

# Co-phthalocyanine/Graphene Quantum Dots/TiO<sub>2</sub> as a New Hybrid for Photocatalytic Degradation of Formic Acid Toward Hydrogen Generation

Sajjad Keshipour\*, Mina Hadidi and Mojtaba Abedi-Mehmandar

Department of Nanotechnology, Faculty of Science, Urmia University, Urmia, Iran

(\* Corresponding author: s.keshipour@urmia.ac.ir  
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## Abstract

Hydrogen has been considered as one of the worthy fuels for the high potential energy and nonpolluting combustion. With increasing the concerns about fossil fuels pollution for the environment, attempts have been concentrated on the improving of new green fuels such as hydrogen. Particularly, the safe and cost-effective production of hydrogen has been widely studied, in which the catalysts deserved remarkable progresses. Herein, photocatalytic activity of cobalt-phthalocyanine/graphene quantum dots/TiO<sub>2</sub> was investigated in the formic acid degradation under visible irradiation toward hydrogen generation. TiO<sub>2</sub> as a semiconductor trapped photons to generate electron/hole pairs and graphene quantum dots made delay in their recombination to provide long time for promoting the hydrogen and carbon dioxide evolution reactions by electrons/holes. Cobalt (II)-phthalocyanine as a catalyst utilized the electrons in the transformation of protons to H<sub>2</sub>, while in the positive region carbon dioxide was producing. The reaction was progressed efficiently affording H<sub>2</sub> with the rate of 3.60 mmol.h<sup>-1</sup> and activation energy was calculated to be 16 KJ.mol<sup>-1</sup>. This three-component catalyst showed satisfying stability to run the reaction for long time. Notable catalytic activity, and employing light power for the reaction done are two significant characteristics of this hybrid.

**Keywords:** Hydrogen generation, Photocatalysis, Green, Phthalocyanine, Graphene, Formic acid.

## 1. INTRODUCTION

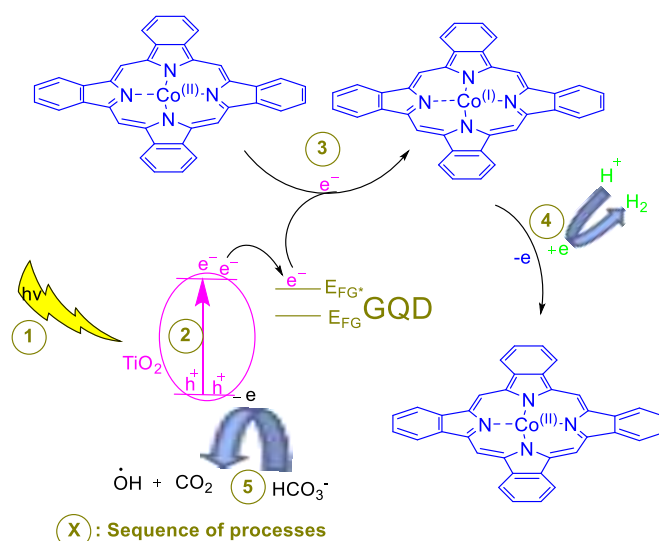
Nowadays, large scale production of green fuels by facile, efficient, and inexpensive approaches is the subject of many researches [1]. Hydrogen as a green fuel gives off water as the combustion gas without any waste [2]. While remarkable sources have been introduced for the hydrogen generation, formic acid (FA) has been widely employed regarding its accessibility, low cost, easy transformation, and waste-less nature [3]. Degradation of FA to hydrogen have been conducted on by various catalysts such as transition metals [4]. However, the low rates of hydrogen evolution from this reaction are considered as the significant issue, which has led to a tremendous study to improve new catalysts for this system. Organometallic compounds like phthalocyanine (Pc) derivatives

revealed superior activity for the hydrogen generation although they are the less studied species in this area. Overall, Pc's of Co, Cu, Ni, Zn, Mg, and Fe were utilized in the hydrogen generation from FA [5-9]. Thin film of CoPc, [5] and water-soluble Co-tetrasulfophthalocyanine catalyzed FA decomposition to H<sub>2</sub> through electrochemical approaches [6]. Fe and Mg phthalocyanines (Pc) were utilized in the deconstruction of FA with detailed study of the reaction mechanism [7]. NiPc and CuPc supported on graphene oxide promoted the reaction in a photocatalytic pathway [8, 9]. The remarkable performance of metallo-phthalocyanines is ascribed to the excellent photochemical activity [10] as well as appropriate redox characteristics [11]. These structures are able to absorb near IR

