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# Clean and effective catalytic reduction of graphene oxide using atomic hydrogen spillover on Pt/γ-$Al_2O_3$ catalyst

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ABSTRACT

We report a clean and eco-friendly method to prepare reduced graphene oxide (RGO) using atomic hydrogen. Pt/γ-$Al_2O_3$ was used as a catalyst for the dissociation of $H_2$ molecules to form atomic hydrogen, which served as a strong reducing agent for the reduction of graphene oxide (GO). The resulting RGO exhibited a high C/O ratio (~8.6) and high electrical conductivity (~4,420 *S/m*). This novel reduction process provides facile, one-pot catalytic reduction of GO on the large scale.



## 1. Introduction

Graphene has attracted a great deal of scientific interest due to its excellent mechanical, electrical, and thermal properties as well as its high specific surface area [1]. The reduction of graphene oxide (GO) is one of the most promising ways to produce graphene platelets on the large scale [2,3]. Generally, GO reduction is facilitated by strong reducing agents such as hydrazine and its derivatives, $NaBH_4$, $LiBH_4$ and hydroiodic acid, which are highly toxic, dangerous, and incompatible for biochemical applications such as biopolymers, biosensors, or drug delivery [4–10]. Recently, clean production of large amounts of graphene has attracted considerable attention due to its potential applications in biochemical fields. Many attempts have been made to develop environmentally friendly approaches for the reduction of GO solutions including bacterial respiration [11], ascorbic acid [12], protein [13], and vitamin *C* [14].

Recently, we demonstrated that nascent hydrogen, generated from the reaction of aluminum and zinc with acid or alkaline solution, is a strong reducing agent for GO reduction to reduced graphene oxide (RGO) with the C/O atomic ratio up to 21 [15]. However, the use of concentrated acidic or alkaline solution is incompatible for most biochemical applications. It is well known that platinum (Pt) is the best catalyst for the dissociation of $H_2$ molecules to form two atomic hydrogens at low temperature [16–18]. On the Pt/γ-$Al_2O_3$ catalyst, hydrogen atoms formed over Pt spill over onto the alumina surface until reaching equilibrium [19–21]. This phenomenon motivated us to examine the use of the spillover of hydrogen over a Pt/γ-$Al_2O_3$ catalyst to reduce GO.

To date, the catalytic reduction of GO using a heterogeneous system have not been investigated. Herein, we report for the first time, a one-pot and clean method for the synthesis of RGO using atomic hydrogen in a heterogeneous Pt/γ-$Al_2O_3$ catalyst system. This novel approach may be extended to other platinum group metals (Pd, Rh, Ru, Ir, and Os) for use as the active component on support materials to prepare clean and biocompatible RGO on the large scale.

## 2. Experimental

An aqueous suspension of GO was prepared by the modified Hummers method with initially expanded graphite prepared by microwave-assisted thermal expansion of expandable graphite [7,22]. Typically, 500 ml of aqueous suspension of GO (1 mg/mL) was introduced into the cylindrical reactor with hydrogen gas at a rate of 50 cc/min entering from the bottom. Pt/γ-$Al_2O_3$ (0.5 wt% of Pt, Sigma-Aldrich) was charged into the reactor with the GO/Pt mass ratio of 50. The reduction was carried out at 80 °C for 24 h under mechanical mixing using an overhead stirrer (250 rpm). The obtained RGO was referred to as hRGO.

## 3. Results and discussion

Atomic hydrogen, which is known as a strong reducing agent, can be effectively used for the reduction of GO, as shown in

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supplementary scheme S1. Hydroxyl groups can be eliminated by the addition of atomic hydrogen followed by a dehydration reaction. Epoxy groups can also be removed by a ring opening reaction followed by addition of atomic hydrogen and dehydration [15]. By mixing GO with Pt/γ-$Al_2O_3$ catalyst in the presence of hydrogen gas, the GO sheets contact with atomic hydrogen spillover on the surface of Pt/γ-$Al_2O_3$ catalyst particles resulting in reduction [19–21]. The reduction of GO to hRGO by atomic hydrogen spillover on surface of Pt/γ-$Al_2O_3$ catalyst particles was confirmed by UV–vis spectra (Fig. 1a). The UV–vis spectrum of GO exhibited a strong absorption peak at 227 nm, which was attributed to the $\pi \rightarrow \pi^*$ transitions of the aromatic C–C bonds, and a shoulder at ~300 nm that was assigned to the $n \rightarrow \pi^*$ transitions of the C=O bonds [15]. The absorption peak of the hRGO redshifted to 269 nm and the absorbance in the whole spectral region ( > 227 nm) increased markedly with increasing reaction time, implying that electronic conjugation within the graphene sheets was restored upon hydrogen reduction [5].

