



Electrocatalytic reduction of CO₂ to CO by Gd(III) and Dy(III) complexes; and M₂O₃ nanoparticles (M = Gd and Dy)



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ABSTRACT

Two Gd(III) and Dy(III) complexes, [M(AyGG)₃(H₂O)₅] (AyGG = Alizarin yellow GG (NaC₁₃H₈N₃O₅)), have been prepared and characterized. The Gd₂O₃ and Dy₂O₃ nanoparticles were prepared by the calcination of the Gd(III) and Dy(III) complexes in air at different temperatures. The nanoparticles were characterized by FT-IR, X-ray diffraction analysis (XRD), and field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The voltammograms in the absence and presence of CO₂ indicate that the Gd(III) and Dy(III) complexes and their nano-oxides can catalyze the electrochemical reduction of CO₂ to CO. The results show that the Dy(III) complex has better electrocatalytic activity than other compounds.

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1. Introduction

Carbon dioxide contributes to the greenhouse effect, which is responsible for the warming of the Earth. The Kyoto Protocol (Japan, 1997) aims to reduce emissions of CO₂ and other greenhouse gases [1–3]. Carbon dioxide is emitted through natural processes (such as volcanic activity, respiration, and decomposition) and human activities (such as deforestation, fossil fuels combustion, and industrial processes). The most effective method to reduce CO₂ emissions is to reduce fossil fuels consumption. The atmospheric mixing ratio of CO₂ is now higher than at any time in at least the last 800,000 years, standing at 385 ppm compared to a pre-industrial high of 280 ppm [3–5]. The current growth rate of 2 ppm per year for CO₂ is a serious warning. This rate has caused much worry in the international community. In 2013, CO₂ accounted for about 82% of all greenhouse gas emissions from human activities [5]. Therefore, the fixation and conversion of CO₂ into a useful chemical feedstock is of potential benefit. Research in the field of electrochemical reduction of CO₂ has grown rapidly in the last few decades. This growing research effort is a response by physical scientists and engineers to the increasing amount of CO₂ in the atmosphere and the steady growth in global fuel (energy)

demand [6,7]. Electroreduction of CO₂ with metal complexes is a feasible technique for the utilization of CO₂ as a C₁ source, though the final products usually have been limited to CO and/or HCOOH [8–16]. Metal complexes with CO₂ as a ligand are considered to play the key role in the electroreduction and photoreduction of CO₂, since the M–η¹–CO₂ bond is easily converted to metal–CO bond through an acid–base reaction in protic media (such as water and alcohols) or through an oxide-transfer to a free CO₂ molecule (uncoordinated CO₂) in aprotic media (such as CH₃CN). CO evolution in the reduction of CO₂ is ascribed to reductive cleavage of the resulting metal–CO [17–22].

In recent years, nanocatalysts have received increasing attention and exhibited many lab- and industrial-scale applications [23–26]. When a nanocatalyst participates in an electrochemical reaction, it is called nano-electrocatalysts. Electrocatalysts are a specific form of catalysts that function at electrode surfaces or may be the electrode surface itself. An electrocatalyst can be heterogeneous (such as a platinum surface or nanoparticles) or homogeneous (such as a coordination complex or enzyme (biocatalyst)) [27–30]. The electrocatalyst assists in transferring electrons between the electrode surface and reactant(s), and/or facilitates an intermediate chemical transformation described by an overall half-reaction. Nanoparticles have emerged as sustainable alternatives to conventional materials, as robust, high surface area heterogeneous catalysts and catalyst supports [31,32]. The nanosized particles increase the exposed surface area of the active

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component of the catalyst, thereby enhancing the contact between reactants and catalyst dramatically and mimicking the homogeneous catalysts. However, their insolubility in common reaction solvents renders them easily separable from the reaction mixture like heterogeneous catalysts, which in turn makes the product isolation stage effortless. Also, the activity and selectivity of a nanocatalyst can be manipulated by tailoring chemical and physical properties such as size, shape, composition, and morphology. The scientific challenge is the synthesis of specific size and shape nanocatalysts to allow facile movement of materials in the reacting phase and control over morphology of nanostructures to tailor their physical and chemical properties. However, the rapid advancement of nano-technology made possible the preparation of a variety of nanoparticles with controlled size, shape, morphology, and composition [30–32].

Here, we report the synthesis and characterization of two new mononuclear Gd(III) and Dy(III) complexes, [M(AyGG)₃(H₂O)₅], where AyGG is Alizarin yellow GG (Fig. 1). In addition, a simple method is reported for the preparation of the Gd₂O₃ and Dy₂O₃ nanoparticles from these precursor complexes by a facile calcination method. The electrocatalytic reduction of CO₂ to CO by the complexes and their nano-oxides is also investigated using cyclic voltammetry (CV) in CH₃CN solution.

2. Experimental

2.1. Materials and methods

GdCl₃·6H₂O, DyCl₃·6H₂O, tetra-*n*-butylammonium hexafluorophosphate, Alizarin yellow GG, and acetonitrile were purchased from Merck. All chemicals and solvents were of high purity and used without any further purification.

