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Graphene oxide modified cobalt metallated porphyrin photocatalyst for conversion of formic acid from carbon dioxide

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ABSTRACT

An increasingly level of one of the important greenhouse gas, CO_2, in the atmosphere from anthropogenic human activities has several adverse consequences and thus, chemical transformation of carbon dioxide into useful, renewable and environmentally friendly products is becoming an important research problem. In the present investigation, we have developed photocatalyst of graphene oxide modified with cobalt metallated aminoporphyrin (GO-Co-ATPP) for conversion of CO_2 to formic acid under visible light. The efficiency of nanohybrid photosynthetic conversion of formic acid from carbon-dioxide is 96.49 μmol for 2 h. We have used XRD, SEM, HR-TEM, AFM, thermogravimetric analysis, BET measurement to establish the structural and physical properties along with infrared spectroscopy and Raman spectroscopy for chemical properties of GO-Co-ATPP. The photocatalyst was significantly effective for NADH photoregeneration with cumulative 48.53% over time and photoelectrochemical measurement showed photocurrent properties. These results strongly suggest that the GO-Co-ATPP photocatalyst materials may open new vistas in conversion of CO_2 into useful and environmentally friendly products as well as energy applications.

1. Introduction

In recent decades, challenging tasks for human society are increasing global temperature and demand of energy using renewable and clean energy resources due to growing global production and population [1–3]. Despite the importance of CO_2 (carbon dioxide) in keeping earth's temperature habbitable and radiation balance, a large increase in CO_2 concentrations is also responsible for global warming, rising sea-level and increasing the acidity of the oceans. The atmospheric CO_2 concentration has increased from 310 ppm to ~390 ppm over the last half-century alone which could lower the pH of ocean from 8.2 to 7.8 by 2095 due to the accumulation and dissolution of CO_2 in ocean water [4]. Therefore, the conversion of carbon dioxide to high value chemicals has attracted much attention in the environmental and energy research areas [5–7]. In addition, artificial photosynthesis using CO_2 and solar energy, a free and abundant renewable source of clean energy, are the most acceptable technology to fulfill future demands of energy [8–11].

Porphyrin nucleus consist of four pyrrole rings joined by four methine bridges to give a near planar macrocycle chromophores based in a 18π-electronic conjugated network. The unique electrochemical and photophysical properties play a key role in natural photosynthetic systems [12–15]. A range of different artificial photosynthesis processes has been developed using different photocatalyst materials, such as transition-metal complexes, semiconductors etc. [16–19]. For example, Yadav et al. [18] have reported a photocatalyst-enzyme coupled artificial photosynthesis system which utilizes solar energy for the synthesis of various useful chemicals and fuels. However, photocatalyst-enzymes coupled artificial photosynthesis process are highly challenging for their practical uses which acts as a photocatalyst in the reduced nicotinamide adenine dinucleotide (NADH) regeneration system and activates enzymatic production of solar chemicals or solar fuel from carbondioxide [18,20]. Covalent attachment of isatin-porphyrin chromophore have recently demonstrated the capability for selective methanol production from CO_2 graphene photocatalyst biocatalyst integrated system [21]. Furthermore, Yaghi et al. have reported covalent organic frameworks in which building unit are cobalt porphyrins for catalytic CO_2 reduction in water [22].

