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IMPROVING PHOTOCURRENT DENSITY GENERATION BY POROUS TIO_2 FILMS MODIFIED WITH POLYSTYRENE PARTICLES

Abstract

The development of porous TiO_2 thin films is of significant interest for photovoltaic and photocatalytic applications owing to their ability to enhance light utilization. Herein, porous TiO_2 films were prepared using 350 nm polystyrene (PS) particles as sacrificial templates, and the effect of PS concentration on photocurrent generation was systematically evaluated. Morphological and optical analyses confirmed the successful formation of porous structures with improved light-harvesting characteristics. Typically, the optimized PS-modified TiO_2 film exhibited a photocurrent density of ~118 μA/cm^2, corresponding to an enhancement of ~20.5% relative to bare TiO_2 film. Integrating sphere measurements revealed increased total absorbance for the porous films, indicating that the improved photocurrent density generation originates from enhanced light trapping within the porous surface. This work highlights the importance of porosity engineering and demonstrates that PS-assisted templating is an effective approach for enhancing the performance of TiO_2-based photoactive thin films.

Keywords: TiO_2 thin films, polystyrene particles, porosity engineering, photocurrent density, light trapping.

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Introduction

TiO_2 semiconductor thin films have been widely employed as n-type layers in a variety of devices, including dye-sensitized solar cells, perovskite solar cells, and photocatalytic systems [1-3]. Over the years, numerous strategies have been developed to enhance photocurrent generation and electrical conductivity in TiO_2 thin films, such as plasmonic sensitization [4], integration with two-dimensional (2D) materials [5], elemental doping [6], and surface nanostructuring [7]. Among these approaches, surface nanostructuring has attracted considerable attention due to its ability to create mesoporous architectures that enhance light harvesting through increased photon scattering, thereby promoting the generation of additional electron-hole pairs. This strategy is particularly attractive from both economic and scalability perspectives, as it does not require costly dopants, plasmonic materials, or 2D nanomaterials. Moreover, nanostructured surfaces exhibit improved resistance to humidity, as previously demonstrated for triboelectric nanogenerators [8].

Nanostructured and mesoporous TiO_2 films can be fabricated using a variety of techniques, including sol-gel synthesis [9], screen-printing [10], electrodeposition [11], and spin-coating [12]. Among these methods, screen-printing and spin-coating are particularly attractive due to their ability to produce uniform films with well-controlled thickness. In addition, the TiO_2 slurry paste used in both techniques can be readily prepared from commercially available TiO_2 nanoparticles (NPs), allowing straightforward adjustment of NPs concentration, solvent composition, and binder content

to achieve the desired viscosity. Furthermore, soft-templating agents, such as monodisperse polymer NPs, can be also incorporated into the slurry paste. During the subsequent calcination process, the polymer templates are completely removed, leaving behind pores that act as light-scattering centers and enhance light harvesting within the TiO_2 film.

In this study, we present a systematic investigation of the relationship between PS particles concentration, film porosity, and photocurrent generation in TiO_2 thin films. To the best of our knowledge, the effect of PS concentration on the photocurrent generation rate of porous TiO_2 films has not been comprehensively explored before. We showed that optimized PS-modified TiO_2 film exhibited a photocurrent density approximately 20.5% higher than that of bare TiO_2 film. Absorbance measurements with an integrating sphere revealed that the enhancement originates from improved light absorption within the porous structure.

Materials and methods

All reagents were purchased from Merck KGaA and used as received without further purification. Monodisperse PS particles with a diameter of 350 nm (2.5 wt.% aqueous suspension) were obtained from Polysciences Inc. To prepare porous TiO_2 films, 50, 100, and 150 μL aliquots of the PS suspension were transferred into separate vials and dried in an oven for several days to ensure complete removal of water.

