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Formation of Deuterium and Helium during Photocatalytic Hydrogen Generation from Water Catalyzed by Pt-Graphene Sensitized with Br-dye under Visible Light Irradiation

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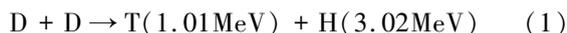
Abstract: ³He is a perfect fuel for nuclear fusion, however, the amount of ³He on the earth is very limited, only around 500 kg. Here, we report that small amount of deuterium and helium can be produced during photocatalytic hydrogen evolution from water catalyzed by Pt-graphene sensitized with Br-dye under visible light irradiation. This work raises a mild route to generate deuterium (D₂) and helium (He) from proton in the water under very mild conditions.

Key words: photocatalytic reduction of proton; formation of deuterium and helium; visible light irradiation

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One of mysterious questions is the source of helium in our universe. It is known that nuclear fusion can produce helium from hydrogen, deuterium and tritium^[1-4]. However, there is difference between the estimated helium abundance and measured helium abundance in the universe^[1]. It is believed that helium can only be generated in nuclear reaction under very high temperature and high pressure. But the fusion in the stars can not account for the abundance of helium in the universe. Now the excess of ⁴He in our universe is thought mainly from the Big-Bang in the very early period of our universe^[1]. Nevertheless, there are several un-covered phenomena which can not be explained by our up to date knowledge. For example, scientists found that there were excess ratios of ³He and ⁴He in submarine hydrothermal water^[5]. The question of energy balance of Jupiter seems also indicate the possibility of low energy fusion reaction there^[6]. Besides, It was found that trace amount of He could be produced by electrochemical method under normal conditions, so

called cold fusion^[7]. In that experiment, Fleischmann and Pons found ³He could be formed via electrochemical route from D₂O. This implied that fusion could be achieved under mild conditions, i. e., collision of heavy hydrogen atoms to T:



Where D is heavy hydrogen, T is tritium and n is neutron. Soon after this work, several hypotheses were present^[8-9]. The rate of fusion is dependent on D nucleus distance. The shortest distance of D nucleus in Pd lattice is about 0.17 ~ 0.28 nm, therefore the fusion rate needs raise at least 50 orders of magnitude can reach Fleischmann and Pons' experiment results. Another is related to the change of the fusion reaction branching ratio. Based on the Bohr model, the reaction (a) and (b) rate was much larger than reaction (c), however, the experiment of Fleischmann and Pons showed that the reaction (c) is dominant (See Table 1).

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Table 1 Branch of tritium nuclear fusion reactions

Branching reaction	Release energy/(MeV)	Reaction rate release 1 W energy/(s ⁻¹)	branching ratio
(a) D + D → ³ He + n	3.27	1.92×10 ¹²	~0.5
(b) D + D →He + n	4.03	1.55×10 ¹²	~0.5
(c) D + D → ⁴ He + γ	23.85	2.61×10 ¹¹	~10 ⁻⁷

Recently, we found that deuterium and helium could be produced during photocatalytic hydrogen evolution from water catalyzed by Pt-graphene sensitized with Br-dye under visible light irradiation. The detected amount of ³He increased with irradiation time increase. This work raises a mild route to generate deuterium and helium from proton in water. These results indicate that proton can be converted to He under very mild condition, under far below the nuclear fusion reaction condition, therefore, are very important because it may account for the difference between the estimated He abundance and measured He abundance in our universe, no matter the generation rate is high or low.

1 Experiments section

All chemicals were commercial purchased and used without further purification. Potassium chloroplatinate (K₂PtCl₆ · 6H₂O, Tianjin Kemiou Chemical Reagent Co., Ltd, AR, ≥99.5%), graphite powder (Sinopharm Chemical Reagent Co. Ltd., ≥99.8%), concentrated sulfuric acid (H₂SO₄, Xilong Chemical Co., Ltd., ≥98.0%), potassium peroxydisulfate (K₂S₂O₈, Xilong Chemical Co., Ltd., ≥99.5%), phosphorus oxide (P₂O₅, Sinopharm Chemical Reagent Co. Ltd., ≥98.0%), potassium permanganate (KMnO₄, Tianjin Kemiou Chemical Reagent Co., Ltd, AR, ≥99.5%), sodium nitrate (NaNO₃, Tianjin Kemiou Chemical Reagent Co., Ltd, AR, ≥99.5%), barium chloride (BaCl₂, Sinopharm Chemical Reagent Co. Ltd., ≥99.8%), hydrogen peroxide (H₂O₂, Xilong Chemical Co., Ltd., 50%), sodium hydroxide (NaOH, Xilong Chemical Co., Ltd., ≥85.0%), hydrochloric acid (HCl, Xilong Chemical Co., Ltd., 36% ~ 38%), Eosin Y (EY, Sinopharm Chemical Reagent Co. Ltd., ≥85.0%), triethanolamine (TEOA, Xilong Chemical Co., Ltd., ≥98.0%),

De-ionized water with a specific resistance of 18.2 MΩ · cm⁻² was obtained by reverse osmosis followed by ion-exchange and filtration (RFD 250NB, Toyo Seisakusho Kaisha, Ltd., Japan).