The most informative analysis used to investigate the degree of reduction of the GO is elemental analysis (Table S1). The percentage of carbon increased dramatically from 54.53% (GO) to 86.18% (hRGO), whereas the percentage of oxygen decreased from 43.29% (GO) to 13.36% (hRGO). The C/O atomic ratio of GO and hRGO was 1.68 and 8.60, respectively, suggesting that atomic hydrogen spillover on the alumina supported platinum is a promising reductant for the reduction of GO. Although the C/O ratio of hRGO is much lower than that of nascent hydrogen reduced graphene oxide [15], it is comparable to RGO produced by using other clean reducing reagents [11–14]. Thermogravimetric analysis (TGA) and the derivative of the thermogravimetric (DTG) were used to further assess the degree of reduction of GO (Fig. 1b). The TGA curve of GO sample showed a significant weight loss with an onset temperature of 150 °C, which was attributed to the elimination of interlamellar water, followed by loss of oxygen functional groups such as hydroxyl, epoxy, and carbonyl from the GO sheets at 250 °C [4,7]. The DTG curve of hRGO revealed that the decomposition peaks at 150 °C and 250 °C disappeared, denoting the removal of oxygen functional groups during reduction. The X-ray photoelectron spectroscopic (XPS) spectra (Fig. 1c) provide further information of the conversion of GO to hRGO. The intensity of the peaks assigned to oxygen functional groups such as hydroxyl, epoxy, peroxide, and carbonyl of GO significantly decreased after reduction, indicating that most of the oxygen functional groups were almost completely removed [4]. The Raman spectra are usually used to reveal changes of the electronic conjugation state. The Fig. 1d shows the redshift of the *G* peak from 1,595 $cm^{-1}$ (GO) to 1,582 $cm^{-1}$ (hRGO) and the increase of the $I_D/I_G$ ratio from 1.0 (GO) to 1.2 (hRGO) which can be attributed to the restoration of $sp^2$ in the form of new graphitic domains that are small in size but numerous [4].

The hRGO can be dispersed in various polar organic solvents such as dimethyl formamide (DMF), methyl pyrrolidone, and acetonitrile by mild sonication (Fig. S1). Fig. 2 shows the atomic force microscopy (AFM) images of GO and hRGO monolayers with the thickness of approximately 1 nm and 1.3 nm, respectively. By suction filtration of hRGO dispersion in DMF using cellulose filtered paper with a 1 μm pore size, free-standing hRGO paper was easily fabricated. Fig. 3 displays scanning electron microscope (SEM) images of free-standing hRGO paper (Fig. 3a) and hRGO powder (Fig. 3b). The SEM cross-sectional image of free-standing paper revealed layer-by-layer structure of hRGO sheets, indicating that the good dispersion of hRGO sheets in DMF. The electrical conductivity of the free-standing hRGO paper characterized by the four-point probe method was approximately 4400 *S/m*, which is comparable to the conductivity of RGO prepared by using other reductants (Table S2).

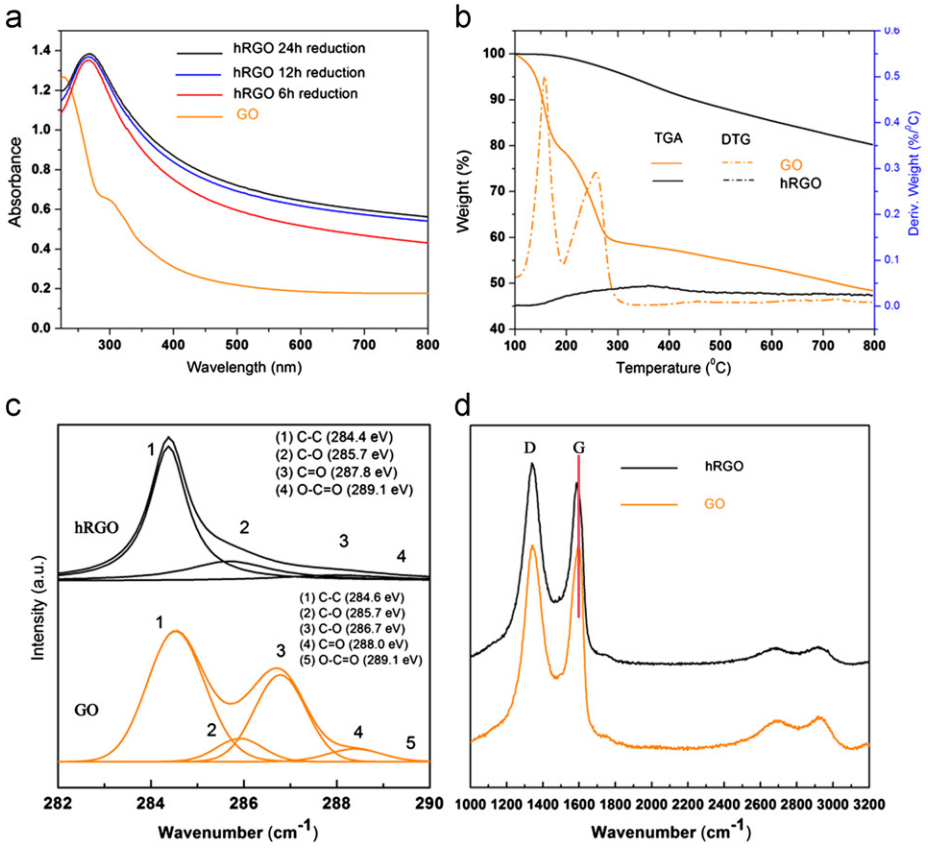


**Fig. 1.** Characterization of GO and hRGO: (a) UV–vis spectra, (b) TGA and DTG thermograms, and (c) XPS C1s spectra and (d) Raman spectra.