and visible light in wavelength ranged from 600-800 nm, and this is a perfect reason for utilization of these structures for light harvesting and promotion of hydrogen generation reactions [12]. Quantum dots based on graphene (GQD) or carbon are classified as a new member of carbon nanomaterials, having sizes less than 10 nm. These nanomaterials are honored in chemistry and material sciences due to some advantages like safety, facile production, inexpensive nature, high solubility, chemical inertness, and easy modification [13]. Innumerable advances have been achieved in the synthesis, properties, and applications of GQDs [14-18]. A hybrid of GQD/TiO<sub>2</sub> was utilized for numerous purposes such as energy, biomedical, electronics, and flexible wearable sensors [19].

In the energy applications usually TiO<sub>2</sub> is in charge of producing electron/hole pairs under light irradiation as a semiconductor. The combination of TiO<sub>2</sub> with GQDs offers some advantages including broadening the light absorption wavelengths, providing active reaction sites, and retarding electron-hole recombination (the combination of charges is a displeasing happen for a semiconductor and leads to its quenching) [19]. One of the energy applications of GQD/TiO<sub>2</sub> is attributed to the H<sub>2</sub> production, which some examples are

highlighted here. GQD/TiO<sub>2</sub> nanotubes catalyzed photocatalytic H<sub>2</sub> generation from water splitting under UV irradiation [20]. After that, the reaction was also reported using rutile TiO<sub>2</sub> nanoflowers instead of the nanotubes [21]. As a worthy report, polymeric O-linked heptazine polymer modified with S, N co-doped GQDs as a photosensitizer produced H<sub>2</sub> under visible irradiation [22]. In continue of our efforts to extend the application of phthalocyanines as the catalysts, [23, 24] herein a new catalytic system consisted of CoPc, GQD, and TiO<sub>2</sub> NPs was used for the efficiently hydrogen production from FA degradation under visible irradiation. With respect to the fact that CoPc as an active catalyst has been employed in the FA decomposition toward hydrogen production through electrochemical reactions, [5] we believed that the electrochemical system could be replaced by a photochemical system in which the electron/holes injection is carried out by TiO<sub>2</sub>. In the meantime, GQD improves the photocatalytic performance of TiO<sub>2</sub> as explained above [19]. Therefore, we conducted the research using TiO<sub>2</sub> as a semiconductor to launch electron flux by photo-irradiation, GQD as sensitizer as well as retardant of charge recombination, and CoPc as the catalyst (Scheme 1) [25].



**Scheme 1.** Photocatalytic H<sub>2</sub> production from FA using CoPc/GQD/TiO<sub>2</sub>.

## 2. EXPERIMENTAL

### 2.1. Material and Methods

All reagents were purchased from Sigma-Aldrich and used without further purification. Anatase form of TiO<sub>2</sub> with the particle size less than 25 nm was purchased from Sigma-Aldrich. Transition electron microscopy (TEM) micrographs were obtained with Philips CM100 BioTWIN transmission electron microscope. GC High Resolution Gas Chromatograph Mass Spectrometer was carried out using thermo scientific. Fourier transform infrared spectroscopy (FTIR) was used to characterize different functional groups of the composite using Jasco 6300 FTIR instrument in the range of 600-4000 cm<sup>-1</sup>. Energy Dispersive X-Ray Spectroscopy (EDX) was carried out by SEM FEI Quanta 200.

### 2.2. Preparation of GQD and CoPc

In this study, GQDs were prepared by direct pyrolyzing method from citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) [15]. For this purpose, 2g citric acid was poured into a 50 ml beaker and then was heated at 200 °C for 15 min. At this time, citric acid was melted and then the color of liquid was changed from colorless to orange, which confirms the formation of GQDs. In order to purification, 20 ml of acetone and 20 ml of NaOH (0.1 M) were added to the mixture. Finally, the oil part was separated from the mixture as GQD.

