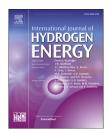
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## Electrochemical hydrogen storage, photocatalytical and antibacterial activity of Fe–Ag bimetallic nanoparticles supported on TiO<sub>2</sub> nanowires

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#### ABSTRACT

In this work, the Fe–Ag bimetallic nanoparticles supported on  $TiO_2$  nanowires (NWs) were synthesized by a facile chemical deposition method. This material subsequently was applied for electrochemical hydrogen storage, photocatalytic degradation of a binary solution of Auramine-O (AO) and Methylene blue (MB) dyes and photocatalytic hydrogen production.

The electrochemical hydrogen storage measurements reveal that  $Fe-Ag/TiO_2$  nanowires have higher hydrogen storage capacity, better cycle stability and higher rate discharge ability than the Fe-Ag/TiO<sub>2</sub> nanoparticles (NPs). Its maximum discharge capacity was 4.29 wt% and remained 3.14 wt% after 25 cycles, and the capacity retention rate was 68% at a high rate current density of 6.2 Ag<sup>-1</sup>. Moreover, the Fe-Ag/TiO<sub>2</sub> NWs supply more significant enhancement in the degradation of a binary solution of AO and MB than Fe-Ag/TiO<sub>2</sub> NPs. The photodegradation rate was 55.99% for Fe-Ag/TiO<sub>2</sub> NWs at 7 min and 29% for Fe-Ag/TiO<sub>2</sub> NPs at 52 min. Furthermore, photocatalytic hydrogen production rates on the as-prepared products are 1269 and 783  $\mu$ mol h<sup>-1</sup> for NWs and NPs, respectively. This significant electrochemical hydrogen storage and excellent photocatalytic performance can be attributed to the increased specific surface area in its one dimension (1D) structure.

It was noteworthy that antibacterial activity experiments illustrated the improved antibacterial activity of Fe–Ag/TiO<sub>2</sub> NPs in comparison to Fe–Ag/TiO<sub>2</sub> NWs because the one-dimensional structure of  $TiO_2$  nanowires makes it difficult to enter the bacterial membrane.

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#### Introduction

Hydrogen is recognized as a most promising candidate to fossil fuels due to crucial advantages such as high efficiency, renewability, abundance and its role for reduction of air pollution [1-3]. However, the most significant challenge to the hydrogen economy is the development of appropriate hydrogen storage materials with large hydrogen-uptake capacity, long-lasting stability and reasonable production costs [4-6]. Nanostructure materials due to their high surface areas have different hydrogen absorption performance compare to their bulk counterparts [7].

Besides hydrogen generation from photo-induced water splitting suggests an excellent route for hydrogen production because of the abundant water resources and tolerable solar energy. Therefore, the development of visible-light active photocatalysts has received increasing attention [8].

Dyes arrival from via wastewater to the different ecosystem as consequence of bleaching, pharmaceutical activity, textile, dyeing, paper and pulp industries [9,10] and discharge of such wastewaters due to the rapid growth of globalization, urbanization, and industrialization lead to serious environmental problems [11,12]. Photocatalytic degradation is known as clean and green purification technology in wastewater treatment process [13]. The poor light distribution is compensated installing a flexible strip light-emitting-diode (LED) around the perimeter of the transparent reactor vessel to get ready uniform light distribution. Such assembly because that photocatalyst particle receives at least the minimum amount of light required for activation [14].

Bimetallic nanostructures catalyst are the best candidate as maintainable energy technology, while supply stability, selectivity and superior specific activity in different applications such as hydrogen generation [15], catalysis [16], fuel cells [17] and hydrogen storage [5,18] compare to their monometallic counterparts. Silver with obvious physiochemical properties able to combine with some other metals such as iron to form bimetallic systems [19] which have higher hydrogen storage compared to the monometallic Fe or Ag particles.

