

Palladium Quantum Dots Sensitized TiO₂ Nanotube Arrays for Highly Efficient Photoelectrocatalytic Hydrogen Generation

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ABSTRACT

In order to further enhance photoelectrocatalytic reactivity, it is desirable to develop a facile and effective technique to obtain high quality Pd@TNTAs with homogeneous dispersion and small enough particle size down to few of nm Pd quantum dots (QDs) on the geometrically-ordered TiO₂ nanotube arrays [1]. In this work, we report a facile synthetic strategy of preparing novel Pd QDs sensitized TiO₂ nanotube arrays (Pd@TiO₂NTs) and their excellent performance in photoelectrocatalytic hydrogen production. Using the prepared Pd@TiO₂NTs (2.05 wt%) both as photoanode and photocathode, a significantly enhanced photocatalytic hydrogen generation rate of about 592 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ was obtained under 320 $\text{mW}\cdot\text{cm}^{-2}$ irradiation with nearly 100% of an incident photon-to-current conversion efficiency (IPCE) value. It demonstrates that the Pd QDs sensitized TiO₂ nanotube arrays can remarkably improving the photocatalytic efficiency for hydrogen generation.

Keywords: TiO₂ nanotube arrays; Palladium quantum dots; water splitting; hydrogen generation; photoelectrochemical activities

1 INTRODUCTION

Sustainable photoelectrocatalytic water splitting is a promising approach for large-scale hydrogen production for renewable energy.^[1,2] The clean hydrogen energy is expected to be an effective way to solve the energy crisis and environmental pollution. Recently, A tremendous amount of research has shown that palladium (Pd) is one of the most versatile catalysts in the hydrogen relevant reactions.^[3] Incorporations of palladium nanoparticles to the TiO₂ nanostructures have attracted significant interest for decades, due to their wide applications such as heterogeneous catalysis based on the unique features combining an active phase of noble metal and a key semiconductor materials [4]. The noble metal (e.g., Pd), which acts as a sink for photoinduced charge carriers, promotes interfacial charge-transfer processes. It is widely accepted that the properties of these kind of composites are strongly dependent on the metal particle size, dispersion, and composition, etc [5]. It is extensively significant to

prepare palladium-loaded TiO₂ nanocomposites with uniform dispersion, tunable particle size, and narrow particle size distribution [6]. Recently, one-dimensional (1-D) highly ordered TiO₂ nanotube arrays (TNTAs) fabricated by electrochemical anodization had been reported to be able to remarkably increase efficiency of photocatalytic water splitting and solar energy conversion applications [7]. In our previous work, we had investigated the attractive activities of TNTAs for photoelectrocatalytic water splitting and the design of superhydrophobic nanostructure models [8-11]. However, the fast recombination rate of photo-generated e^-/h^+ remains an essential problem restricting the photocatalytic applications of the TNTAs. Thus, the palladium-loaded TiO₂ nanotube arrays (Pd@TNTAs) with their prominent charge-transfer properties and photocorrosion stability are expected to have excellent reactivity in hydrogen generation owing to their complementary features [12].

In this paper we report the fabrication of Pd QDs sensitized highly ordered TiO₂ nanotube arrays (Pd@TiO₂NTs) and their excellent performance in hydrogen production by photoelectrocatalytic water splitting. It is noted that, using the prepared Pd@TiO₂NTs (2.05 wt%) as both photoanode and photocathode, a significantly enhanced photocatalytic hydrogen generation rate of about 592 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ was obtained under 320 $\text{mW}\cdot\text{cm}^{-2}$ irradiation with nearly 100% of an incident photon-to-current conversion efficiency (IPCE) value. These results clearly demonstrate that the Pd QDs sensitized TiO₂ nanotube arrays are capable of remarkably improving the photocatalytic efficiency for hydrogen generation.

