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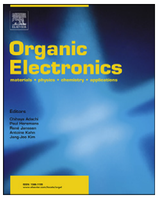

High-efficiency counter electrodes using graphene hybrid with a macrocyclic nickel complex for dye-sensitized solar cells

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ABSTRACT

Nanocomposites using graphene hybrid with a fully conjugated macrocyclic nickel complex were successfully prepared via a simple redox reaction of graphene oxide and an octaaza-bis-α-diimine macrocyclic nickel complex. The dye-sensitized solar cells fabricated with the graphene/macrocyclic nickel complex-based nanocomposite counter electrode reached a power conversion efficiency of 8.30%, which was higher than that of the platinum counter electrode under the same conditions. The nanocomposites exhibited excellent electrocatalytic performance for the reduction of triiodide due to the well-distributed catalytic nickel center on the graphene surface.

1. Introduction

Since Grätzel and his colleagues reported the dye-sensitized solar cells (DSSCs) in 1991 [1], DSSCs have attracted much attention due to their various merits, such as relatively high efficiencies, simple device structures, easy fabrication, potentially low cost, and variety and flexibility in applications [2–5]. These features have made DSSCs attractive for solar energy applications in the face of increasing energy and environmental challenges [6]. A typical DSSC consists of a transparent conductive substrate, a porous thin-film photoelectrode composed of TiO_2 nanoparticles, dyes, an electrolyte, and a counter electrode (CE) [7]. The CE is an important component in DSSCs. The functions of the CE include electron collection from external circuits and electron transfer from the CE interface to the electrolyte by an electrocatalytic reduction of I_3^-. The requirements for the CE in DSSCs are low charge-transfer resistance, high reversibility/current density for the effective reduction of the oxidized species, and good chemical/electrochemical stability in the electrolyte systems. Normally, platinum (Pt) is used as the CE material because of its excellent electrocatalytic activity and good chemical stability for high efficiency DSSCs. However, the cost of Pt is relatively expensive for the large-scale application of DSSCs. Therefore, developing a low-cost and high-efficiency CE to replace Pt electrodes is a meaningful issue for the cost reduction of DSSCs. Several previous studies have endeavored to replace Pt CEs with other more cost-effective CE materials that have favorable electrochemical properties such as metal oxide [8,9], conductive polymers [10–12], carbon nanotubes [13,14], graphene [15–17], and composite materials [18–20].

Graphene has attracted much research and it has been applied in various areas because of its excellent properties such as high specific surface area, mechanical properties, chemical/thermal stability, and conductivity [21–25]. Due to its exceptional properties, graphene-based electrodes may have the potential as CEs for DSSCs. Several research teams have used graphene to fabricate DSSC CEs [15,26–31]. Kavan et al. fabricated graphene sheets on a fluorine-doped tin oxide (FTO) substrate for use as a DSSC CE and achieved satisfactory catalytic activity [29]. Roy-Mayhew et al. used functionalized graphene sheets as DSSC CEs and determined that increased oxygen-containing functional groups enhance the surface catalytic activities of graphene [30,32]. Wan et al. fabricated graphene thin films on various substrates by using low-cost room-