For the preparation of CoPc, phthalic anhydride (8 mmol), urea (40 mmol), ammonium molybdate (0.005 g), and CoCl<sub>2</sub>.6H<sub>2</sub>O (0.6 g) in a round-bottom flask were mixed and then, the obtained mixture was irradiated under microwave using a 900 W instrument for 3 min [11]. The mixture was treated with HCl (50 ml, 0.1 M) and mixed for 10 min and then, NaOH (50 ml, 0.1 M) was added to the vessel. Next, the solids were filtered off, washed with H<sub>2</sub>O

(5 × 10 ml), and dried in a drying oven at 80 °C to give blue color CoPc.

### 2.3. A Setup for Degradation of FA for Hydrogen Evolution

Photocatalytic degradation of FA was performed using a 200 W xenon lamp ( $\lambda > 420$  nm). Initially, 0.05 g (18  $\mu$ mol) of CoPc, 0.1 g GQD, and 0.04 g TiO<sub>2</sub> were added to 30 ml of FA. Then to disperse catalysts, the mixture was stirred without any light irradiation for 30 min. Next, the mixture exposed to light irradiation to run a photochemical reaction while continuously being stirred. The reaction vessel was linked by a hose to an inverted burette filled with water to trap the produced gas and the volume of the replaced water with produced gas was used in the following equation to obtain the mol of gas:

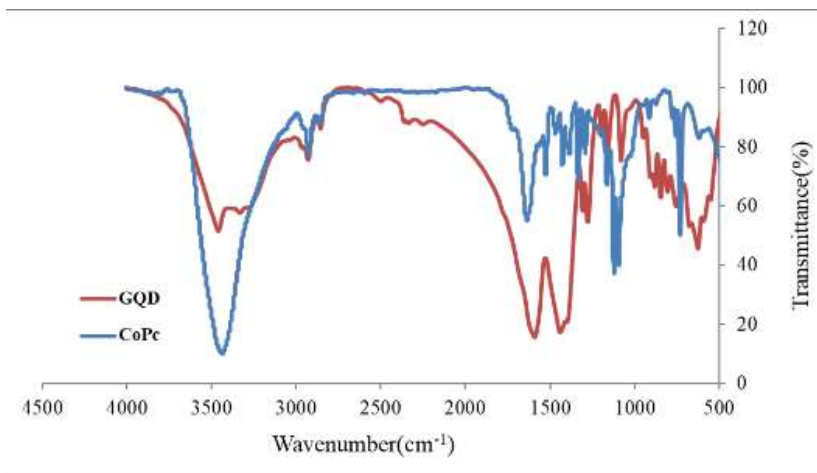
$$PV=nRT$$

where,  $P$ ,  $V$ ,  $n$ ,  $R$ , and  $T$  are atmospheric pressure (atm), gas volume (L), mol of gas, ideal gas constant, and temperature (K), respectively.

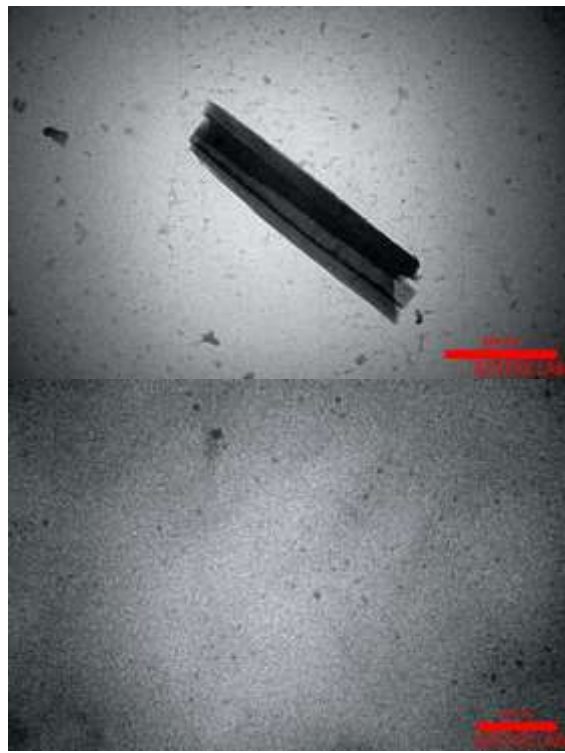
## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of GQD and CoPc