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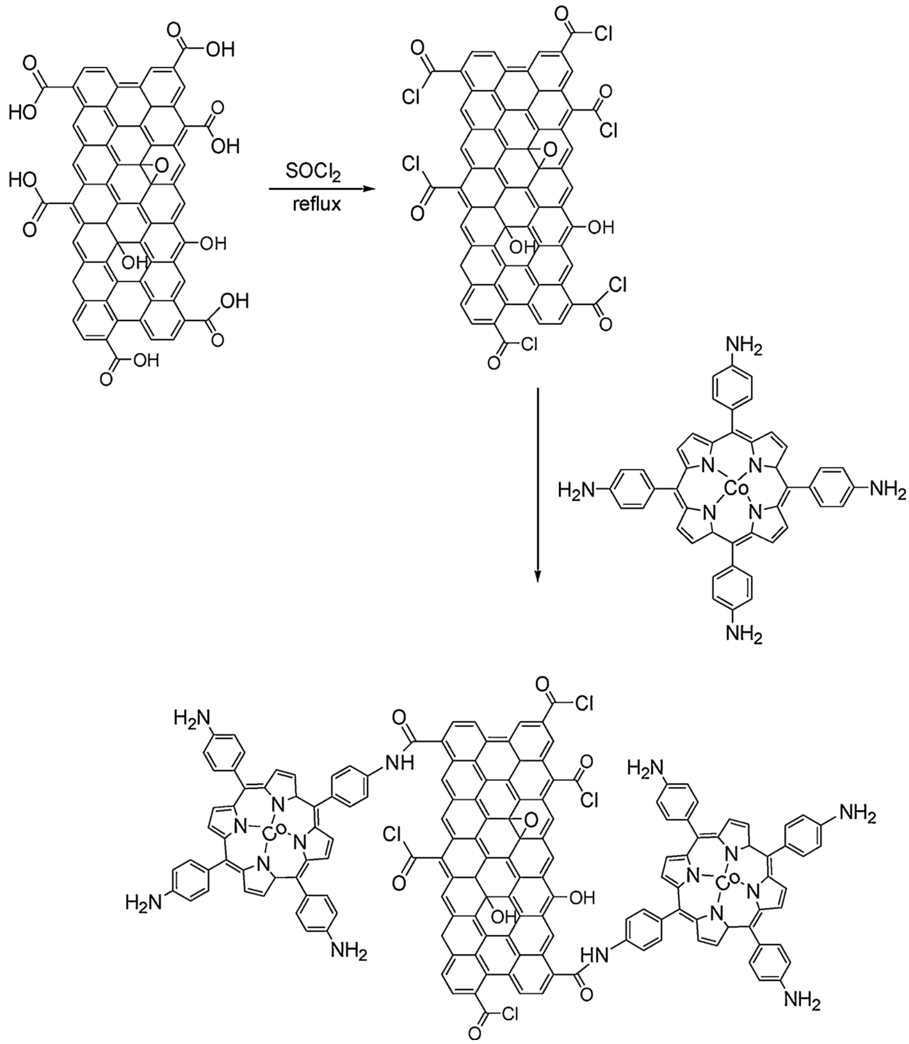

Scheme 1. Schematic illustration of the synthesis of GOCl and GO-Co-ATPP.

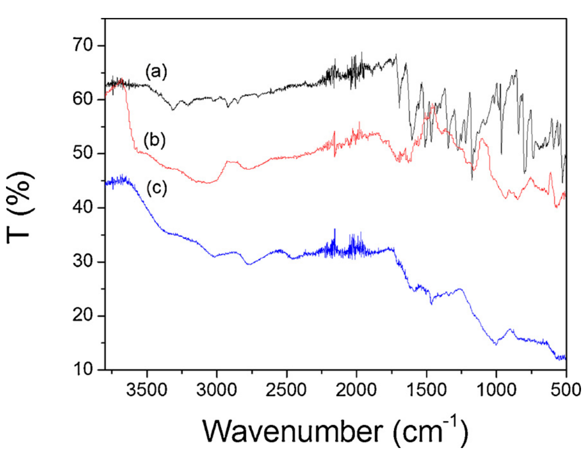

Fig. 1. ATR-IR of ATPP (a), GO (b) and GO-Co-ATPP (c).

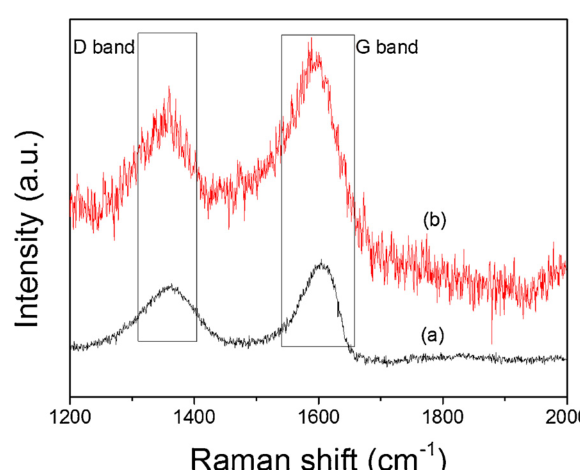

Fig. 2. Raman spectra of GO (a) and GO-Co-ATPP (b).

Carbon materials are more important inorganic materials for artificial photosynthesis, since carbon is one of the most available elements in our ecological system and more environmental friendly. Graphene oxide has diverse applications, not only as central optoelectronic but also as a energy conversion and storage material for nanoscale engineering [23]. In addition, graphene oxide has many exceptional properties, including its biological function, mechanical, thermal and biomedical applications [24–31]. Several researchers have taken advantage of these unique aspects of grapheme oxide and a variety of modification of nanohybrid materials have been produced with properties derived both from biological functions and structural characteristics of nanohybrid molecules. Furthermore, various chemical properties of graphene has facilitated its application in conversion and storage of energy [26,32–35]. Recently, photoreduction of CO_2 to methane