The TiO_2 slurry paste was prepared according to the previously reported procedure [13], with the concentration of TiO_2 NPs adjusted to approximately 59-60 mg/mL. Subsequently, 0.3 mL of the TiO_2 slurry was added to each vial containing dried PS particles, and the mixtures were stirred at 500 rpm for 48 h to obtain homogeneous dispersions. The resulting pastes were deposited onto cleaned fluorine-doped tin oxide (FTO) glass substrates (12-16 Ω/cm^2) using a three-step spin-coating procedure. First, a TiO_2 underlayer was deposited using a bare TiO_2 slurry paste at 500 rpm for 5 s, followed by 5000 rpm for 20 s. Second, a layer of either bare or PS-modified TiO_2 slurry paste was deposited under identical spin-coating conditions on a top of first TiO_2 underlayer. Finally, a solution consisting of titanium isopropoxide (0.1 mL) and isopropanol (1.0 mL) was spin-coated at 500 rpm for 5 s with subsequent acceleration to 2000 rpm for 20 s. After the deposition of each layer, the films were annealed at 500 °C to obtain solid TiO_2 layers on the FTO substrates. The photocurrent generation performance of all samples was evaluated using a conventional three-electrode configuration. TiO_2-coated FTO substrates served as the working electrodes, while a platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All measurements were performed in 0.1 M Na_2SO_4 aqueous electrolyte and repeated at least three times to ensure reproducibility. The reported values represent the average of the obtained results, with only minor variations observed between measurements. Simulated solar irradiation was provided by a Newport LCS-100 solar simulator (AM 1.5G, Newport-Spectra Physics), calibrated to one-sun intensity (100 mW cm^{-2}) using a certified silicon reference cell. Chronoamperometry (CA) measurements were carried out using a PalmSens4 potentiostat at an applied potential of 0.6 V versus Ag/AgCl under chopped illumination conditions.

The morphology of the TiO_2 films was characterized using a field-emission scanning electron microscope (FESEM, ZEISS Crossbeam 540). Crystal structure analysis was performed by X-ray diffraction (XRD) using a SmartLab diffractometer (Rigaku Corp.). The surface chemical composition of the optimized sample was investigated by X-ray photoelectron spectroscopy (XPS, NEXSA system). Total absorbance measurements were carried out using a Quantaurus-QY spectrometer (Hamamatsu Photonics K.K.) equipped with an integrating sphere.

Results and discussion

It is well-known that optimized surface porosity can improve light trapping and thereby enhance the photocurrent generation of semiconductor structures [14]. Figure 1 shows the CA responses of

TiO_2 films prepared with different PS concentrations. Under solar light illumination, all samples generate electron-hole pairs, which are subsequently separated and transported through the system, resulting in measurable photocurrent. Once the illumination is removed, the photocurrent rapidly decreases to nearly zero, confirming that the observed current is solely associated with photoinduced processes. The reproducible light on-off cycles further demonstrate that the photocurrent generation occurs only under sunlight illumination.

On the other hand, clear differences in photocurrent density generation can be observed among the investigated samples. In particular, the TiO_2 films modified with 50 and 100 μL of PS particles exhibited the maximum photocurrent densities of 118.28 and 118.22 μA/cm^2, respectively, corresponding to an enhancement of approximately 20.5% compared to the bare TiO_2 film (98.17 μA/cm^2). In contrast, the sample prepared with 150 μL of PS particles generated a photocurrent density of only 97.65 μA/cm^2, which is slightly lower than that of the unmodified TiO_2 film. The photocurrent density measurements were repeated using at least for four different samples per batch, with a photocurrent density deviation below 2-3%, demonstrating good reproducibility of the cells. The observed trend indicates the existence of an optimal porosity level, beyond which further increases in porosity may negatively affect the photocurrent generation performance of the TiO_2 films. The decrease in photocurrent at higher PS concentrations can be attributed to excessive porosity, which may reduce film connectivity and hinder efficient charge transport within the TiO_2 films.

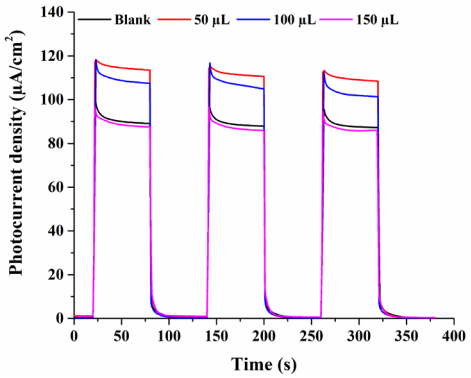

Figure 1 – Chronoamperometry results
for bare and PS-modified TiO_2 films

Next, the bare and optimal PS-modified TiO_2 (50 μL) films were investigated using FESEM to visualize the effect of PS incorporation on the film morphology. Figures 2a and 2b show the corresponding FESEM images obtained at 5000× magnification. In the case of the bare TiO_2 film, a relatively flat and uniform surface can be observed, indicating that the TiO_2 NPs are evenly distributed and form a continuous mesoscopic layer. In contrast, the PS-modified TiO_2 film reveals the presence of numerous pores with diameters comparable to or larger than the size of the original PS particles. The existence of these pores confirms the successful incorporation of PS particles into the TiO_2 slurry paste and their complete removal during the thermal treatment process. Some pores appear larger than expected, which is most likely due to the aggregation of several PS particles in the same area prior to heat treatment. Overall, the FESEM results confirm that PS-assisted templating is an effective approach for generating porous TiO_2 films with increased surface roughness and pore density.

