

Au/ZnO nanostructures for photocatalytic applications

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Abstract

Heterogeneous photocatalytic processes, based on the use of semiconductor nanoparticles as photocatalysts, have been gaining increasing commercial interest worldwide mostly in the fields of environmental cleanup (water/air purification/disinfection), construction and architecture (self-cleaning surfaces), energy generation (photovoltaics and H₂ production) and synthesis of high added-value compounds such as fuels and fine chemicals. These processes have salient advantages, such as the possibility of being conducted at ambient conditions of pressure and temperature, with the additional benefit of being driven by sunlight, an inexhaustible and clean energy source.

The wide spread use of titanium dioxide (TiO₂) in conjunction with other specialty materials, such as paints, sunscreens and food colouring, led to massive consumption of this commodity and triggered the interest on alternative materials capable of efficiencies similar, or even higher, than TiO₂ for specific applications.

Zinc oxide (ZnO) with a bandgap similar to that of TiO₂, has been investigated as a potential alternative in photocatalytic applications specially because its great morphological versatility and lower cost [5]. Depending on the synthesis method and preparation conditions, ZnO materials showing different shapes at the micro- and nanoscale can be obtained, such as nanospheres, nanowires, nanotubes, nanorings and nanotetrapods.

However, its similarity to TiO₂ is simultaneously, its major drawback, namely with its 3.2 eV bandgap mostly absorbs UV light, which accounts for only 5% of the total solar spectrum reaching Earth's surface. Numerous attempts have been made to improve the inherently low efficiency of ZnO (and TiO₂) in harvesting sunlight by shifting the spectral response into the visible and/or by retarding the recombination of electrons and holes. The major practices involve catalyst modification by metal and non-metal doping, metal loading, dye photosensitization, mixing with other semiconductors, and addition of inert supports or carbon materials [1].

One promising strategy to enhance the photocatalytic activity of semiconductor materials is the introduction of noble metal nanoparticles such as Au, Ag or Pt onto their surfaces. The first report on the positive effect of adding metal nanoparticles to semiconductor photocatalysts dates back to the 70s, with the pioneering work of Fujishima and Honda on the photoelectrochemical generation of hydrogen by using a Pt/TiO₂ electrode [2]. Since then, many studies have focused on the role of metal nanoparticles as co-catalysts in semiconductor-based photocatalysts. A variety of explanations have been advanced for rationalizing the observed improvement in photoefficiency, including: i) increased absorption due to surface plasmons and light-trapping effects; ii) improved charge separation as a result of localized electromagnetic field; iii) promotion of electron transfer to adsorbed species; or iv) electron storage effects that can drive the Fermi level to more negative potentials. Moreover, different effects are observed depending on the type of metal nanoparticles, their sizes and shapes.

Metal nanoparticles of silver and gold exhibit surface plasmons in the visible spectral range and can absorb visible light via surface plasmon resonance, i.e., through collective oscillations of the conduction band electrons in the metal particles driven by the electromagnetic field of incident light. The plasmonic effect is often presented as the main contribution for the enhanced photoactivity of Au-loaded metal oxides upon visible light excitation. However, it has been found that photocharging effects, which would arise from storage of electrons within the metal core, may also play a role. Moreover, the optical properties of Au nanoparticles are influenced by many factors, namely the dielectric constants of both the metal and the surrounding material, the particle size, the particle shape of the metal and the surrounding environment.

Several authors have reported on the positive effect of loading Au onto ZnO materials in photocatalytic applications, mostly dealing with water decolourization, but also with organic synthesis and hydrogen production.

In this work, gold was loaded with minute amounts of Au nanoparticles (< 1 wt.%) by a double impregnation method on several ZnO samples with different micro/nanoscale morphologies (Figure 1): "needle"-like structures (ZnO-n), rods (ZnO-r), "flower"-like ZnO (ZnO-f) and spheroidal/needle structures (ZnO-t). Materials were characterized by spectroscopic, microscopic and N₂ adsorption techniques, and

tested for two distinct applications: solar photocatalytic oxidation of phenol in aqueous solutions and photocatalytic production of H_2 from ethanol.

Results indicate that the photoefficiency of the Au/ZnO materials depend on the ZnO morphology, gold nanoparticle dimensions and shapes. Also, Au/ZnO photoexcitation mechanisms vary depending on the wavelength of irradiation and also on the intrinsic properties of the catalyst, namely ZnO radiation absorption and gold nanoparticle size.

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Figures

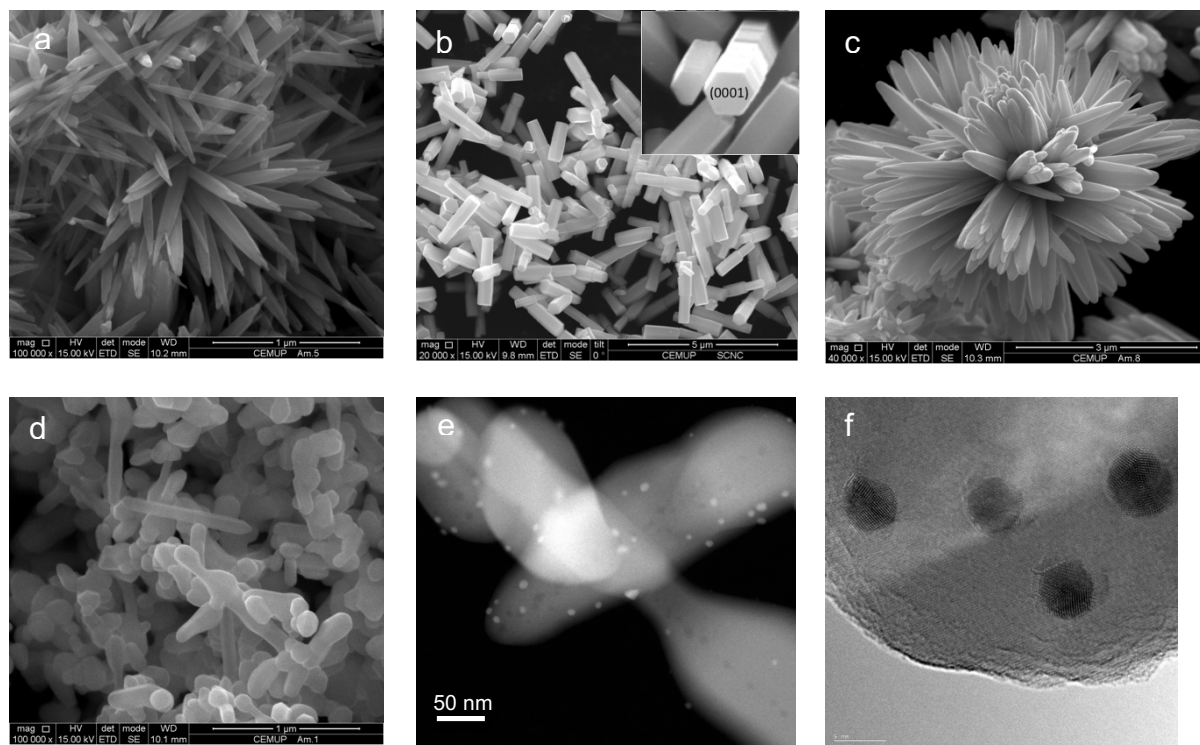


Figure 1. SEM micrographs of ZnO-n (a), ZnO-r (b), ZnO-f (c) and ZnO-t (d); STEM and HRTEM micrographs of Au/ZnO-t (e and f, respectively).