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SILICON NANOSTRUCTURES FOR SOLAR HYDRGEN GENERATION: ADVANTAGE AND PERSPECTIVES

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ABSTRACT

Nowadays, modern technical solutions in various spheres of human activity from the opto-electronics up to nanobiotechnology are increasingly dependent on the level of technology. Applied research on nanomaterials plays a key role in the development of nanotechnologies. The nanostructured silicon is one of the materials attracting the special attention of researchers in various applied areas. A new and widely discussed application of nanostructured silicon is a possibility of their usage in the process of efficient hydrogen generation.

The present paper is devoted to a brief review of recent advances in the study of the applicability of porous silicon nanostructures for hydrogen generation. The main possible mechanisms of the photocatalytic activity of silicon nanostructures, as well as the influence of such parameters as their shape, size and degree of surface development on the hydrogen generation efficiency of the material are discussed. In addition, based on literature overview, an analysis regarding the most likely paths for the development of this area of semiconductor materials science and an assessment of the feasibility of using silicon nanostructures for hydrogen generation has been made.

Keywords: silicon nanostructures, photocatalysis, water splitting.

INTRODUCTION

Due to the ever-increasing pollution of the environment and the depletion of fossil energy sources, the issue of developing and introducing environmentally friendly and efficient technologies for energy production and environmental cleanup is becoming increasingly urgent. In this regard, hydrogen energy can offer one of the main solutions to the mentioned problems. Hydrogen energy is one of the type of perspective alternative energy with high energy density, cleanliness and storability [1].

It is very important to choose high-performance, low-cost and earthabundant photocatalysts for realizing large-scale production of hydrogen. In this respect, Si is an attractive candidate for photocatalytic water splitting, because Si is earth abundant,

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relatively cathodically stable semiconductor material with high solar energy utilization efficiency [2]. However, due to the high reflective index of Si more than 30% of incident light is reflected back [3]. This obstructs to the hydrogen generation on Si. Intuitively, this limitation can be circumvented by forming nanostructures of silicon of different shape and morphology.

The present paper is devoted to consider briefly the recent advances in using of silicon nanostructures for hydrogen generation.

SYNTHESIS OF SILICON NANOSTRUCTURES

Silicon nanostructures offered as photoactive materials for hydrogen generation can be obtained by various known methods, with both technological approaches top-down and bottom-up. The most interesting recent results were reported on silicon nanostructures in the form of porous nanolayers, nanowires, mesoporous flakes, and silicon nanoparticles as well as in composition with other semiconductor and metal mamomaterials. The common feature of silicon nanostructures proposed for the generation of hydrogen is the presence of a developed active surface. There are several wide spread attractive top-down (reactive ion etching, electron-beam lithography, nanosphere lithography, nanoimprint lithography, chemical and electrochemical etching) and bottom-up (chemical vapor deposition, molecular beam epitaxy, thermal evaporation) approaches for silicon nanostructures formation [4]. Among top-down approach methods, metal-assisted wet chemical etching (MAWCE) attracts some attention due to its low cost and good opportunities for control the geometrical parameters and morphology of resulting nanostructures. This approach based on the deposition of silver or other noble metals nanoparticles, followed by redox reaction in hydrofluoric acid solution [5]. The great advantage of this method is the ability to use both bulk silicon and thin silicon films. MAWCE is low-cost and simple method of obtaining silicon nanostructures with ability for controlling parameters (such as length, diameter, orientation, type and level of doping) [6-8]. This method does not need use of special, expensive vacuum equipment and allows fabricating structures unlimited in size and area.

PHOTOCATALYTIC PROPERTIES OF SILICON NANOSTRUCTURES

When considering the processes of hydrogen generation using silicon nanostructures, two possible mechanisms are discussed in the literature. The first is associated with pure oxidation of the nanostructure to a stable silicon dioxide, and the smaller the nanostructure, the more intense the reaction that can be accelerated by adding alkali. This process is well studied and has been successfully used to generate hydrogen on porous nanoparticles of small diameter [9].

The second approach, explaining the release of hydrogen using silicon nanostructures, is the process of photocatalysis on their well-developed chemically active surface. Heterogeneous photocatalysis is a promising method in the redox reaction. Thus, a number of researchers recently emphasizes the possibility of implementing the process of water splitting on the surface of silicon nanostructures under the illumination with light source. The possibility of hydrogen generation due to the photocatalytic reaction

on the surface of silicon nanostructures is an open question and one of the actively developing areas.

