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# Titania@gold plasmonic nanoarchitectures: An ideal photoanode for dye-sensitized solar cells



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### ABSTRACT

Rapid depletion of fossil fuel leads to increasing energy demand in the near future and it will force us to seek alternative eco-friendly and renewable energy resources. Dye-sensitized solar cells (DSSCs) represent one of the most promising emerging technologies for light-to-electrical energy conversion. Titania is the most widely used photoanode, but its limited performance due to poor interfacial charge transfer and limited optical properties has motivated the quest for modified titania materials to overcome this issue. The emergence of gold–titania nanocomposite materials (Au–TiO<sub>2</sub>) as a new component to fabricate the DSSCs has opened up new ways to effectively utilize renewable energy sources. This review article mainly focuses on the superior photovoltaic performance of Au–TiO<sub>2</sub> nanocomposite materials based photoanode in DSSCs. The review justifies how plasmonic Au influences the visible light absorption, electrons transfer process and solar energy conversion efficiency. Data supporting and confirming the superiority of Au on TiO<sub>2</sub> or TiO<sub>2</sub> on Au are briefly presented to justify the possibility of electron transfer from dye to conduction band of the TiO<sub>2</sub> through Au. This account further highlights the recent developments in these area and points out some specific Au–TiO<sub>2</sub> plasmonic nanoarchitectures as photoanode for improved device performance.

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#### 1. Introduction

Extensive use of fossil fuels leads to depletion of its natural resources and increasing the demand of energy and make the environmental impact [1]. The development of a clean, green and renewable energy carrier that does not utilize fossil fuels is a great scientific and technological challenge [1,2]. The renewable energy source meets the essential criteria, such as ideally clean, abundant, inexpensive and widely distributed regionally in the world. Among the various renewable energy sources, solar energy is a decentralized and inexhaustible natural resource, with the magnitude of the available solar power striking the earth's surface at any one instant equal to 130 million of 500 MW power plants [1-4]. Solar energy, besides fusion, has the largest potential to satisfy the future global need for renewable energy sources but it cannot be used as such and it must be captured and converted into useful forms of energy. Scientists have taken significant efforts in the development of renewable-energy technologies, such as photovoltaic cells [5-7], photoelectrochemical cells [8-10] and photocatalytic [11–13] systems.

## 2. Dye-sensitized solar cells: components and working principle

Dye-sensitized solar cells (DSSCs) represent one of the most promising emerging technologies for light-to-electrical energy conversion [5-7,14-15]. A typical DSSC consists of a photoanode of a wide band-gap semiconductor (such as, TiO<sub>2</sub>, ZnO, Nb<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, etc) with a monolayer of dye molecules adsorbed on it as a sensitizer, an electrolyte (tri-iodide and iodide redox couple) and a catalyst (Pt, carbon, etc) coated conducting substrate as cathode [5-7,14-18]. The schematic representation of a dye-sensitized solar cell and operation are shown in Fig. 1. Upon illumination, the dye molecule absorbs incident photons of wavelength corresponding to the energy difference between its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Electrons from the ground electronic state of the dye (S) are now promoted to excited state (S\*), and this excited state dye (S\*) injects the electron into the conduction band (CB) of TiO<sub>2</sub>. The electrons after being injected into CB of TiO<sub>2</sub> are transported through the semiconductor layer by diffusion to reach the conducting layer, FTO. The iodide ion now donates electron to the oxidized dye  $(S^+)$  at anode and regenerates the dye molecule. The oxidized species of the electrolyte, *i.e.*, triiodide in iodide-triiodide complex, is reduced to iodide at the cathode. The above processes goes in cycle and consequently current flows through the external circuit as long as the cell is illuminated under a light [5–7,14–18].

## 2.1. Limitations associated with the components of dye-sensitized solar cells

Till date, the first report by O'Regan and Gratzel in 1991 on DSSC with TiO<sub>2</sub> nanocrystalline film combined with a ruthenium–

polypyridine complex dye and the efficiency above 7% was achieved [14]. Following this idea, several DSSCs were developed with nanocrystalline TiO<sub>2</sub> film. However, the use of TiO<sub>2</sub> nanoparticles as photoanode in DSSC is not ideal in structure in view of electron transport. The first non-ideality results from the lack of macroscopic electrostatic potential gradient in the film due to the fact that the film is permeated with a concentrated electrolyte [18]. Therefore, the electron transport in the nanoparticle film is dominated by the process of diffusion instead of drift. The second non-ideality comes from the fact that the electron transport in the nanoparticle film undergoes a trapping and detrapping process, i.e., the injected electrons can be captured by the trap states and, however, can again be thermally emitted back to the conduction band [19,20]. The trapping, which may result in an energy loss to the injected electrons, is particularly serious in the case of nanoparticle film because of numerous grain boundaries existing in the nanoparticle film [21]. In order to overcome this limitations, several methodologies were adopted in the photoanode, such as employing low-dimensional nanostructures [22,23], anisotropic nanomaterials [24], surface treatment [25,26], coupling with another semiconductor [27], core-shell [28] and metalsemiconductor nanocomposites [29,30].

#### 2.2. Low dimensional nanostructures

When the DSSCs consists of  $TiO_2$  nanoparticles are usually as a random network of misaligned structure and lattice mismatches at the grain boundaries thus leads to the charge recombination and electron scattering. Low-dimensional nanostructures have an aligned structure that can act as single crystal, thus facilitate the rapid electron transport through unidirectional manner and show potential in obtaining high performance devices [31]. The



**Fig. 1.** Schematic representation of a dye-sensitized solar cell constructed with a photoanode consisting of a dye-sensitized semiconducting oxide film, a counter electrode made of Pt coated glass substrate, and an electrolyte filled between the dye-adsorbed photoanode and counter electrode, reprinted with permission from Ref 17, Copyrights (2012) Royal Society of Chemistry.

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