2 EXPERIMENTAL SECTION

An electrochemical anodization of the titanium foils (0.1 mm thick, 99.5% purity) was carried out in ethylene glycol containing 0.3 wt% NH₄F + 2 v% H₂O with Pt counter electrode. In the first-step of anodization, the 50 V potential was applied for 4 h, then the as-anodized Ti foil was ultrasonically rinsed in acetone to strip the anodized TiO₂ nanotubular layer from the titanium substrate. Subsequently, a second-step of anodization was conducted on the Ti substrate at 50 V for the further growth of nanotubes. After the ultrasonically removal of the TiO₂ layer again, the exposed Ti foil was then treated for 5 min

for the third anodization. All the three-step anodizing experiments were conducted in fresh electrolyte with a magnetic agitation at room temperature. The as-prepared amorphous TiO₂ nanotube arrays were finally annealed in air at 450°C for 2 h with a heating rate and cooling rate of 5°C/min to convert to crystalline phases.

The morphologies of the prepared samples were observed by a field emission scanning electron microscope (SEM, S4800, Hitachi) and transmission electron microscopy (TEM, JEM2100) equipped with an energy-dispersive X-ray spectrometer. The crystalline structure of the samples was identified by x-ray diffraction (XRD, Philips, Panalytical X'pert, Cu KR radiation). The elemental composition of the nanotube array films was analyzed by x-ray photoelectron spectroscopy (XPS, VG, Physical Electrons Quantum 2000 Scanning Esca Microprob, Al K_α radiation).

The photoelectrochemical cell used for photocurrent measurements was consisted of Pd@TNTAs both as photoanode and photocathode, a SCE reference electrode, and an electrolyte (0.5 M aqueous KOH solution). To evaluate the photovoltaic performance, the water splitting experiment was carried out in a gas-closed circulation system equipped with a three electrode photoelectrochemical cell and a volumetric device with a vacuum line. The photoelectrochemical cell was immersed in a cooling water bath to maintain the solution temperature at 290 K during photoirradiation. The volume of the electrolyte with 2 M Na₂CO₃ + 0.5 M ethylene glycol was 150 mL. The electrolyte was purged with N₂ gas for over 30 min to get rid of the oxygen at the beginning. A 300 W Xe lamp (PLS-SXE300, Beijing Bofeilai Technology Co, Ltd.) was used as an artificial solar light source under 320 mW·cm⁻² irradiation.

3 RESULTS AND DISCUSSION

Figure 1a is a typical SEM image of the as-synthesized TiO₂ nanotube arrays, which reveals a compact and highly ordered one-dimensional architecture of TiO₂ film. It can be seen that the average diameter of the TiO₂ nanotubes is about 80 nm, and the tube length is about 1.2 μm (Figure 1a, inset). The wall thickness of these TiO₂ nanotubes is found to be in a range of 30–40 nm. Figure 1b and c show that the Pd QDs are uniformly deposited onto the highly ordered TiO₂ nanotube arrays. It is obvious that the Pd QDs are dispersed very homogeneously over the entire length of the nanotube walls from bottom to top (Figure 1b and c), and the Pd QDs synthetic process does not damage the architectural structure of TiO₂ nanotube array. Figure 1d is a TEM image of the Pd QDs onto a single TiO₂ nanotube, showing a homogeneous distribution of Pd QDs both outside and inside TiO₂ nanotube with very small particle size ranged from 2.5 to 4 nm. The lattice spacing of 0.35 nm in the left part of the high-resolution TEM (HRTEM) image (Figure 1e) corresponds to (101) plane of anatase

TiO₂ [13], and the lattice spacing of 0.22 nm is attributed to the (111) plane of metallic Pd [14].

The composition of the electroanodized TiO₂ nanotube and deposited QDs characterized by X-ray photoelectron spectroscopy (XPS) further confirms that the nanotube composites are composed of TiO₂ nanotubes and Pd QDs (2.15 wt %), shown in **Figure 2**. The as-anodized TiO₂ nanotubes are generally amorphous, and after annealed at 450°C for 2 h in air, the prepared TiO₂ nanotubes are mainly converted to crystal phase as seen from **Figure 3**. No any additional peak attributed to Pd metal phase is found, suggesting a small nanoparticle size on the nanotubes surface [15].

