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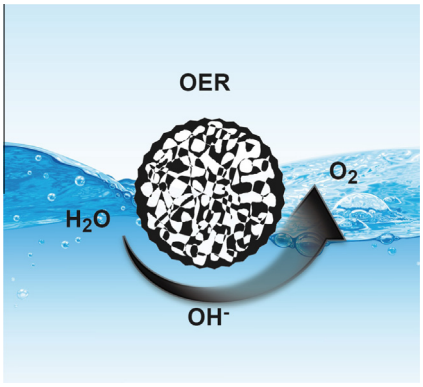
Short Communication

Spray-drying of milk for oxygen evolution electrocatalyst and solar water splitting

Chenyi Cai [a,1], Min Kuang [b,1], Xiling Chen [a], Hao Wu [b], Hongtao Ge [b], Gengfeng Zheng [b,*]

[a] The Fuzhou No. 1 Middle School, Fuzhou 350001, China
[b] Laboratory of Advanced Materials, Department of Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai 200438, China

GRAPHICAL ABSTRACT



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ABSTRACT

The development of efficient and robust electrocatalyst has been the central of the solar water splitting-based hydrogen fuel acquisition. In this work, we reported the use of cow milk, with addition of tetraethyl orthosilicate (TEOS) and melamine, for the synthesis of nitrogen-doped mesoporous carbon microspheres. Due to the large surface and enhanced charge transport behavior, the obtained samples enabled low overpotentials and a small Tafel slope toward oxygen evolution reaction, which were close or comparable to the best OER catalysts of carbon materials reported previously. Further incorporation of this catalyst and a Pt wire to a commercial solar cell, the direct solar-to-hydrogen conversion was realized, with a stability of over 30 h.

The electrochemical or photoelectrochemical water splitting has been attracting substantial research interest and efforts in the past few decades, as it can provide clean and renewable hydrogen fuel with minimum carbon emission to the environment, which has the promise to relieve the significantly increased pressure from fossil fuel consumption and depletion [1]. Although hydrogen is one of the most abundant elements in the world, the free hydrogen molecules do not exist naturally. To date, hydrogen produced via water splitting only accounts for ~4% of global hydrogen production, which requires the use of electrocatalysts for the two half reactions, i.e., the water reduction and oxidation. Nonetheless, the best electrocatalysts used today has still been limited to noble metal-based materials, such as Pt [2] and RuO_2

* Corresponding author.
E-mail address: gfzheng@fudan.edu.cn (G. Zheng).
[1] C.C. and M.K. contributed equally to this work.

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materials [3] used. The scarcity of these materials and the associated high cost substantially limit the potential scale up of utilizing these materials for industry production. Searching new earth-abundant materials for the water splitting electrocatalysts have thus become the central research focal point in this field [3–6].

The water oxidation half-reaction (i.e., oxygen evolution reaction, OER) is widely known for its sluggish kinetics and thus requires a high overpotential to drive [3]. A variety of earth-abundant materials, including metal oxides [3,7–9], hydroxides [10,11], sulfides [12], and selenides [13], have been developed to reduce the OER overpotential. Among these material candidates, the metal-free carbon-based materials have attracted increasing interest, due to their intrinsic high electrical conductivity and excellent mechanical/chemical stability under a large pH range [14–17]. Nitrogen element has also been incorporated into the carbonaceous framework, either by in situ or post-growth doping [14,15], or forming CN compounds such as carbon nitride [17], to increase the electrical transport and catalytic activity. For instance, coaxial nanocables with carbon nanotube cores and N-doped carbon shells were synthesized to achieve a high electrical conductivity of 3.3 S cm^{-1} and a good OER activity [14]. Chen et al. reported the fabrication of a graphene-carbon nanotube hydrogel film with simultaneous doping of both nitrogen and oxygen elements, which enabled a high OER performance [15]. Peng et al. also demonstrated the growth of C_3N_4 of on carbon nanotubes and carbon fiber, via thermal pyrolysis of a mixture of commercial cotton cloth and melamine [17]. The increased OER performance was attributed to the high nitrogen content of C_3N_4 and the enhanced electrical conductivity through this carbonaceous framework.

