



Noble metal doped graphene nanocomposites and its study of photocatalytic hydrogen evolution



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ABSTRACT

This work reports the deposition of platinum (Pt) nanoparticles on the surface of graphene nanosheet by a simple approach, using a microwave-assisted method. The photocatalytic activity has been investigated for hydrogen evolution. The hydrogen evolutions were attributed to graphene, due to its high photoelectron transport properties, and the Pt nanoparticles attached on the surface of graphene sheet, which act as reaction centers for H₂ evolution. The “as-prepared” composites were characterized by Brunauer Emmett Teller (BET) surface area measurement, X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and UV–vis diffuse reflectance spectra (DRS). This work highlights the potential application of graphene-based materials in the field of energy conversion.

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1. Introduction

Environmental pollution, caused by the burning of fossil fuels and the increasing energy crisis, has led scientists to search for renewable and environmental friendly energy resources. The world is considering evolution from an oil-based economy to a hydrogen-based economy, due to the limitation of the earth's reserve of fossil fuels. Hydrogen energy is considered as the most important form of clean and storable energy [1–4]. Much research has been dedicated to the search for stable and high efficient photocatalysts [5–7]. TiO₂ nanoparticles on layered MoS₂/graphene hybrid were synthesized by simple hydrothermal method and enhanced hydrogen evolution was observed. Enhanced catalytic activity was attributed to the synergetic effect between MoS₂ and graphene in the composites [8]. Q. Xiang summarizes the problems and advantages of the graphene based materials in photocatalysis. The critical review summarizes the recent progress in the design and fabrication of graphene-based semiconductor photocatalysts through various strategies as well as in situ growth, solution mixing, hydrothermal and/or solvothermal methods [9]. Chemically reduced graphene oxide was functionalized by (EY) eosin via non covalent

fictionalization method. The photocatalytic H₂ evolution were observed by using the functionalized (EY-RGO) as a photocatalyst material. Improved catalytic activities were reported by comparing with RGO under UV–vis light irradiation [10]. Similarly, the synthesis and photocatalysis of a novel nanohybrid composed of bipyridine ruthenium complex ((2,2'-bipyridyl)-4-pyridylchlororuthenium (II), Ru (bpy)₂(py)Cl) covalently functionalized graphene were carried out successfully and improved photocatalytic behavior was observed under UV- irradiation [11]. Noble metal free dye-sensitized graphene oxide was synthesized and generation of hydrogen gas from water/methanol mixtures was observed by using visible or solar light [12]. TiO₂ based materials have been widely studied for water splitting [13–15].

The main barriers, from the recombination of photogenerated electrons and holes, back reaction and reduced activation by visible light, limit its further development [16]. To overcome these deficiencies much research has been conducted to enhance catalytic efficiency, such as metal doping [17,18], and composite semiconductors [19]. To impede electron recombination, the presence of an efficient electron relay is essential [20,21]. Graphene, with its flexible 2D nature, tunable band gap, high electrical conductivity, and higher work function, has a potential support in accepting and transferring electrons [22]. Due to functional groups on the surfaces of GO, it can be used as anchoring sites for metal nanoparticles [23], so it is possible to use them as a support to produce graphene

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hybrids. A combination of graphene and functional nanoparticles may lead to materials with interesting properties for a variety of applications, and in particular, they are expected to have enhanced photocatalytic activity [24]. Several groups have investigated Pt/graphene nanocomposites, with different synthesis techniques and organic media. The catalytic properties of these nanocomposites were investigated for hydrogen evolution. In this context Shixiong et al. synthesized Pt/graphene nanocomposite via the hydrothermal method, using rose bengal and eosine dyes. The observed H₂ evolution rate was found to be 350 μmol/10 h, by using 250 W, UV light sources. The catalytic activity was enhanced by using the co catalyst TiO₂ [22]. Lei et al. studied the synthesis of trimethylamine functionalized graphene decorated with Pt nanoparticle via solvothermal process, after heat treatment of 5 days at 125 °C–135 °C. The hydrogen evolution rates were found to be 14 μmol/6 h [25]. In this paper, we report the preparation of Pt/graphene nanocomposite by fast and facile microwave assisted method. The Pt/graphene nanocomposites were achieved by irradiation of microwave for only 300 s. The application of Pt/graphene nanocomposite as a photocatalyst for hydrogen evolution was investigated. The hydrogen evolution took place in aqueous solution containing Na₂S/Na₂SO₃ and methanol as sacrificial reagent. The hydrogen evolution rate was found to be markedly high, as compared to other reports. The research reveals that methanol behaves as a hole scavenger, graphene as a light absorber and electron acceptor/transferor, and Pt nanoparticles provide a reaction center for hydrogen evolution.

2. Experimental sections

2.1. Materials

Graphite oxides were prepared from natural graphite by the Hummers Offman method [26]. Hydrogen hexachloroplatinate (IV) hydrate (H₂PtCl₆·nH₂O n = 5.5), purchased from Kojima Chemical Co. Ltd, Japan, was used as a platinum source. Sodium sulfide pentahydrated (Na₂S·5H₂O) and sodium sulfite (Na₂SO₃) were purchased from Samchun Pure Chemical Co. Ltd, Korea. Ethylene glycol was purchased from Dae-Jung Chemical and Metals Co. Ltd, Korea. All chemicals were used without further purification.

