



Design of multicomponent aerogels and their performance in photocatalytic hydrogen production



Rafael O. da Silva^a, Florian J. Heiligtag^b, Michael Karnahl^{a,c}, Henrik Junge^a, Markus Niederberger^b, Sebastian Wohlrab^{a,*}

^a Leibniz Institute for Catalysis at the University of Rostock (LIKAT), Albert-Einstein-Str. 29a, 18059 Rostock, Germany

^b Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland

^c University of Stuttgart, Institute of Organic Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany

ARTICLE INFO

Article history:

Available online 17 September 2014

Keywords:

Mesoporous TiO₂

Aerogel

Pt cocatalyst

Reduced graphene oxide

Photocatalytic hydrogen production

ABSTRACT

Multicomponent aerogels were prepared from the preformed components (i) crystalline TiO₂ nanoparticles, (ii) Pt nanoparticles as well as (iii) multilayer reduced graphene oxide (m-rGO) and were subsequently tested for photocatalytic H₂ evolution. The multicomponent photocatalysts showed a 3D architecture consisting of crosslinked TiO₂ nanoparticles which are decorated with (1–2 nm) platinum nanoparticles with embedded m-rGO. The three-component materials retained the mesoporosity and high surface area of pure TiO₂ aerogels, as illustrated by transmission electron microscopy and nitrogen sorption experiments. This architecture is responsible for the enhancement of the photocatalytic activity, which reached a maximum hydrogen production rate of 11.61 mmol H₂ g⁻¹ h⁻¹ for the TiO₂ aerogel with a cocatalyst content of 0.4 wt% Pt. In comparison, a Pt/TiO₂ reference powder produced only about 3.28 mmol H₂ g⁻¹ h⁻¹. In this way, the aerogel architecture enables the design of compositions other than Pt/TiO₂ or even the co-assembly of further active materials such as conducting components into the aerogel matrix as shown by the addition of m-rGO to the Pt/TiO₂ aerogels.

© 2014 Elsevier B.V. All rights reserved.

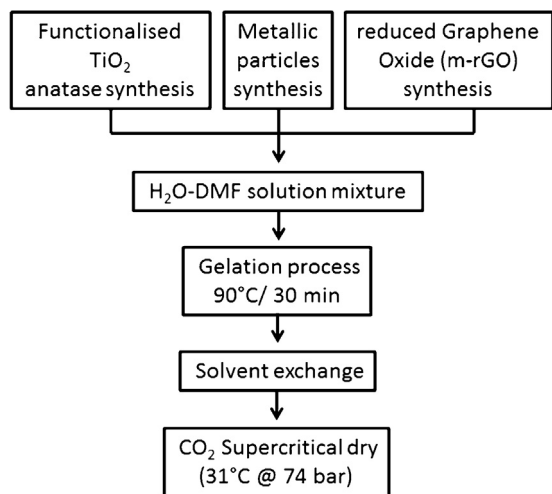
1. Introduction

A sustainable energy vision of our future focuses on the need of a secure energy supply, including the use of renewable resources as well as the mitigation of carbon dioxide emissions [1,2]. In this respect, hydrogen is supposed to play an important role as an alternative fuel and energy carrier due to its high gravimetric energy storage capacity [3]. Its relevance has increased over the last years due to considerable advances in hydrogen production, storage and conversion [4–6]. In particular, hydrogen can be obtained by light driven reduction of protons from water, which is subject of intense research [7]. Despite significant efforts to date, the present challenge in materials chemistry is to develop highly active photocatalysts [8,9]. However, the search for photocatalyst materials is more and more directed towards the combination of single components in order to obtain multifunctional materials. Thus, beside photocatalyst synthesis the mixing with other activity enhancing materials plays a significant role in light-driven photocatalytic

water splitting and photoelectrochemical hydrogen generation [10–12]. Recently we showed the influence of particle size of gold decorated NaTaO₃ semiconductors on the photocatalytic water splitting in solution mixture with conducting multilayer reduced graphene oxide (m-rGO) [13]. Although the catalytic performance was significantly increased in the case of nanoscale NaTaO₃, the interactions between the multilayer graphene oxide and the catalyst are rather random since no chemical or physical attachment of the components was achieved.

Aerogels are a class of highly porous materials that combine unique properties like high specific surface area, low density and low thermal conductivity in a continuous 3D network of meso- to micropores which makes them attractive for photocatalytic applications [14–16]. Gathering in this manner, all the desired properties for a physical composite architecture, like high surface area, photoactivation of the semiconductor, a co-catalyst and conducting carbon platelets could be brought together. In this context, the multicomponent aerogel strategy reported by Niederberger et al. provides a good approach to physically combine several different materials into one single architecture on the base of a TiO₂ model system [17,18]. This work reports on such an assembly of multicomponent aerogels and their application in photocatalytic H₂ production. The catalysts consist of chemically synthesized

* Corresponding author. Tel.: +49 381 1281 328; fax: +49 381 1281 51328.
E-mail address: Sebastian.Wohlrab@catalysis.de (S. Wohlrab).



Scheme 1. Multicomponent aerogel preparation process.

conductive carbon layers (m-rGO) and chemically synthesized platinum nanoparticles embedded in a porous semiconductor TiO₂ anatase matrix. Upon combination of catalytic active and conducting components in aerogels an increase in photocatalytic activity was found for such catalyst architectures.

2. Materials and methods

Multicomponent aerogels were prepared by the following materials and techniques, which can be summarized by [Scheme 1](#). In details: (i) chemical synthesis of trizma-functionalized TiO₂ anatase; (ii) synthesis of metallic nanoparticles free of surface ligands or stabilizers; (iii) preparation of multilayer graphene oxide and further reduction by a solvothermal treatment to m-rGO; (iv) mixing the previously prepared materials to prepare one single dispersion; (v) gelation of the mixed dispersion and (vi) solvent exchange and supercritical drying of the samples.