TiO<sub>2</sub> nanostructures are widely applied in many fields including electrochemical biosensors, supercapacitors, dyesensitized solar cells, lithium batteries, photocatalysis, photoelectrochemical and pharmaceutical applications [20-24]. TiO<sub>2</sub> with high redox activity has superior charge storage capability, high chemical stability, non-toxicity, low cost and excellent electrochemical properties is attractive for energy storage and is consider as one of the most promising materials for photoelectrochemical water splitting [8,25,26]. The size and surface site distribution of particles have an important role in the electrochemical performance of hydrogen storage materials [27]. One-dimensional (1D) TiO<sub>2</sub> nanostructures such as nanotubes (NTs), nanowires (NWs) and nanorods attain appreciable attention in photocatalysis applications due to their special physical properties, thermal stability and supplying direct wide band gap that can split photoinduced electron and holes [28,29].

Recently, deposition of noble metal (e.g. Pt, Ag and Au) nanoparticles on  $TiO_2$  is good for efficient surface modifiers to enhance its photoactivity [30,31] and accordingly metal- $TiO_2$ 

semiconductors owing to their applicability as electron trapping sites significantly increase the light harvesting efficiencies and subsequently improve charge transfer processes at the interfaces between  $TiO_2$  and metal. Besides, bimetallic loaded  $TiO_2$  also exhibit better photocatalytic activities for organic degradation than the monometallic nanoparticles loaded  $TiO_2$  [32–34].

Besides,  $TiO_2$  nanostructures attracting a great deal of interest to enhance purification of the environmental source.  $TiO_2$  nanomaterials know as the glamour of recent medical research due to its antibacterial effect to treat different disease-causing organisms [35]. The antibacterial effect of  $TiO_2$  nanoparticles on bacteria is excessive importance due to the ability of pathogenic bacteria to enter in ecosystem food chain [36].

Silver nanoparticles are applicable as bactericide due to their effective action on cellular metabolism and inhibiting cell growth [37,38]. Therefore, Ag/TiO<sub>2</sub> reveal excellent antibacterial properties and photocatalytic properties, which candidate this material as photocatalytic bactericide decomposition [24,39].

Determining the bacterial activity of each nanoparticle as antibacterial agent requires preliminary experiment to measure minimum inhibitory concentrations (MICs) and minimum bactericidal concentrations (MBCs) [40]. In this work, facile chemical deposition approach was used to prepare Fe-Ag bimetallic nanoparticles supported on TiO<sub>2</sub> nanowires. Since the 1D TiO<sub>2</sub> nanostructures were modified by various metals to obtain unique sites that strongly affect activity of the catalyst [28] and accordingly nanostructured TiO<sub>2</sub> NWs were synthesized by simple hydrothermal method. The electrochemical hydrogen storage performance of Fe-Ag/TiO<sub>2</sub> NWs with a three-electrode system in 6 mol L<sup>-1</sup> KOH solution were investigated compared to the Fe-Ag/TiO<sub>2</sub> NPs. The Fe-Ag/TiO<sub>2</sub> NWs exhibit high maximum discharge capacity (4.29 wt%), good cycling stability (3.14 wt% after 25 cycles), and high rate of discharge ability (68% at high rate current density of 6.2 Ag<sup>-1</sup>) owing to its unique morphology. The Fe–Ag/TiO<sub>2</sub> NWs exhibit excellent photocatalytic performance toward the degradation of the binary solution of Auramine-O (AO) and Methylene blue (MB) in aqueous solution. The photodegradation is 55.99% for Fe-Ag/TiO<sub>2</sub> NWs at the 7 min and 29% for Fe-Ag/TiO<sub>2</sub> NPs at the 52 min. The photocatalytic H<sub>2</sub>production rates on the samples are 1269 and 783  $\mu$ mol h<sup>-1</sup> for NWs and NPs, respectively. Moreover, the antibacterial activity of the Fe–Ag/TiO<sub>2</sub> NWs and NPs on Staphylococcus aureus, Pseudomonas aeruginosa, and Escherichia coli bacterial species were examined to search and find a novel trend. The results reveal that Fe-Ag/TiO<sub>2</sub> NPs is a good candidate as a antibacterial activity in comparison to the Fe-Ag/TiO2 NWs due to the 1D structure of Fe-Ag/TiO2 NWs which makes possible to apply them as bacterial membrane.

#### Experimental

#### Chemicals

The chemicals used in this investigation were  $TiO_2$  P25, iron (III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and silver nitrate

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