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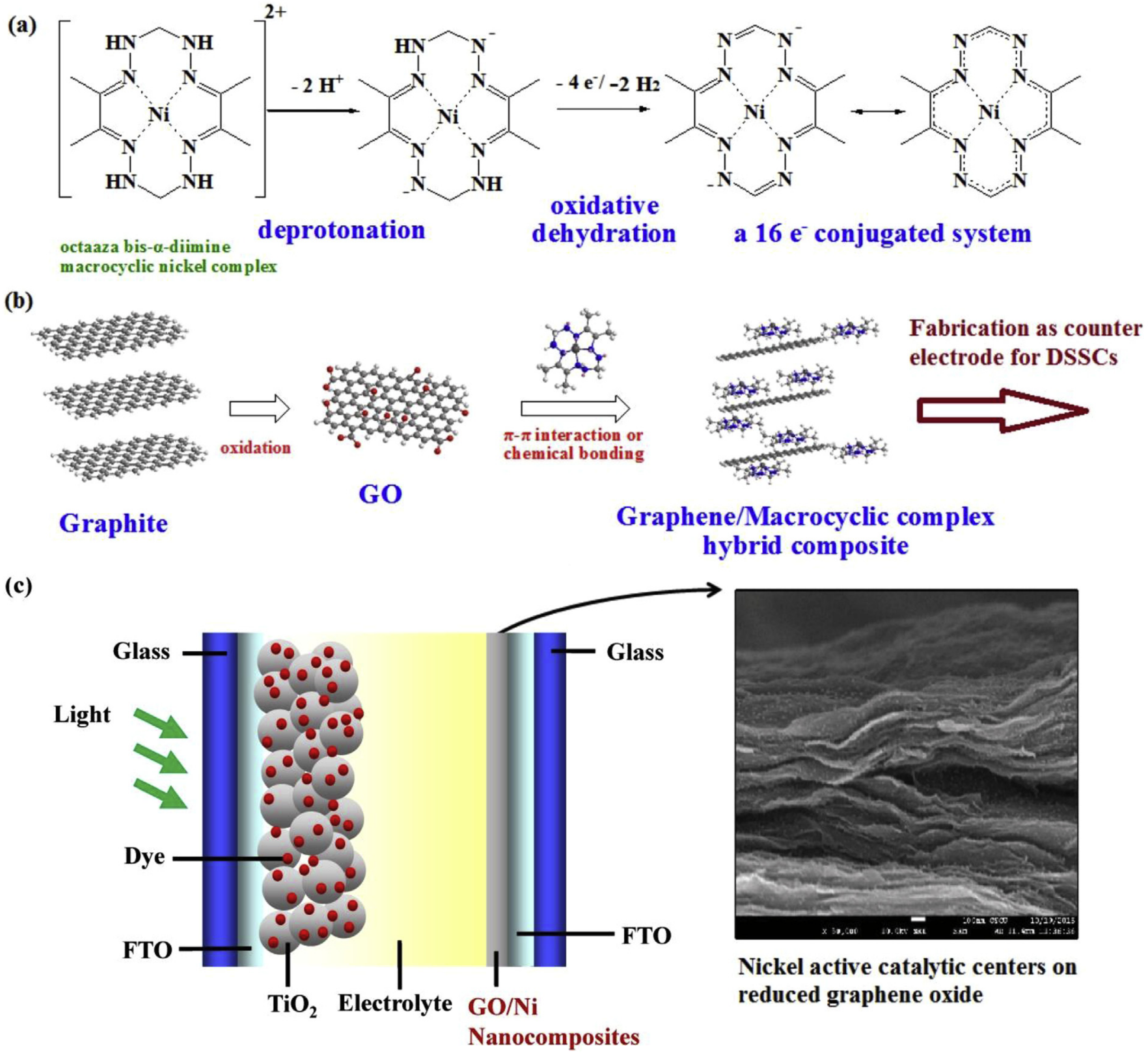
temperature solution processes and determined that graphene can be applied to DSSCs, supercapacitors, fuel cells, and chemical sensor devices [31].

In this study, we developed a novel molecular hybrid graphene-based electrocatalytic system as the CE for DSSCs. A new series of graphene/macrocyclic nickel (Ni) complex-based hybrid materials were synthesized and successfully applied as the CEs of the DSSCs. A metallic catalyst was grafted onto the graphene surface to prepare a nanoscale and well-distributed metal hybrid material for the CE. The results showed that DSSCs based on this system could achieve efficiency better than those based on Pt-based CEs. An octaaza bis-α-diimine macrocyclic Ni complex, $[Ni(C_{10}H_{20}N_8)]Cl_2$, was selected for the preparation of the graphene-based hybrid materials because the macrocyclic system could be chemically transformed to a completely conjugated 16π-electron system of the dihydrooctaaza [14]annulene complex $[Ni(C_{10}H_{14}N_8)]_2$ through the deprotonation and oxidative dehydrogenation reaction of the octaaza Ni complex via 2 proton subtraction and 4 electron oxidation (Scheme 1(a)). The well-distributed macrocyclic molecules on the surface of the graphene can be induced by the incorporation of the octaaza bis-α-diimine macrocyclic Ni complex because the secondary amine of the octaaza bis-α-diimine macrocyclic Ni complex may react with functional groups such as carboxylic acid and epoxide of graphene oxide (GO). Therefore, chemical bonding could be a driving force that leads to molecular grafting on the GO layers. Furthermore, a redox reaction between the octaaza bis-α-diimine macrocyclic Ni complex and GO occurred because the high oxidation state of GO induced the oxidative dehydrogenation reaction of the octaaza bis-α-diimine macrocyclic Ni complex.

The redox reaction is proposed to reduce GO to a more reduced oxidation state, i.e. reduced GO (RGO), at a mean time, leading to the oxidation of the macrocyclic Ni complex to a fully conjugated oxidation state. The π-π interaction between the RGO and the conjugated Ni complex is expected, which could enhance the deposition of the macrocyclic complex on the graphene surface and form a uniform nanoscale deposition. Considering the generality of this simple reaction of molecular-level materials, our method might stimulate interest in the growth of a very broad range of graphene-modified systems exhibiting various properties and



Scheme 1. Preparation processes of (a) octaaza-bis-α-diimine Ni macrocyclic complex and (b) graphene hybrid with a fully conjugated macrocyclic Ni complex. (c) DSSCs fabricated with the graphene/macrocyclic Ni complex-based nanocomposite counter electrodes.