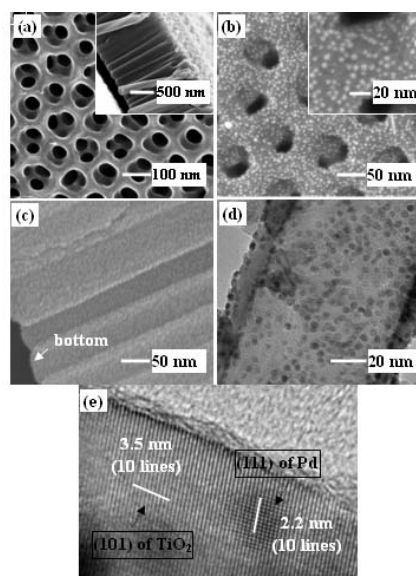


Figure 1: (a) Top and cross-sectional view (inset) SEM image of the TiO₂ nanotube array film by the third-step electrochemical anodization; (b) top at low and high magnifications and (c) cross-sectional view of the Pd QDs deposited TiO₂ nanotube-array film; (d) TEM images of the TiO₂ nanotube film after Pd QDs were deposited into the film; (e) HRTEM image of a Pd QDs deposited nanotube.

Figure 4a summarizes the incident photon-to-current conversion efficiency (IPCE) obtained from the photoelectrochemical cell using pure TiO₂ nanotubes and Pd@TiO₂NTs (2.15 wt%) as photoanodes at 0.8 V_{SCE}. The absorption edges of Pd@TiO₂NTs show an obvious blue-shift, which is believed to be attributed to the quantum effect from the Pd nanoparticles. It is indicated that the IPCE_{max} for the prepared Pd@TiO₂NTs photoanode is about 98.6%, while for the photoanode of pure TiO₂ nanotubes is only about 69.8%, when using Pd@TiO₂NTs as photocathode. In line with photocurrent results, the hydrogen evolution rate using the prepared Pd@TiO₂NTs both as photocathode and photoanode for photoelectrocatalytic water splitting is up to 592 μmol·h⁻¹

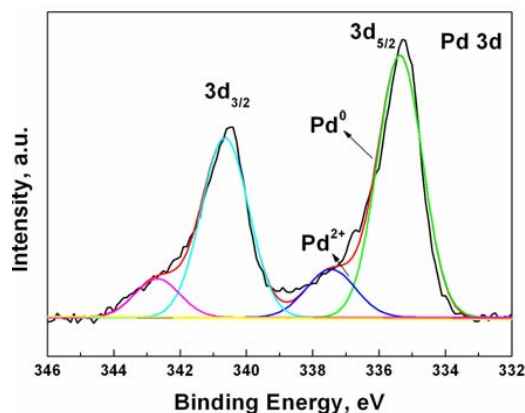


Figure 2: XPS spectra of Pd_{3d} of the prepared Pd/TiO₂NTs (2.15 wt%, 2.5-4 nm).

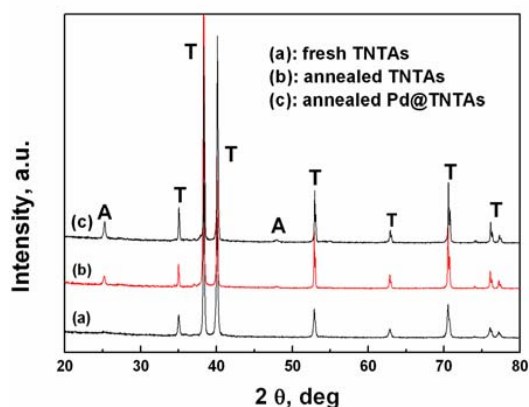


Figure 3: XRD profiles of fresh TiO₂ nanotubes arrays (TNTAs) and TiO₂ nanotubes annealed at 450 °C before and after Pd QDs deposition (2.15 wt%, 2.5-4 nm).

$^1\text{-cm}^{-2}$ in 2 M Na₂CO₃ + 0.5 M ethylene glycol at bias voltage of -0.3 V_{SCE} depicted in figure 4b. This unusually high hydrogen generation rate is a significant improvement to the previous relevant works to the best of our knowledge [18]. In the hydrogen generation experiment at bias voltage of -0.3 V_{SCE}, the evolved O₂ amount was found about 105 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$, which was less than the stoichiometric value ratio consideration (H₂:O₂ = 2:1). This may be resulted from the holes consumed by the addition of electron donor in the electrolyte and the absorbed oxygen on the surface of the photocatalyst under UV irradiation [16,17]. This markedly enhanced photocatalytic activity for hydrogen production should be resulted from the strong synergy between the highly ordered nanotubular TiO₂ support and