In addition to using those inorganic compounds for carbon sources, it will also be interesting to discover the capability of using natural organic materials as possible precursors for creating new carbon-based materials. Very recently, it has been reported by our group that eggs, one of natural living organisms that contain abundant organic and biological molecules, can be used to synthesize carbon materials for rechargeable Zn-air batteries [18]. Inspired by this work, herein, we developed the synthesis of nitrogen-doped mesoporous carbon microspheres from plain liquid cow milk, using a fast and convenient spray-drying technique. The mesoporosity and nitrogen level can be facilely tuned by varying the amount of tetraethyl orthosilicate (TEOS) and melamine added into the milk precursor. Compared to samples prepared without TEOS or melamine, the obtained nitrogen-doped mesoporous carbon microspheres exhibited a much better OER performance under alkaline condition, with an overpotential of 320 mV for a current density of 10 mA cm^{-2}, a Tafel slope of 89 mV s^{-1}, and excellent stability with ~86% current density retention over 20 h. Further coupling of a commercial silicon solar cell enabled the direct solar-to-hydrogen conversion under simulated sunlight, thus suggesting new opportunities of searching potential precursors, even from common food or commodities, for fabrication of efficient catalytic materials.

The synthesis of the milk-oriented materials was carried out in a spray-drying process, which is illustrated in Fig. 1a. The milk precursor, obtained directly from commercial fresh milk, was mixed with TEOS and melamine (Methods in the Supporting Information). Ammonia water was added to the solution mixture to tune the pH, and thus TEOS was hydrolyzed and condensed into SiO_2 frameworks, described by the chemical equation shown in Fig. 1a,b. This mixture was then pumped through the spray-drying instrument with controlled flow rate and carrier gas feed, which resulted into formation of small liquid particles, which was collected and calcined (Fig. 2a). During this calcination process, milk and melamine were thermally converted into N-doped carbon framework, interlaced with the mesoporous SiO_2 framework. Further etching of the SiO_2 framework by KOH (6 M) resulted in nitrogen-doped mesoporous carbon microspheres (designated as C-NMS).

Scanning electron microscopy images show that these C-NMS samples have a concaved sphere morphology, with an average particle size of 3–5 μm (Fig. 2b). This concaved sphere morphology is attributed to the difference between the receding droplet surface and the evaporation rate of the liquid droplet during the

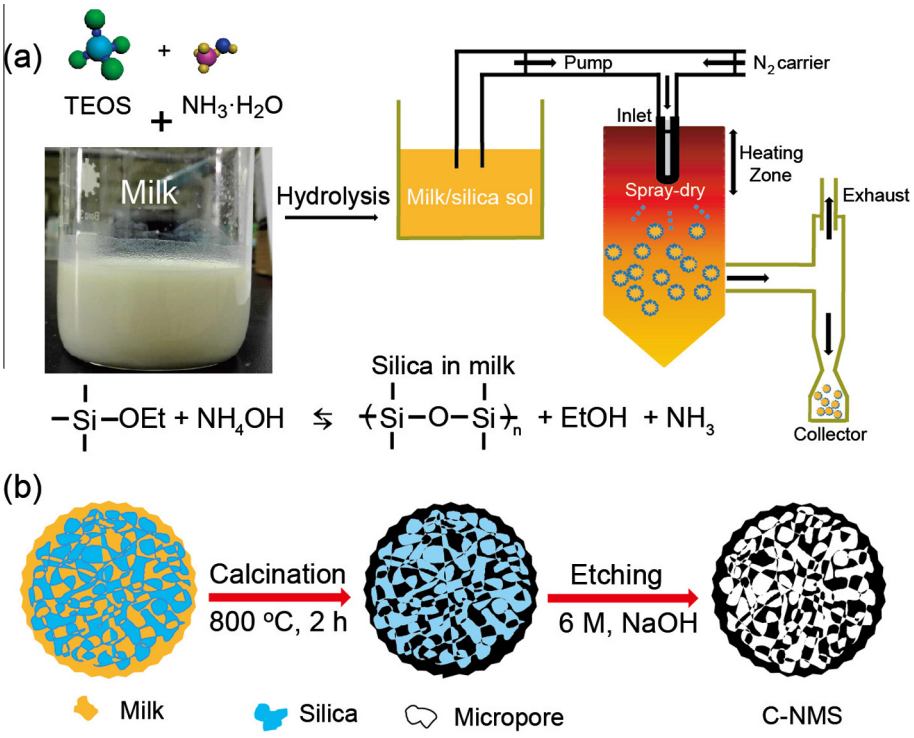

Fig. 1. (a) Schematic of the spray-drying process. (b) Schematic illustration of fabrication of the C-NMS catalyst.