Both films were further compared using XRD analysis. Figure 3 presents the diffraction patterns of the FTO-coated glass substrate, blank TiO_2 film, and the optimal PS-modified TiO_2 (50 μL) film deposited on FTO-coated glasses. It can be seen that both TiO_2 films exhibit characteristic diffraction peaks of the anatase phase located at 25.4°, 37.8°, 48.2°, 54.0°, 55.2°, and 62.8°, corresponding to the (101), (004), (200), (105), (211), and (204) crystal planes, respectively [12]. The diffraction peaks originating from the FTO substrate are also visible in all patterns. Importantly, no noticeable shifts in peak positions or significant changes in peak intensities were observed after PS particles

incorporation, indicating that the modification process does not affect the crystal structure or phase composition of the TiO_2 films.

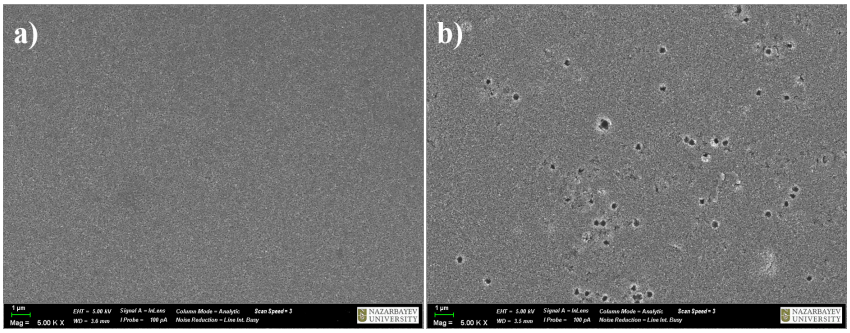

Figure 2 – FESEM images of (a) bare
and (b) optimal PS-modified TiO_2 (50 μL) films

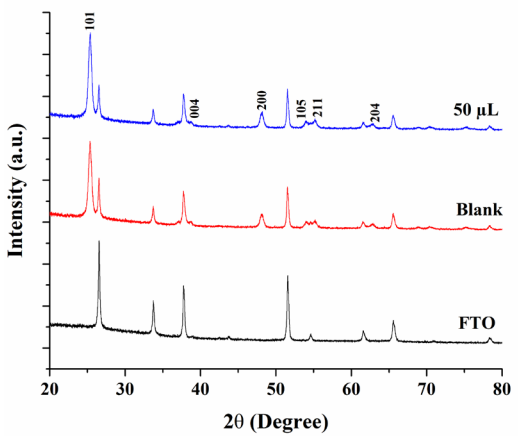

Figure 3 – XRD patterns of FTO-coated glass,
bare and optimal PS-modified TiO_2 (50 μL) films

Moreover, the oxidation states of titanium and oxygen in the bare and optimal PS-modified TiO_2 (50 μL) films were investigated using XPS to confirm that the incorporation of PS particles does not alter the surface chemical composition of the films. Figures 4a and 4b present the high-resolution XPS spectra of the optimal PS-modified TiO_2 (50 μL) film only, as both samples exhibited nearly identical spectral features. The Ti 2p spectrum displays characteristic Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks at 458.2 and 463.9 eV, respectively, confirming the titanium oxidation state to be Ti^{4+} [12]. Similarly, the O 1s spectrum can be deconvoluted into peaks centered at 529.5 and 530.2 eV, which are attributed to Ti-O bonds and surface-adsorbed oxygen-containing species (or hydroxyl/water groups), respectively. Therefore, the XPS analysis confirms that both films consist of chemically identical TiO_2 structures and that no changes in oxidation states occur after PS incorporation. Combined with the XRD results, these findings suggest that the enhanced photocurrent generation originates primarily from the increased surface porosity and light-trapping capability of the PS-modified TiO_2 films rather than from changes in their crystal structure or surface chemistry.

To verify the improved light-harvesting capability of the optimal PS-modified TiO_2 (50 μL) film compared to bare TiO_2, total absorbance measurements were performed using an integrating sphere in the wavelength range of 325-500 nm. As shown in Figure 5, the bare TiO_2 film exhibits strong absorption in the UV region, followed by a sharp decrease in absorbance above ~ 390 nm, which is consistent with the reported bandgap of anatase TiO_2 (3.18-3.20 eV) [5, 12]. In contrast, the optimal PS-modified TiO_2 (50 μL) film displays slightly higher absorbance in the UV region as well

as an extended absorption tail in the visible range. This behavior highlights the beneficial effect of increased surface porosity on the optical properties of the film. The enhanced absorbance is attributed to stronger light-scattering effects within the porous structure, which increase the effective optical path length and promote more efficient light harvesting. Consequently, the improved light absorption of the PS-modified TiO_2 film is consistent with its higher photocurrent density observed during CA measurements.

