



Photoelectrocatalysis of Rhodamine B and Solar Hydrogen Production by TiO₂ and Pd/TiO₂ Catalyst Systems



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ABSTRACT

There has been extensive research on the modifications of TiO₂, the most heavily investigated photocatalyst, to improve its lack of visible light harvesting and fast electron and hole recombination rate. Metal loading is one of most common ones that focus on enhancing light absorption and efficient charge separation. Here, a hybrid Pd/TiO₂ photocatalyst system was developed where metallic Pd nanoparticles were photochemically deposited onto TiO₂ nanorods. The photoelectrochemical performance of the bare TiO₂ and hybrid Pd/TiO₂ samples were compared through the decolourisation of a standard commercial textile dye Rhodamine B (RhB) and solar hydrogen production in different electrolyte solutions at various applied voltage values. The results are discussed proposing possible reaction mechanisms with an emphasis on the charge trapping role of Pd nanoparticles. The discussions are supported by detailed measurements of Mott-Schottky plots, electrochemical impedance spectroscopy and j-v curves with shifts in the flat band and onset potentials after the deposition of Pd nanoparticles.

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1. Introduction

Since the discovery of TiO₂'s capability for water-splitting and the photocatalytic degradation of organic compounds, almost every suitable semiconductor has been analysed for environmental and energy applications [1,2]. The most heavily investigated is still TiO₂ due to its chemical stability, low cost and good photocatalytic efficiency [3]. The main drawback of TiO₂ is its limited optical response. Due to its large band gap (E_g ~3.2 eV), the photoresponse of TiO₂ is limited to UV light which comprises only 5% of solar energy [4]. There have been extensive studies on a variety of modifications of TiO₂ to improve wavelength range response to boost charge generation and induce efficient charge separation to avoid recombination [5]. Techniques for modifications of TiO₂ include metal loading [6,7], ion doping [8], semiconductor coupling [9,10] and dye sensitisation [11].

Precious metals or rare earth metals deposition on semiconductors is one of the most commonly studied methods for photocatalytic enhancement of TiO₂. There are two main reasons responsible for such achievement: formation of Schottky junction for efficient charge separation and localised surface plasmon

resonance (LSPR) for higher charge generation due to the absorption of visible light. For TiO₂, Au [12–14] and Ag [15–17] are the most popular noble metals to enhance the photocatalytic activity but plasmonic photocatalysis with Pt, [18,19] Pd [20–22] and Ru [23] has also been reported. Comparative studies on the performance of TiO₂ with different metals have been done where the discussions of photoreactivity were based on the work function of the metals [24,25].

However, metal deposition on TiO₂ does not necessarily result in an enhancement of photoelectrochemical performance. Declines in photoactivity and photocurrent by the addition of Ag [26] and Au [27] on TiO₂ have also been reported. This is related to the complex charge transfer mechanism between the metal, TiO₂, substrate and the surrounding electrolyte solution. The relative positions of band levels of the semiconductor, work function of the deposited metal and redox potentials of the solution are the key aspect for understanding the mechanism. There are two features of electron transfer between TiO₂ and deposited metal nanoparticle. First mechanism is the transfer of electrons from conduction band of TiO₂ to metal nanoparticles which is thermodynamically favourable as Fermi level of the metal has lower energy than that of conduction band of TiO₂. These electrons are the excited within band gap of TiO₂ by UV light and further injected to the electrolyte solution by the metal nanoparticles. The charge separation induced by the metal in this way surpasses the recombination [28,29].

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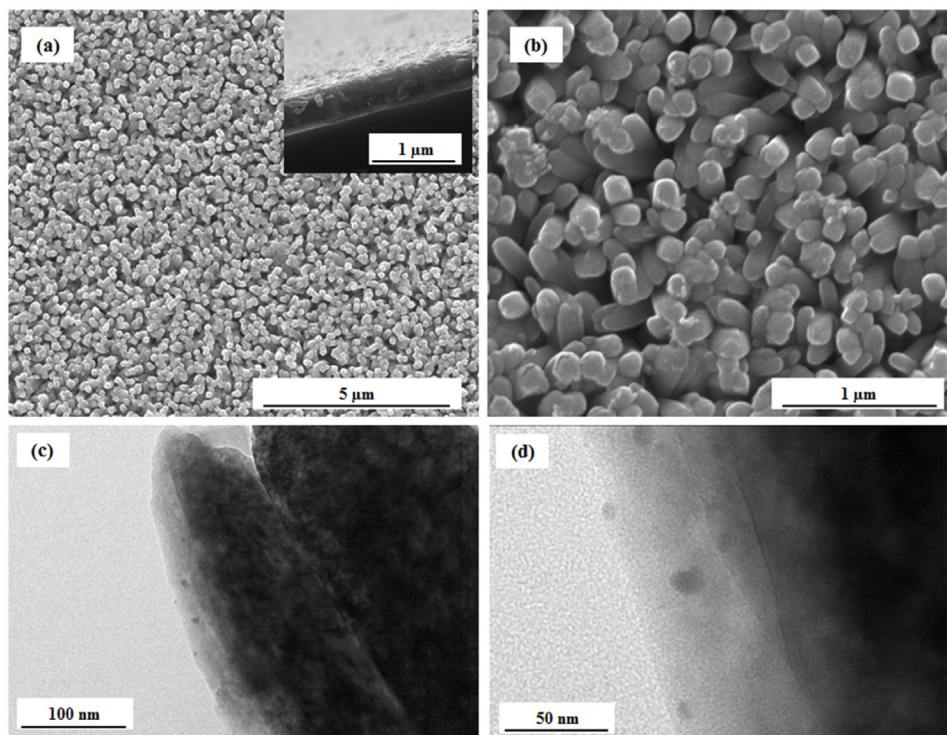