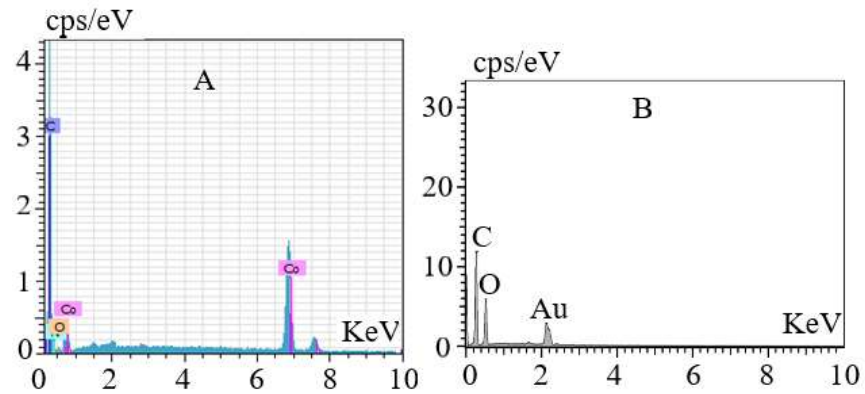
In order to confirm properly formation of GQDs and CoPc, the prepared samples were subjected to FTIR spectroscopy, which is an absorbance-based technique for monitoring functional groups. As shown in GQD spectrum (red), the appearance of sharp peaks in about 1710 cm<sup>-1</sup> is related to the C=O [15]. A broad band in a higher wavenumber, 3599 cm<sup>-1</sup>, is ascribed to the hydroxyl groups. On the other hand, formation of CoPc observed by appearance a characteristic peak at 1698 cm<sup>-1</sup>, which is attributed to C=C or C=N groups [24]. The appearance of weak peaks in the range of about 3000 cm<sup>-1</sup> was ascribed to the aromatic C-H bonds of CoPc structures.



**Figure 1.** FT-IR spectra of GQD and CoPc.



**Figure 2.** TEM images of CoPc (top) and GQDs (bottom).



**Figure 3.** EDX analysis of CoPc (A), and GQD (B).

TEM micrographs were prepared for CoPc and GQD (Figure 2). The CoPc micrograph showed formation of rod like structures with about 270 nm diameter (the first image; scale bar 500 nm). Moreover, TEM image of the synthesized GQD showed formation of uniform nanoparticles with the size of 12-15 nm (the second image; scale bar 50 nm).

EDX analysis was performed on CoPc, which revealed the presence of the expected elements including C, N, and Co. The result obviously confirms formation of CoPc. Also, the spectroscopy for GQD was revealed C, and O as the ingredients of GQD. It worthy to note that the majority of the GQD structure involves C=C, C=O, and C-O bonds (Figure 3).

### 3.2. Catalytic FA Degradation

Totally, photocatalytic H<sub>2</sub> production is impressed by some factors such as wavelength of irradiation, efficiency of electron donating system, power of catalyst and so on. Furthermore, the operation range for a photocatalyst is considered as a significant factor in which the visible area is preferred. CoPc is known as a photocatalyst with a broad absorption in the visible region [26]. This capability of CoPc is ascribed to the  $\Pi$  system with absorption areas at 620-700 nm known as Q band and about 350 nm known as Soret B band. Herein, a three-component catalyst of CoPc/GQD/TiO<sub>2</sub> was employed in the photocatalytic H<sub>2</sub> generation from FA under Vis irradiation at ambient conditions (Table 1). The catalyst degraded FA toward production of H<sub>2</sub>/CO<sub>2</sub> with the rate of 3.60 mmol H<sub>2</sub>.h<sup>-1</sup> (calculated in 10 min) using optimized amounts of 0.1 mmol of CoPc/0.1 g of GQD/0.04 g TiO<sub>2</sub>. The reaction afforded 0.36 mmol of H<sub>2</sub> in the absence of TiO<sub>2</sub>, which showed that CoPc could also act as a semiconductor to absorb photons and proceed the reaction. However, existence of TiO<sub>2</sub> increased the reaction rate by improving the electron injection. For screening the effect of GQD on the reaction, H<sub>2</sub> evolution was examined using

CoPc/TiO<sub>2</sub> and the result demonstrated the rate of 0.44 mmol.h<sup>-1</sup>. As described in the introduction, GQD impresses the photocatalytic reactions by retarding the electron-hole recombination which increases available electrons any time. In all experiments, signals assigned to H<sub>2</sub> and CO<sub>2</sub> were detected by GC without any CO signal.