In [10] Liu et. all report the exploration of water splitting on Si nanowires by performing measurements in pure water under light illumination and yield of H_2 production of 1.2–1.7% at incident light wavelengths of 350–550 nm. The research team also tried to explain the mechanisms of photocatalytic water splitting on silicon nanowires and demonstrated that the production of hydrogen gas on Si nanowires occurs through the cleavage of Si-H bonds and the formation of Si-OH bonds, resulting in the low probability of generating oxygen. The reactions occurring on SiNWs in the presence of Si-H:

Oxidation: $h^+ + Si + H_2O \rightarrow Si\text{-}OH + H+$ (a)

Reduction: $e^- + Si - H + H+ \rightarrow Si + H_2$ (b)

The reaction of O_2 production:

Oxidation: $h+ + Si\text{-}OH \rightarrow Si\text{-}O + H+$ (d)

Si-OH bond, which was formed at the result of reaction (a) would prefer to hosting the reaction (c) and suppressing H_2 production:

Reduction: $e- + Si - OH + H+ \rightarrow Si + H_2O$ (c)

Song et.all [11] used the other form of silicon nanostructures as mesoporous silicon spheres with high crystallinity, large specific surface area and optimal band structure to enable the efficient and stable photocatalytic H_2 evolution (1785μmol $h^{-1}g^{-1}$) under visible light, emphasizing that the highly crystalline mesoporous structure in improving charge separation and promoting surface reactions. In addition, porous structures can be controlled simply by changing the conditions of synthesis, which, in turn, leads to the appearance of the band gap, easy cleaning, charge separation and surface reaction.

Dai et. all [12] used a bottom-up synthesized mesoporous crystalline silicon for hydrogen generation by chemical reaction with KOH solution, which production rate was 0.095 g H_2 s^{-1} g^{-1}Si. In the work synthesis route of mesoporous crystalline silicon is based on $SiCl_4$ reduction utilizing salt by-products as pore templates and heating at different temperatures. The excellent chemical H_2 generation rate is related to the high surface areas of such material. More importantly, the high surface areas and mesoporous structure combined with the nanosized, crystalline primary particles enable much improved H_2 evolution rate and extended working life compared with the previously reported result.

Another group synthesized mesoporous silicon nanosheets from natural clay and used them for hydrogen generation [13]. The silicon nanosheets have a high surface area, were ultrathin (~5 nm) and contain mesoporous structures derived from the oxygen vacancies in the clay. These advantages allowed to perform some experiments on the generation of hydrogen from a water–methanol mixture. Further, when the silicon nanosheets are combined with platinum as a cocatalyst, they exhibit high activity in

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KOH (15.83 mmol H_2/s * mol Si) and excellent photocatalytic activity with respect to the evolution of hydrogen from a water–methanol mixture (723 μmol H_2/h*g Si).

It is well known that porous silicon nanostructures exhibit a visible emission at the red-infrared wavelengths region and the overall absorption band of porous silicon nanowires is much broader than those of TiO_2 which is one of the widely spread photocatalyzers. It covers entire spectral range from UV to visible and near IR. These mentioned properties of silicon nanowires are expected to be successfully implemented in the photocatalytic field. Researchers from California were incorporated Pt nanoparticles with 3–4 nm diameters onto porous silicon nanowires for enhancing photocatalytic activity [14]. They have compared photocatalytic activities of porous silicon nanowires, PtNP loaded porous silicon nanowires (PtNP–pSiNW) and photocatalytic degradation of indigo carmine (IC), 4-nitrophenol. After 60 minutes of irradiation, 37.2% and 86.9% of porous silicon nanowires and PtNP–pSiNW was degraded IC, while only 4.7% of IC molecules were degraded with the same irradiation conditions without PtNP–pSiNW photocatalysts. 4-nitrophenol photodegradation does not changed. From this investigation it was convinced that Pt-loaded porous silicon nanowires are much more efficient photocatalysts than only porous SiNWs. Incorporating Pt nanoparticles facilitate electron–hole separation and promote the electron transfer process in catalytic photodegradation reaction.

In [15] Shao et al. employed HF-treated silicon nanowires (SiNWs) as catalysts in the degradation of rhodamine B, as well as oxidization of benzyl alcohol to benzoic acid. To elevate the photocatalytic efficiency of the degradation, they also used a noble metal-modified SiNWs, which were generally recognized as effective due to their easy separation of charges with electrons collected in metal particles. For this purposes they have used platinum, palladium, gold, rhodium, and silver particles. The unexpected and unusual results were that SiNWs exhibited better photocatalytic activity than Pd-, Au-, Rh-, or Ag-modified ones in the degradation of rhodamine B. To explain these results researchers supposed that on the surface of SiNWs, there are monohydride (SiH), dihydride (SiH_2), and trihydride (SiH_3) species. Their *ab initio* calculations showed that the charge on the H atom in these three hydrides is in the range 0.09-0.13 au, therefore these H atoms are electron-deficient and may serve as an electron sink. When a photon with energy equal to or greater than the band gap of the SiNW reaches the catalyst's surface, it results in the generation of an electron in the conduction band and a hole in the valence band. The induced hole receives the electron from adsorbed water and results in OH free radical groups. Hydrogen atom has a large Pauling electron negative value of 2.2, consequently, the terminated hydrogen atom with a charge of 0.09-0.13 au may serve as an electron sink and accelerate the separation of the electron and hole. Here, terminated hydrogens accelerate the separation of photoinduced electrons and holes and promote the photocatalytic efficiency. Finally, the reactive *OH* radicals oxidize and degrade organic adsorbed pollutants.

