



Sub 1 nm aggregation-free AuPd nanocatalysts confined inside amino-functionalized organosilica nanotubes for visible-light-driven hydrogen evolution from formaldehyde



Shengbo Zhang^{a,1}, Hua Wang^{a,1}, Lei Tang^a, Mei Li^a, Jianhang Tian^a, Yue Cui^a, Jinyu Han^a, Xinli Zhu^a, Xiao Liu^{a,b,*}

^a Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

^b Key Laboratory of Pesticide & Chemical Biology of the Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China

ARTICLE INFO

Keywords:

Amino-functionalized
Organosilica nanotubes
AuPd alloy
Photocatalytic hydrogen evolution
Formaldehyde

ABSTRACT

Novel amino-functionalized organosilica nanotubes (AM-NT) were facilely synthesized by the hydrolysis and condensation of 3-aminopropyltrimethoxysilane (APTMS) with 1,4-bis(triethoxysilyl)benzene (BTEB) using a simple micelle-templating approach. Through adjusting the ratios of organosilane precursors, the very short AM-NT with ~60 nm in length and ~6 nm in pore diameter could be controllably obtained. By using the unique AM-NT as the supports, a series of AuPd alloy nanoparticles with the average size of sub 1 nm could be synthesized after the liquid phase reduction of HAuCl₄ and H₂PdCl₄ in water, which were mostly confined inside the short organosilica nanotubes and further applied for the hydrogen evolution from formaldehyde aqueous solution. These bimetallic AuPd nanocatalysts in the organic-modified nanotubes exhibited remarkably improved catalytic activity under visible light irradiation and the highest initial TOF value of 241.7 h⁻¹ could be achieved at the room temperature. Furthermore, these ultrasmall nanocatalysts exhibited high reaction stability and no aggregation of metal nanoparticles was observed even after 5 recycles. The superior catalytic activity was mainly attributed to the uniform and ultrafine AuPd nanostructure, benefiting from the synergetic stabilizing effects of amino and benzene groups in the nanotube frameworks. The fast electron transfer from much smaller Au with localized surface plasmon resonance (LSPR) to active Pd sites could efficiently occur, resulting in the excellent photocatalytic activity.

1. Introduction

Hydrogen is widely utilized in the petroleum and chemical industries, such as the upgrading of fossil fuels, ammonia production and proton exchange membrane fuel cells (PEMFC), which may play a vital role in the future to satisfy the energy demand [1–6]. Most of the hydrogen employed today in industry is supplied from coal gasification and steam reforming, leading to the continuous consumption of limited fossil resources. Moreover, the controllable storage and safe delivery of hydrogen still restrict its widespread application. From the point of view of sustainable development, it is highly desirable to explore more mild and maneuverable manners for hydrogen production using alternative technologies. Recently, the hydrogen evolution from liquid-phase chemical hydrogen storage materials, such as formic acid [7–14],

methanol [15,16], sodium borohydride [17–19], ammonia borane [20,21], and formaldehyde [22–25] has been attracted much research attention and intensively studied. Among them, the reduction of formaldehyde (HCHO) to H₂ using water as one of the hydrogen donors (HCHO + H₂O → HCOOH + H₂) can be considered as an efficient and promising hydrogen generation strategy due to its atomic economy and nonflammable hydrogen carrier of formaldehyde. More importantly, the resulting gas is only pure hydrogen without CO or CO₂ generation in alkaline solutions, which can greatly meet the criteria of hydrogen production from cost, safety and purity, especially for PEMFC.

Many studies have confirmed that some metal nanoparticles can act as catalysts and significantly accelerate the hydrogen evolution rate from formaldehyde alkaline solution, such as monometallic Cu [26], Pt [27], Ag [25,28], Ni [26], Au [29] and bimetallic AgPd alloy [30].

* Corresponding author at: Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China.

E-mail address: liuxiao71@tju.edu.cn (X. Liu).

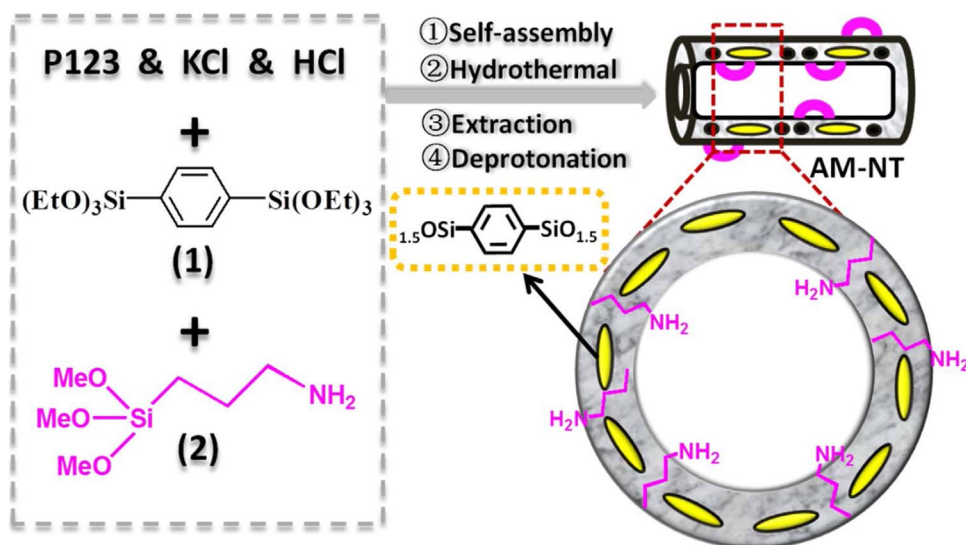
¹ These authors contributed equally.