**Table 1.** H<sub>2</sub> production by various catalysts from FA degradation reaction.

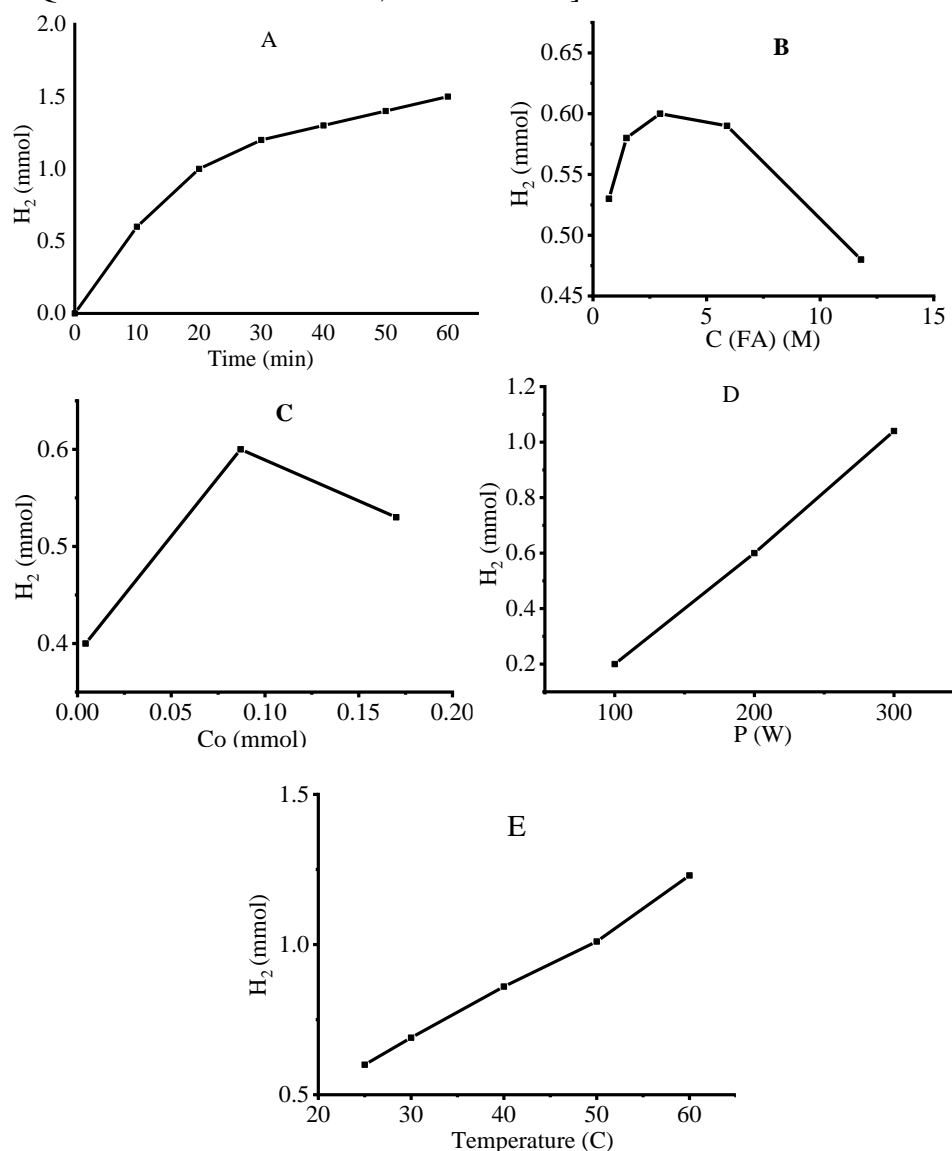
Entry	catalyst	H <sub>2</sub> (mmol)
1	TiO <sub>2</sub>	-
2	CoPc	-
3	GQD	-
4	TiO <sub>2</sub> (0.04 g)/CoPc (0.05 g)	0.44
5	CoPc (0.05 g)/GQD (0.10 g)	0.36
6	TiO <sub>2</sub> (0.04 g)/CoPc (0.05 g)/GQD (0.10 g)	0.60
7	TiO <sub>2</sub> (0.03 g)/CoPc (0.05 g)/GQD (0.10 g)	0.54
8	TiO <sub>2</sub> (0.04 g)/CoPc (0.05 g)/GQD (0.09 g)	0.57
Reaction conditions: FA (30 ml), catalyst, r.t., xenon irradiation (200 W), 10 min.		