Elemental analysis (C, H and N) were performed using a Leco, CHNS-932 elemental analyzer. Fourier transform infrared spectra were recorded on an FT-IR JASCO 680-PLUS spectrometer in the region of 4000–400 cm⁻¹ using KBr pellets. Electronic absorption spectra were recorded on a JASCO 7580 UV–vis–NIR double-beam spectrophotometer using quartz cells with a path length of 10 mm. XRD analyses were performed using a PHILIPS PW3040/60 diffractometer with CuK α radiation. Morphology of the nanoparticles was observed using a field-emission scanning electron microscope (FE-SEM, HITACHI; S-4160). Transmission electron microscopy (TEM) images were obtained on a Philips CM30 transmission electron microscope with an accelerating voltage of 300 kV. Voltammetric experiments were performed on a SAMA Research Analyzer M-500. All measurements were carried out in a 5 mL cell which was fitted with a Teflon lid incorporating a three-electrode system comprising of a glassy carbon electrode ($\varphi = 2$ mm) as the working electrode, a platinum wire as the auxiliary electrode, and a silver wire as the pseudo-reference electrode (the potential values reported vs. SCE). The glassy carbon working electrode surface was freshly cleaned with alumina polish on a micro cloth before each scan and was rinsed with doubly-distilled water between each polishing step. The cyclic voltammograms of [Gd(AyGG)₃(H₂O)₅] and [Dy(AyGG)₃(H₂O)₅] were recorded in acetonitrile using tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting

electrolyte. Ferrocene ($E^\circ = 0.665$ V vs. NHE) was used as an internal reference at the end of each experiment. The solutions were purged by N₂ or CO₂ flows during study. All spectral and electrochemical data were collected at ambient temperature.

All gas chromatograms were recorded with a Varian STAR 3400 gas chromatograph with He as the carrier gas at a flow rate of 30 mL/min and a temperature of 230 °C. After each electrolysis step (at least 3 h at a controlled potential) in the presence of the electrocatalysts ([Gd(AyGG)₃(H₂O)₅], [Dy(AyGG)₃(H₂O)₅], Gd₂O₃, or Dy₂O₃), the gas sample was taken using a gas-tight syringe and the gaseous reaction product, *i.e.* CO, was detected by GC and IR. No detectable quantity of the target product (CO) was found in the headspace of the blank solution (containing the supporting electrolyte (TBAH) + solvent (CH₃CN) under CO₂) after electrolysis in the absence of the electrocatalysts for 3 h at room temperature. In all samples, no hydrogen (H₂) peak was detected by GC.

2.2. Synthesis of [Gd(AyGG)₃(H₂O)₅]

[Gd(AyGG)₃(H₂O)₅] was synthesis by the reaction of Alizarin yellow GG and gadolinium(III) chloride hexahydrate in 30 mL water. Alizarin yellow GG (0.93 g, 3 mmol) was dissolved in 15 mL of water under stirring at 80 °C until a dark yellow solution resulted. To the solution was then added a solution of GdCl₃·6H₂O (0.37 g, 1 mmol) in 15 mL water. The reaction mixture was refluxed for 5 h. The dark orange precipitate was filtered and washed with water and dried in air at room temperature (Scheme 1). Yield: 0.95 g, 86%. Anal. Calc. for GdC₃₉H₃₄N₉O₂₀ (MW = 1105.99 g/mol): C, 42.35; H, 3.10; N, 11.40 % Found: C, 42.64; H, 3.21; N, 11.51%.

2.3. Synthesis of [Dy(AyGG)₃(H₂O)₅]

Alizarin yellow GG (0.93 g, 3 mmol) was dissolved in 15 mL of water under stirring at 80 °C until a dark yellow solution resulted. To the solution was then added a solution of DyCl₃·6H₂O (0.38 g, 1 mmol) in 15 mL water. The reaction mixture was refluxed for 12 h. The red–orange precipitate was filtered and washed with water and dried in air at room temperature (Scheme 1). Yield: 0.97 g, 87%. Anal. Calc. for DyC₃₉H₃₄N₉O₂₀ (MW = 1112.12 g/mol): C, 42.15; H, 3.08; N, 11.34 % Found: C, 42.23; H, 3.19; N, 11.48%.

2.4. Synthesis of Gd₂O₃ and Dy₂O₃ nanoparticles

To prepare the nanoparticles, the precursor complexes, [Gd(AyGG)₃(H₂O)₅] and [Dy(AyGG)₃(H₂O)₅], were calcined up to 600 °C. The brown gadolinium oxide (Gd₂O₃) nanoparticles and white dysprosium oxide (Dy₂O₃) nanoparticles were obtained by subjecting 0.3 mg of the as-prepared Gd(III) and Dy(III) complexes powder to heat treatment in air at given temperatures ranging between 400 and 600 °C. An average temperature increase of 20 °C every minute was selected before the temperature reached to the target temperature, and after keeping the thermal treatment at the target temperature for 2 h, it was allowed to cool to room temperature naturally. A series of further experiments were carried out to investigate the reaction conditions. The detailed reaction conditions and corresponding results are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization of complexes

The reaction of Alizarin yellow GG with GdCl₃·6H₂O and DyCl₃·6H₂O is shown in Scheme 1. The complexes were prepared in good yield. The elemental analyze of the complexes were entirely consistent with their proposed composition. Fig. 2 shows the



Fig. 1. Molecular structure of Alizarin yellow GG (AyGG).

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