Pd QDs. Firstly, the crystalline nature of the smooth nanotubes and the film geometry may provide a

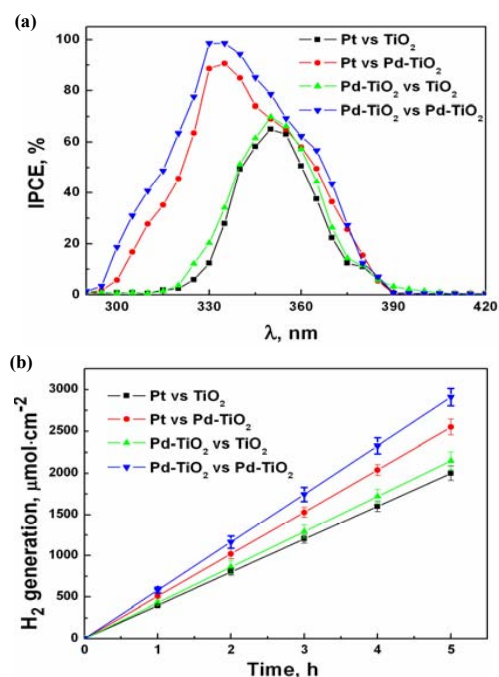
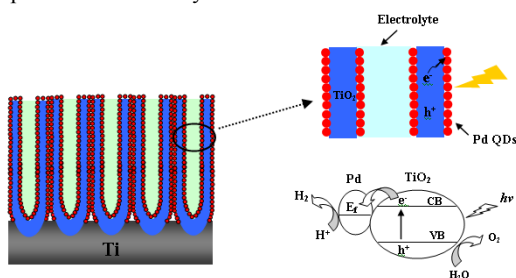


Figure 4: (a) IPCE values (incident photo-to-photocurrent efficiency) measured at 0.8 V_{SCE} in 0.5 M KOH and (b) the amount of hydrogen generated by the TiO₂ nanotubes and the Pd@TiO₂NTs film photoanodes in the PEC cell vs Ptfoil and Pd@TiO₂NTs film as a cathode at -0.3 V_{SCE}.

large surface area with a fast and efficient photogenerated electrons transfer. And secondly, the uniform Pd QDs, acting as electron sinks, reduces the recombination of photogenerated electrons and holes and prolongs the lifetime of the electron-hole pairs leading to a significantly improved photocurrent and efficiency [18]. Finally, the homogeneous distributed Pd QDs onto the TiO₂ nanotube may play a role of highly effective catalytic centers for promoting the H₂O decomposition and H₂ formation.

In **Scheme 1**, we depicted the main features of the Pd@TiO₂NTs photoelectrode and the charge-transfer processes between TiO₂ nanotubes and Pd particles activated by the the light. It is considered that the crystalline nature of the ordered and smooth TiO₂ nanotubes and the film geometry may provide a large surface area with a fast and efficient photogenerated electrons transfer. The uniform Pd QDs deposited on the nanotube surface, acting as electron sinks, can prevent the recombination of the photo-induced electrons and holes, and prolong the lifetime of the electron-hole pairs. On the other hand, the incorporation of Pd QDs onto the TiO₂ surface is able to increase the rate of electron transfer from

the semiconductor surfaces and reduction of H^+ at the Pd nanoparticles in electrolytes.



Scheme 1: Sketch showing the nanostructure of Pd QDs modified TiO_2 nanotube film electrode and charge-transfer processes between Pd and TiO_2 .

4 CONCLUSION

In summary, our present results demonstrate a facile and efficient strategy for preparing the highly uniform Pd QDs with a very narrow particle size distribution (~2.5-4 nm) loaded on the ordered TiO_2 nanotubes by using a modified hydrothermal method. The significantly increased efficiency of photoconversion and notable photocatalytic hydrogen production rate achieved here confirm that the unique structures of the Pd@ TiO_2 NTs nanocomposite facilitate the charges transfer and separation of the photogenerated electrons-holes, as well as the high activity of Pd QDs catalysis for accelerating the H_2O decomposition and H_2 formation. It is resonanted a promising strategy of the development of Pd@ TiO_2 NTs nanocomposite in hydrogen production by photocatalytic water splitting.

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