Effects of various parameters were studied on the reaction yield such as FA concentration, catalysts loading, light power, and temperature (Figure 4). Like the majority of reports, the reaction indicated decrease in the reaction rate after 10 min (Figure 4A). For example, the reaction rates were calculated as 3.6, 2.4, and 1.2 mmol H<sub>2</sub>.h<sup>-1</sup> for the 0-10, 10-20, and 20-30 min, respectively. The concentration of FA was found as a significant factor on the reaction yield with the maximum rate of 3.6 mmol.h<sup>-1</sup> for the 2.95 M of the acid (calculated for 10 min). Both increasing and decreasing the acid molarity reduced the reaction rate (Figure 4B). The catalyst loading was also evaluated on the reaction, in which the 0.1 mmol of the catalysts gave the best result (Figure 4C). The increasing of the catalyst amount from 0.1 mmol induced negative

impacts on the reaction may be due to the interfering of the excess catalyst together. The power of the light source demonstrated direct impress on the reaction yield with higher yields in higher intensities (Figure 4D). The reaction temperature indicated an important influence on the catalytic activity of the hybrid where higher yields obtained at higher temperatures (Figure 4). Moreover, the activation energy ( $E_a$ ) was calculated to be 16.0 kJ/mol for the reaction by CoPc/GQD/TiO<sub>2</sub>. This  $E_a$  is significantly lower than most previously obtained  $E_a$  values [27].

A hot filtration test was also carried out on CoPc/GQD/TiO<sub>2</sub>. For this reason, the

catalyst was removed from the mixture after 5 min using centrifuge and the reaction progress was monitored which showed that the gas releasing was stopped confirming heterogeneously progressing of the reaction. Finally, the catalyst stability was surveyed in FA. In order to do this test, the light source was turned off after 10 min and turned on again after 24 h. The reaction produced 3.24 mmol H<sub>2</sub>.h<sup>-1</sup> in the second round, indicating the stability of the catalytic system in the FA solution. It should be highlighted that the stability of the catalyst is considered as one of the significant factors for the durability [28-30].



**Figure 4.** Effects of time, concentration of FA, Co amounts, lamp power, and temperature on the produced H<sub>2</sub> by CoPc/GQD/TiO<sub>2</sub>.

#### 4. CONCLUSION

A hybrid of CoPc/TiO<sub>2</sub>/GQD was employed in the photocatalytic degradation of formic acid. While CoPc has been used as an electrocatalyst in this reaction, present research revealed that the reaction is executable under visible light via an appropriate system capable to produce electron flux. Results demonstrated that TiO<sub>2</sub> as a semiconductor, and CoPc as a semiconductor as well as catalyst contribute in this reaction. Furthermore, GQD by improving electron injection efficiency and retarding the charge recombination in semiconductors accelerates the reaction.

#### DECLARATION

**Conflict of Interest.** The authors declare no competing financial interest.

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#### Authors Contribution.

Sajjad Keshipour: Conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, supervision, validation, visualization, writing-original draft, and writing-review & editing.

Mina Hadidi: Data curation, formal analysis, investigation, methodology, resources, validation, visualization, and writing-review & editing.

Mojtaba Abedi-Mehmandar: Data curation, formal analysis, investigation, methodology, resources, validation, visualization, and writing-review & editing.



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