<http://dx.doi.org/10.1016/j.apcatb.2017.08.043>

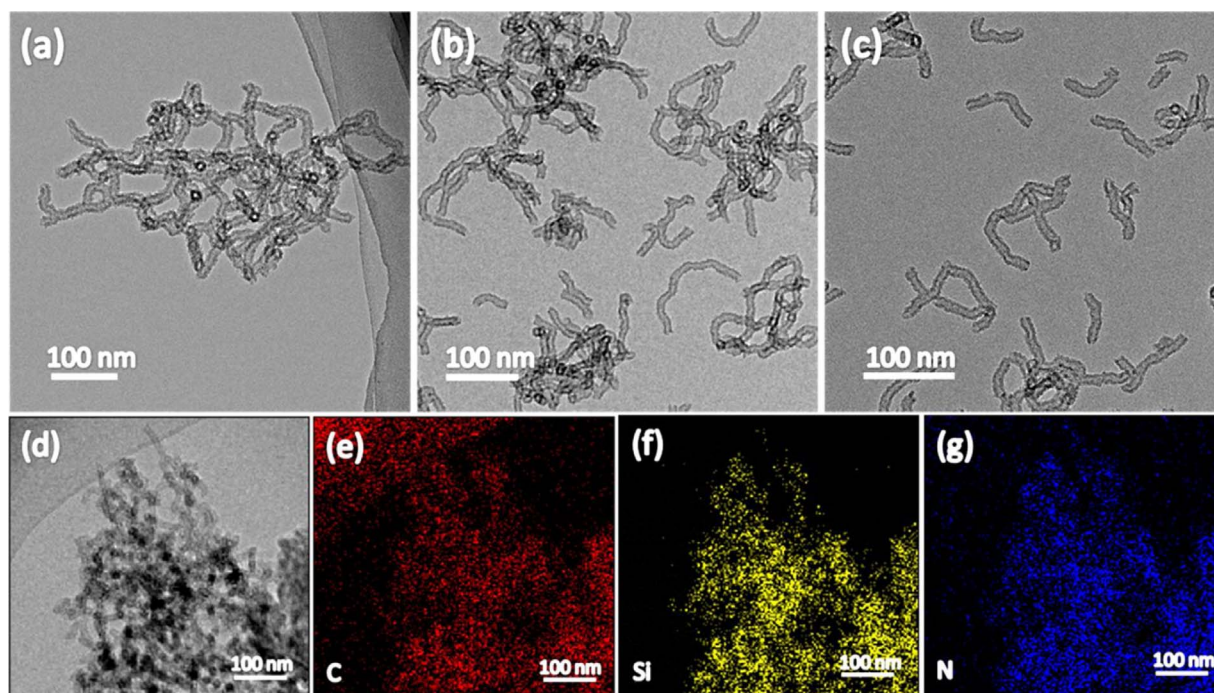
Received 29 June 2017; Received in revised form 11 August 2017; Accepted 14 August 2017

Available online 19 August 2017

0926-3373/ © 2017 Elsevier B.V. All rights reserved.



Scheme 1. Synthetic routes of amine-incorporated organosilica nanotubes.

Fig. 1. The TEM images of (a) $\text{AM}_{0.1}$ -NT, (b) $\text{AM}_{0.2}$ -NT, (c) $\text{AM}_{0.4}$ -NT. (d) Dark field STEM image and (e-g) the elemental mapping images of $\text{AM}_{0.4}$ -NT.

Especially, ultrasmall metal nanoparticles are of great interest due to their unique nanostructure-dependent properties, such as high dispersion, high surface-to-atom ratio, abundant edge and corner atoms and quantum confinement effects, which drastically differentiate their catalytic performance from that of bulk metals [7–9,31–39]. However, using small metal nanoparticle as catalysts suffers from one fatal drawback: small metal nanoparticles tend to aggregate or coalesce owing to their low Tammann temperatures and high surface energies, which seriously makes the active sites and catalytic performance decrease. Therefore, it still remains a challenge for the synthesis of well-dispersed and ultrafine metal nanoparticles with high activity and stability. On the other hand, the hydrogen evolution from alkaline formaldehyde solution has also been achieved from semiconductors under visible light irradiation [40,41]. However, as far as we know, there is no any report about the Au- or Ag-containing bimetallic alloys for visible-light-driven hydrogen evolution from formaldehyde, in the utilization of the localized surface plasmon resonance effect of Au or

Ag.

Organosilica nanotubes containing various organic functionalities in the frameworks are a new kind of organic-inorganic hybrid mesoporous material, which possess the distinct properties such as robust nanostructure, high surface areas, large channel structure and tunable hydrophilicity/hydrophobicity [42–46]. Our previous study has demonstrated that the organic groups in the frameworks could facilitate the formation of smaller metal nanoparticles to enhance the reaction activity [42,47]. Considering the much stronger stabilizing effect of amino groups for metal nanoparticles, herein, we report the synthesis of benzene-bridged organosilica nanotubes containing amino groups in the framework and its encapsulation of AuPd alloys in the nanotube channels. Interestingly, the very short amino-incorporated organosilica nanotubes with ~ 60 nm in length and pore diameter of ~ 6 nm could be controllably synthesized. A series of well-dispersed and ultrafine AuPd nanoparticles supported on cut-short organosilica nanotubes were successfully obtained and applied for the hydrogen evolution from

Download English Version:

<https://daneshyari.com/en/article/6453602>

Download Persian Version:

<https://daneshyari.com/article/6453602>

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