Aerogel derived catalysts are abbreviated according to the following nomenclature: “Pt/Xm-rGO/TiO₂ aerogel” with 0.4 wt% Pt and X: wt% m-rGO, both related to the overall mass in the TiO₂ aerogel network (for details, see [Table 2](#)). Furthermore, variations in Pt content revealed catalysts named “1.0Pt/0m-rGO/TiO₂ aerogel” with 1.0 wt% Pt and “0.1Pt/0m-rGO/TiO₂ aerogel” with 0.1 wt% Pt, respectively. Reference catalysts are denoted as “mixture Pt/Xm-rGO/TiO₂”.

2.1. Materials and syntheses

Titanium(IV) chloride (>99.0%), benzyl alcohol (≥99.0%) and chloroform (≥99.8%) were purchased from Merck. 2-Amino-2-(hydroxymethyl)-1,3-propanediol (trizma ≥99.7%) and graphite powder (<20 μm) were purchased from Sigma–Aldrich. N,N-dimethylformamide (DMF 99.8%) were purchased from Acros and ethanol (≥99.5%), sulphuric acid (H₂SO₄ 96%) and potassium permanganate (KMnO₄ ≥99.%) were purchased from Carl Roth. Chloroplatinic acid was isolated after treatment in aqua regia using pure platinum metal >99.99% as precursor. All gases used during the experiments were purchased from Linde and/or Air Liquide. Only deionized water (DI) was used throughout the experiments. All chemicals were used as received.

(i) *Synthesis of trizma-functionalized TiO₂* was adapted from a published synthesis protocol [17]. 6.49 mmol (786 mg) 2-amino-2-(hydroxymethyl)-1,3-propanediol (trizma), was

dissolved in 170 ml benzyl alcohol by heating to 80 °C for 30 min. After cooling to room temperature 77.52 mmol (8.5 ml) TiCl₄ was added dropwise under stirring. The reaction solution was heated to 80 °C for 24 h. Afterwards, the solution was cooled to room temperature and the resulting material were separated from the solvent by centrifugation. The yellowish supernatant was decanted; the white precipitate was washed with chloroform by re-dispersing the precipitate. The washing step was repeated at least three times with chloroform followed by centrifugation. The wet precipitate was dried in oven under vacuum (60 °C, 12 h), grinded and finally redispersed in water. The final concentration of trizma functionalized anatase nanoparticles was 120 mg/ml.

(ii) *Synthesis of the platinum nanoparticles:* 179 mg H₂PtCl₆ were dissolved in 60 ml DMF and stirred for 15 min at room temperature. Aliquots of 30 ml were poured into 50 ml Teflon vessels, sealed and heated in a CEM Mars laboratory microwave for 30 s at 220 °C with a maximum power of 600 W. The resulting nanoparticle dispersion was used without further treatment. The final solution concentration of 0.94 mg/ml was determined using induced coupled plasma atomic emission spectroscopy (ICP).

(iii) *Synthesis of multilayer reduced graphene oxide (m-rGO):* First graphite powder was exfoliated and oxidized using a modified Hummer's method [19,20]. In detail, 5.0 g graphite and 2.5 g NaNO₃ were added to 120 ml concentrated H₂SO₄ and the mixture was cooled to 0 °C. KMnO₄ (15.0 g) was added slowly under stirring in order to keep the reaction below 30 °C. Afterwards, the slurry was stirred at 35 °C for 0.5 h and then 230 ml water were added slowly in order to keep the reaction temperature around 98 °C for 15 min. The suspension was quenched by adding 700 ml of water and the remaining unreacted KMnO₄ was consumed by adding 12 ml of H₂O₂ (30%). After cooling to room temperature the black slurry was purified as follows. The filtrate was centrifuged (4000 rpm for 1 h) and its supernatant decanted away. The remaining solid was washed extensively with water, two times with HCl (30%) solution and with ethanol afterwards and with acetone finally. For every washing cycle centrifugation was used to collect the precipitate (4000 rpm/15 min) except for the washing with ethanol and acetone (10,000 rpm/0.5 h). The final obtained brown solid precipitate was dried overnight at 40 °C. For the reduction step, 1.0 g of the dried material was dispersed into 100 ml of 99.5% ethanol and sonicated for 0.5 h prior to pour the solution into a Teflon autoclave and submit it to solvothermal treatment at 150 °C for 24 h.

(iv) *Pre-mixing of nanoparticle dispersions for aerogel preparation:* For the preparation of a mixture of Pt and TiO₂ nanoparticles, the aqueous TiO₂ anatase dispersion is mixed with the platinum dispersion in DMF in a volume ratio of 2:1. For dispersions containing m-rGO, the proportional amount of m-rGO powder is dispersed in the as-synthesized platinum colloid dispersion and sonicated for 30 min. Then, the TiO₂ dispersion is added in a volume ratio of 2:1. For the preparation of dispersions without platinum, the pure DMF is used instead.

(v) *Preparation of (mixture Pt/Xm-rGO/TiO₂) reference samples:* For the particle mixture the same procedure was performed as described above (item iv). The as prepared mixed dispersions were stirred and afterwards sonicated for 10 min and dried in vacuum overnight at 60 °C. A fine powder was obtained after grinding the dry product.

(vi) *Gelation of the nanoparticle dispersions (Pt/Xm-rGO/TiO₂):* After pouring the dispersions in a Teflon container, the container is sealed and the gelation is induced by heating the containers

Download English Version:

<https://daneshyari.com/en/article/54220>

Download Persian Version:

<https://daneshyari.com/article/54220>

[Daneshyari.com](https://daneshyari.com)