2 Preparation of Graphite Oxide

GO was prepared from natural graphite by a modified Hummers method. Briefly, graphite powder (10 g) was added to a mixture solution of concentrated H₂SO₄ (15 mL), K₂S₂O₈ (5 g), and P₂O₅ (5 g) under the condition of 80 °C. The resultant mixture was isolated, and cooled down to room temperature. Then the mixture was diluted with distill water (0.75 L) and the product was filtered, washed with distilled water until the filtrate pH become neutral. The product was dried in air at room temperature for 24 h. Subsequently, the preoxidized graphite (2 g) and NaNO₃ (1 g) were added to cold concentrated H₂SO₄ (0 °C, 46 mL). Then the KMnO₄ (6 g) was added gradually with stirring so that the temperature of the mixture was kept below 20 °C, followed the mixture was stirred at 35 °C for 2 h. Distilled water (92 mL) was slowly added to the mixture, and stirred for 15 min. The reaction was terminated by adding distilled water (0.28 L) and H₂O₂ solution (5 mL, 30%), subsequently. The product was filtered, washed repeatedly with HCl (1 : 10, v/v) and distilled water until sulfate could not be detected with BaCl₂, and then dried in an oven at 60 °C for 24 h.

3 Preparation of Pt/RGO and catalyst activity measurement

Synthesis of catalysts and measurements of the photocatalytic H₂ evolution activity were performed in a sealed Pyrex flask (150 mL) with a flat window (an efficient irradiation area of 10.2 cm²) and a silicone rubber septum for sampling. The amount of hydrogen

evolution was measured using gas chromatography (Aglient 6820, TCD, 13x column, Ar carrier). Synthesis of catalysts details and measurements of photocatalytic H_2 evolution activity were described as follows (The pH of 10 v/v% TEOA aqueous solution): 2 mL of graphene suspensions (3 mg/mL) was dispersed into 80 mL of TEOA- H_2O solution with the ultrasound treatment (25 kHz, 250 W) about 10 minutes, 600 μL of aqueous K_2PtCl_6 (5 mg/mL) was added and followed by magnetic stirring for 30 min, and then Eosin Y ($1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) was added. The photoreaction dispersion was irradiated under visible light ($> 420 \text{ nm}$). The detection of D_2 and He were carried out in a GC-MS (Aglient, 5975C, Triple-Axis Detector), a Quadrupole Mass Spectrometer (LC-D200M), and a Rare Gas Isotope Mass Spectrometry System (Nobleless SFT).

4 Results and discussion

Fig. 1 present the time curves of products during photocatalytic hydrogen generation. With reaction time increased, the formed hydrogen gradually increased.

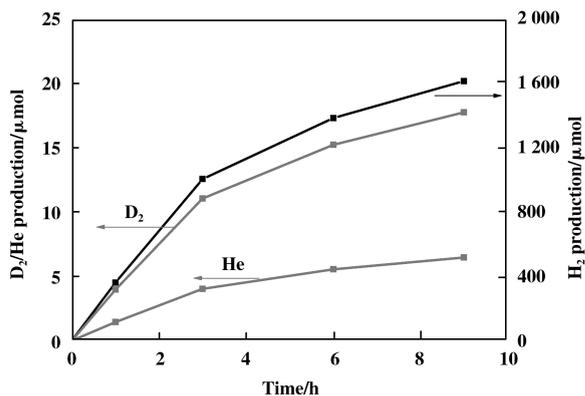


Fig. 1 The products of photocatalytic reaction over EY dye Pt-RGO photocatalyst

Surprisingly, D_2 and He were also detected. The formed deuterium and helium were confirmed by a gas chromatography-mass spectrometer (GC-MS), a GC-MS (Aglient, 5975C, Triple-Axis Detector), a Quadrupole Mass Spectrometer (LC-D200M), and a Rare Gas Isotope Mass Spectrometry System (Nobleless SFT) respectively.

The hydrogen was formed by reduction of proton

with light excited electron from Br-dye on Pt sties over graphene^[10]. Due to the heavy atom effect, the efficiency of hydrogen formation was significantly enhanced^[11]. During the reduction of proton by excited electron, the complex of proton and electron is electronic neutral, and this complex can further combine with electron reduced proton, i. e., hydrogen atom to form deuterium and helium. Although the detail mechanism of combination of electronic neutral complex with hydrogen atom is unknown, we believe this combination is feasible because the excited electrons can attack H atom and can make the H atom show some kind of electronegativity (denoted by H^-). Then the H^- combines with H^+ to form deuterium, and two D atoms form helium.

We realized that the results reported here raised more questions than provided answers, and that many further works are required on this topic. However, the observation of the generation of He and of D_2 from photocatalytic water splitting is very surprising. Evidently, it is necessary to reconsider the quantum mechanics of electrons in such photocatalytic reaction. In addition, some extra questions required further verification: (1) the reaction heat during photocatalytic reaction, (2) some extra particles should be detected, and (3) the specific ratio of helium isotopes should be confirmed. The detail experiments and analysis will be carried out in future.

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溴染料敏化担载 Pt 石墨烯催化可见光制氢、氘和氦

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摘要: ^3He 是理想的核聚变燃料, 但是地球上 ^3He 的储量十分有限, 大约只有 500 kg. 我们报道了在可见光光照条件下, 溴染料敏化担载 Pt 石墨烯催化水还原为氢气过程中伴生少量氘和氦的实验现象. 结果表明在温和条件下自水中的质子生产氘和氦的是可能的.

关键词: 光催化还原质子; 生成氘和氦; 可见光辐照