2.2. Preparation of photocatalyst

Graphene oxides were prepared by further ultrasonication of graphite oxide. In the typical synthesis, GO (50 mg) and H₂PtCl₆ (0.5 mmol) were dispersed in ethylene glycol (EG) solution (20.0 mL) under vigorous stirring, to form a stable suspension. After mixing together by being stirred for several minutes, the solution was then transferred into a 120 mL reaction vessel, and placed in a conventional microwave oven (Samsung, RE-406B 700 W). The solution was then irradiated with microwave at full power for 5 s on and 5 s off for 300 s, and cooled at room temperature, washed several times with hot water, and transferred into a dry oven for 6 h. The weight ratios of GO to H₂PtCl₆ were 0.15%, 0.25%, 0.50%, 0.75% and 1%, and the obtained samples were labeled as Pt/G1, Pt/G2, Pt/G3, Pt/G4 and Pt/G5 respectively.

2.3. Characterization

The BET surface areas of the photocatalyst Pt/graphene nanocomposite were determined through nitrogen adsorption at 77 K, using BET analyzer (Monosorb, USA). The crystal structures and phases of the samples were obtained by XRD (Shimata XD-D1, Japan) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in the range of 2θ from 10 to 80°, at a scan speed of 1.20 m⁻¹. The decomposition

kinetics for the photocatalytic activity was measured in the range between 300 and 700 nm, by spectrometer (Optizen POP, Mecasys, Korea). The morphology of the samples were studied by SEM (JSM-5200 JOEL, Japan). Energy dispersive X-ray spectroscopy (EDX) was also employed for elemental analysis. Transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) was used to observe the surface state and structure of the photocatalyst composites at an acceleration voltage of 200 kV. TEM was also used to examine the size and distribution of the Pt particles deposited on the graphene sheet. X-ray photoelectron spectroscopy (XPS) was performed using VG scientific VISACA lab 2000, and a monochromatic Mg X-ray radiation source. Survey (wide scan) spectra and high-resolution spectra of C1s, and the element contained within sample, were recorded. C/O ratios were evaluated from the wide scan spectra, by using relative sensitivity factors. UV–vis absorption spectra were obtained, by using a scan UV–vis spectrophotometer (Neosys-2000), equipped with an integrating sphere assembly.

2.4. Photocatalytic reaction and mechanism study

The photocatalytic reaction was carried out at room temperature. The photocatalyst powder 50 mg Pt/graphene were dispersed by magnetic stirrer, in 150 mL aqueous solution containing 0.1 mol L⁻¹ Na₂S and 0.04 mol L⁻¹ Na₂SO₃ and 20% methanol as a sacrificial reagent. UV light source having 356 nm in wavelength was used at a distance of 20 cm from the glass reactor. The amount of hydrogen gas evolved was detected by Minimax (X13010683) XP H₂ sensor.

3. Results and discussion

3.1. Growth and characterization of Pt/graphene nanocomposites

The BET surface area (S_{BET}) of samples gradually increases with increasing graphene content in the sample, as shown in Table 1. The increased surface area of Pt/graphene photocatalyst will provide more active sites for the reaction, and will make charge transport easier, leading to enhancement of the photocatalytic performance [27]. The phase structures of the samples were examined by XRD measurements. Fig. 1 shows the XRD patterns for Pt/G1, Pt/G2, Pt/G3, Pt/G4 and Pt/G5 samples. In this figure the (002) diffraction peak of graphene shifts to higher angle ($2\theta = 26.2^\circ$). During microwave radiation, graphene oxide is partially converted to graphene, and its crystalline structure is restacked. The XRD pattern of Pt/graphene nanocomposites describe strong diffraction peaks at 39.7°, 46.0°, 67.4°, 80.1°, 85°, which are in good agreement with the (111), (200), (220) and (311), (222) crystal planes of pure Pt with face-centered-cubic (fcc) phase (JCPDS 65-2868) [24]. From the XRD spectra the position of the 002 diffraction peak at 26.2° indicates that GO is further converted to the crystalline graphene, and the conjugated graphene network (sp² carbon) has been reestablished [28,29].

The EDX analysis of the Pt/graphene nanocomposites indicates that the nanocomposites were synthesized successfully. From the

Table 1

The comparison of hydrogen evolution rate of Pt/graphene nanocomposites and the degradation rate constant.

Samples	H ₂ evolution μmol/9 h 20% Methanol	H ₂ evolution μmol/9 h with Na ₂ S/Na ₂ SO ₃	S _{BET} surface area m ² /gm	K _{app} (min ⁻¹) Rh·B
PT/G1	370	379	66	9.4 × 10 ⁻⁴
PT/G2	374	412	86	1 × 10 ⁻³
PT/G3	390	426	96	1.6 × 10 ⁻³

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