CONCLUSION

In summary, we have made a short review, pointing the main interesting tendencies in the research of the possibility of using silicon nanostructures for photocatalytical hydrogen generation. In this paper, we reviewed a number of recent reports on the possibility of using silicon nanostructures as a material for hydrogen generation not only

due to oxidation, but also due to photocatalytic water splitting. In recent years, interest in photocatalysis has focused on the use of semiconductor materials as photocatalysts for the removal of ambient concentrations of organic and inorganic species from aqueous or gas phase systems in environmental clean-up, drinking water treatment, industrial and health applications. From the listed in the review works, in which the results of effective hydrogen evolution are shown, it is clear that silicon nanostructures with a developed and chemically active surface can be used as a photocatalytic agent for the generation of hydrogen. Since, as has been shown, there is a huge variety of ways to obtain silicon nanomaterials, and a very rich choice of structure morphology, the mechanisms of photocatalytic reactions are not fully understood. Therefore, the definition of clear mechanisms of photocatalytic reactions for one form or another of silicon nanostructures and their dependence on various external parameters remains an open question for a solution in the near future.

REFERENCES

[1] Parra D.,Valverde L., Pino F.J., Patela M.K. A review on the role, cost and value of hydrogen energy systems for deep decarbonisation, Renewable and Sustainable Energy Reviews, vol.101, pp 279-294, 2019.

[2] Ji J, Zhang H., Qui Y., Wang Y., Luo Y., Hu L. Plainum nanoparticle decorated silicon nanowire arrays for photoelectrochemical hydrogen production, Journal of Materials Science: Materials in Electronics, vol. 24, pp. 4433-4438, 2013.

[3] Mussabek G.K., Assilbayeva R.B., Yermukhamed D., Yar-Mukhamedova G.Sh., Timoshenko V.Yu. Features of total optical reflection in silicon nanostructures obtained by metal assisted chemical etching. Proceedings of 17-th SGEM 2017, 29 June-5 July 2017, Albena, Bulgaria, V.17. Nano, bio, green and space technologies for sustainable future. Issue 61, pp. 141- 147, 2017

[4] Schmidt V., Wittemann J.V., Senz S., Gosele U. Silicon nanowires: a review on aspects of their growth and their electrical properties, Advanced Materials, vol. 21, pp. 2681-2702, 2009.

[5] Galopin E. Metal-assisted chemical etching of silicon: Preparation of silicon nanowire arrays, Electrochemical Society Meeting Abstracts, pp. 2, 2008.

[6] K.K. Dikhanbayev, V.A. Sivakov, F. Talkenberg, G.K. Mussabek, Ye.T. Taurbayev, N.N. Tanatov, E. Shabdan. Electron backscatter diffraction in the silicon nanowires, Physical Sciences and Technology, vol.2, No 2, pp. 4-11, 2015.

[7] Schmidt V., Senz S., Gosele U. Diameter-dependent growth direction of epitaxial silicon nanowires, Nano Letters, vol. 5, pp. 931-935, 2005.

[8] Sagyndykov A.B., Kalkozova Z.K., Yar-Mukhamedova G.Sh., Abdullin K.A. Fabrication of nanostructured silicon surface using selective chemical etching. Technical Physics, vol. 62, No.11, pp. 1675-1678, 2017.

[9] Litvinenko S., Alekseev S., Lysenko V., Venturello A., Geobaldo F., Gulina L., Kuznetsov G., Tolstoy V., Skryshevsky V., Garrone E., Barbier D. Hydrogen production from nano-porous Si powder formed by stain etching, Int. J. Hydrogen Energy, vol. 35, p 6773, 2010.

https://doi.org/10.5593/sgem2019/6.1

[10] Liu D., Li L., Gao Ya., Wang Ch., Jiang J., Xiong Yu. The nature of photocatalytic "water splitting" on silicon nanowires. Angew. Chem. Int. Ed. vol. 54, pp 2980 –2985, (2015)

[11] Song H. Liu D., Yang J., Wang L., Xu H., Xiong Yu. Highly crystalline mesoporous silicon spheres for efficient visible photocatalytic hydrogen evolution. ChemNanoMat, Vol. 3, No.1, pp. 22-26, 2017.

[12] Dai F., Zai J., Yi R., Gordin M. L., Sohn H., Chen Sh., Wang D. Bottom-up synthesis of high surface area mesoporous crystalline silicon and evaluation of its hydrogen evolution performance. Nature Communications, vol.5, 3605, pp. 1-11, 2014.

[13] Ryu J. , Jang Y. J., Choi S., Kang H. J., Park H., Lee J. S., Park S. All-in-one synthesis of mesoporous silicon nanosheets from natural clay and their applicability to hydrogen evolution. NPG Asia Materials vol. 8, pp. e248, 2016.

[14] Qu Y., Zhou H., Duan X. Porous silicon nanowires, Nanoscale, vol. 3, pp. 4060-4068, 2011.

[15] Shao M., Cheng L., Zhang X., Duo D., Ma D., Dee Sh. L. Excellent photocatalysis of HF-treated silicon nanowires. Journal of American Chemical Society, vol. 131, pp. 17738–17739, 2009.