Fig. 1. SEM micrographs of (a) TiO₂ nanorods hydrothermally grown on FTO with subsequent annealing at 550 °C for 3 h. The inset picture shows the cross-section of the sample indicating a length of 2.2 μm (± 0.2 μm) for nanorods. (b) Pd/TiO₂ sample where the morphology was not affected by Pd deposition and deposited Pd could not be observed. TEM micrographs of Pd nanoparticles deposited onto TiO₂ nanorods showing (c) the distribution of the particles and (d) the spherical shapes of nanoparticles with diameter of 5–10 nm.

Second one is the migration of electrons oscillated by the surrounding localised plasmon resonance from the metal nanoparticles to the conduction band of TiO₂ [6]. These electrons are then transferred to the FTO coated glass substrate and the counter electrode Pt via a conducting wire to form the photocurrent. Charge trapping role of the deposited metals influences the photocurrent as the electrons scavenged by the nanoparticles end up not being transferred to the counter electrode results in decreased photocurrent [26]. The extent of metal loading should also be discussed because an excessive amount can have detrimental effects on the resulting photoreactivity as higher amount of loading may create recombination centres [30,31]. The active sites of the semiconductor are also decreased by the excessive amount of metal deposition on the surface which limits the charge generation and charge transfer at the interface of the semiconductor [5].

Here, we report the synthesis of a hybrid Pd/TiO₂ photocatalyst system where metallic Pd nanoparticles were photochemically deposited onto TiO₂ nanorods hydrothermally grown on FTO coated glass substrate. The photoelectrochemical performance of the bare TiO₂ and hybrid Pd/TiO₂ samples were compared through the decolourisation of a standard commercial textile dye Rhodamine B (RhB) and water splitting to produce photogenerated hydrogen gas in different electrolyte solutions at various applied voltage values. Hybrid photocatalyst Pd/TiO₂ showed enhanced photoelectrocatalytic activity in decolourisation of aqueous RhB solution. For the case of solar hydrogen production, Pd/TiO₂'s photoelectrochemical performance was superior with methanol solution whereas bare TiO₂ samples produced a higher amount of hydrogen in 0.01 M Na₂SO₄ and aqueous solutions under same conditions. The results are discussed with proposition of possible charge transfer mechanisms with an emphasis on the charge

trapping role of Pd nanoparticles. The key point in understanding the difference between photoelectrocatalytic performance of TiO₂ and Pd/TiO₂ lies in the fate of photoelectrons trapped by the Pd nanoparticles. Whether the trapped electrons by Pd do reduction chemistry with the solution on the surface prior to recombination with the holes determines the performance of the Pd/TiO₂ catalyst system.

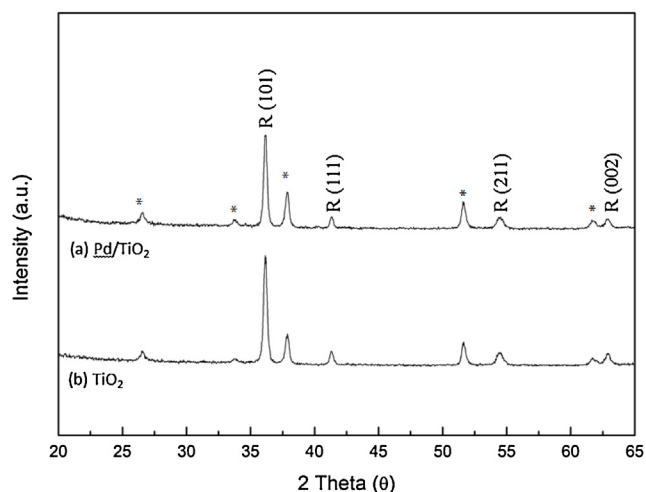


Fig. 2. XRD pattern of TiO₂ and Pd/TiO₂ hydrothermally grown on FTO coated glass substrates. The crystalline peaks were indexed to rutile (R) phase of TiO₂ excluding the peak for the FTO substrate (*). There was no observable change after the deposition of Pd nanoparticles and Pd peak was not observed.

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