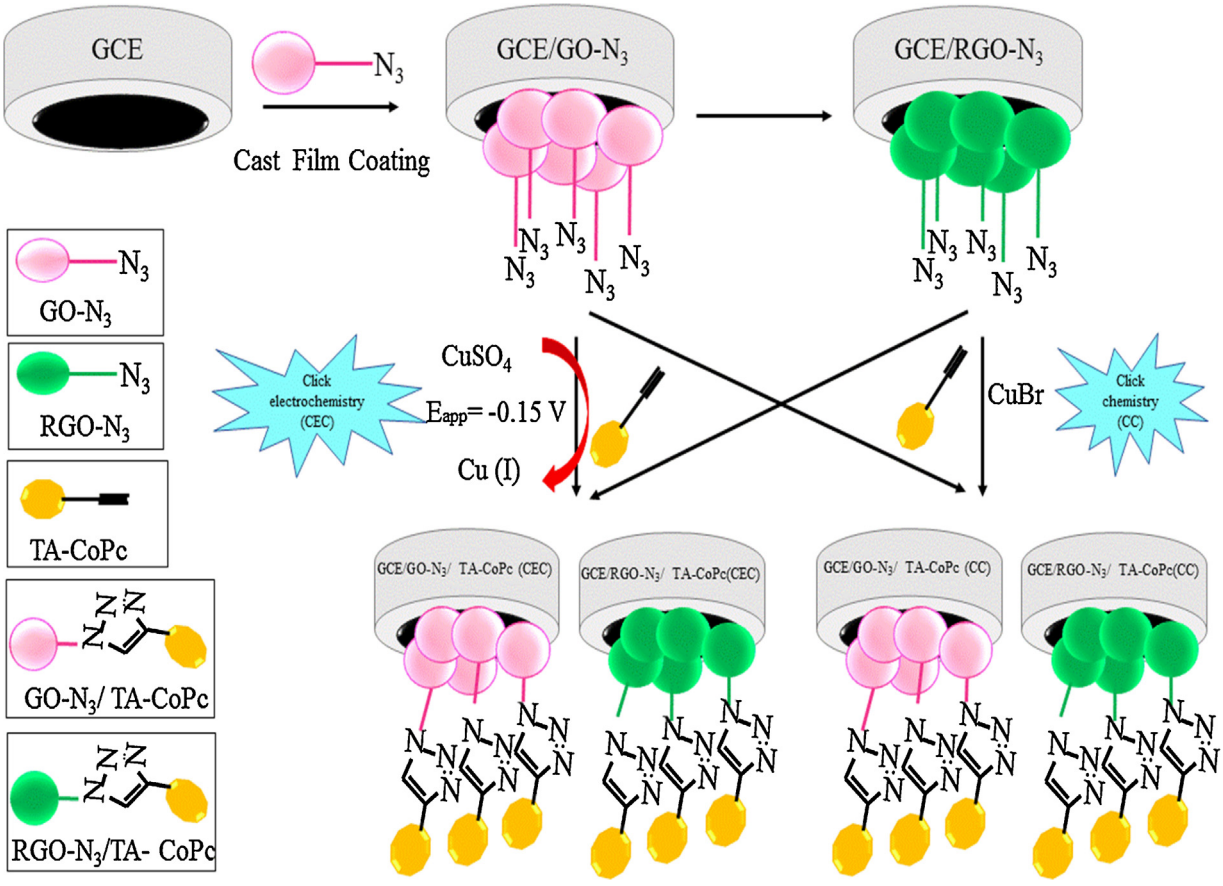
ductivity can be recovered by restoring the π-network, one of the most important reactions of graphene oxide is its reduction to reduced graphene oxide (RGO) [25]. Thus, RGO is both conductive and has chemically active defect sites making it a promising candidate for the active material in various technological applications, such as, molecular sensors [26,27], catalysts [23,28,29], solar cells [30], and supercapacitors [31,32]. Due to the higher electrically and optically activity of RGO with respect to GO, RGO has been preferred as active photocatalysts [29,33,34] and photoelectrocatalyst [35,36] for the hydrogen production from water splitting reac-



Scheme 1. Synthetic pathways for the phthalonitriles and phthalocyanines (i) $CoCl_2$, DBU, *n*-pentanol, heat, N_2.



Scheme 2. Electrode modification via the "click chemistry" (CC) and the "click electrochemistry" (CEC) between **GO-N_3**, **RGO-N_3**, and ***TA-CoPc***.