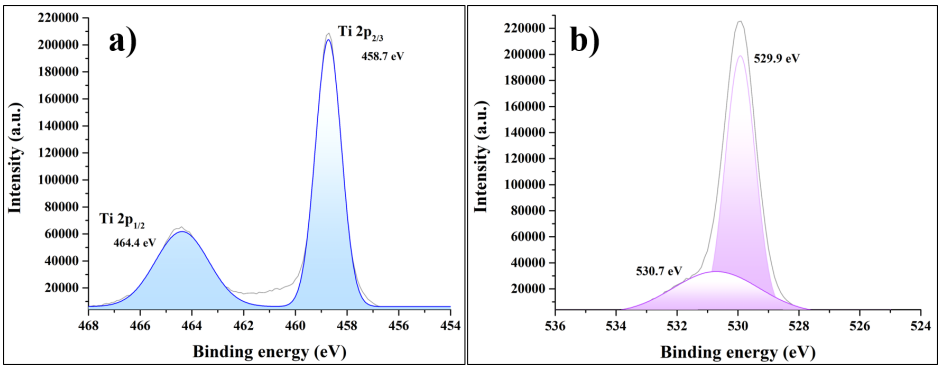

Figure 4 – High resolution XPS survey of (a) titanium
and (b) oxygen elements in optimal PS-modified TiO_2 (50 µL) film

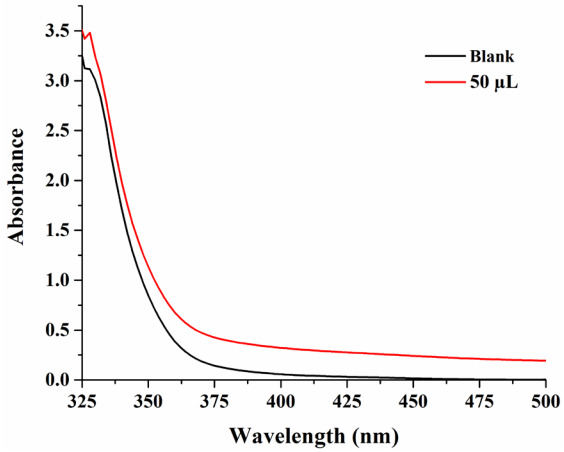

Figure 5 – Total absorbance measurements
of bare and optimal PS-modified TiO_2 (50 µL) films

Conclusions

In summary, porous TiO_2 thin films were successfully fabricated through PS-assisted templating using monodisperse 350 nm PS nanoparticles at different concentrations. Chronoamperometry measurements revealed that the incorporation of an optimal amount of PS particles (50 µL) increased the photocurrent density from 98.17 to 118.28 µA/cm^2, corresponding to an enhancement of approximately 20.5% compared to bare TiO_2 films. FESEM analysis confirmed the formation of a porous surface morphology after PS removal, while XRD and XPS measurements demonstrated that the crystal structure and surface chemical composition of TiO_2 remained unchanged after modification. Total absorbance measurements performed using an integrating sphere revealed enhanced light-harvesting capability of the porous films, which was attributed to increased light scattering and a longer optical path within the TiO_2 film. These findings indicate that the observed

photocurrent enhancement originates primarily from porosity-induced optical effects rather than changes in the intrinsic properties of TiO_2. Overall, PS-assisted surface nanostructuring represents a simple, scalable, and cost-effective strategy for improving the photocurrent density of TiO_2 thin films and may be applicable to other photovoltaic and photocatalytic systems.

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ПОЛИСТИРОЛ БӨЛШЕКТЕРІМЕН МОДИФИКАЦИЯЛАНҒАН КЕУЕКТІ TiO_2 ҚАБЫҚШАЛАРЫ АРҚЫЛЫ ФОТОТОК ТЫҒЫЗДЫҒЫНЫҢ ГЕНЕРАЦИЯСЫН АРТТЫРУ

Аңдатпа

Кеуекті TiO_2 жұқа қабықшаларын әзірлеу жарықты тиімдірек пайдалануға мүмкіндік беруіне байланысты фотоэлектрлік және фотокаталитикалық қолданбалар үшін үлкен қызығушылық тудырады. Бұл жұмыста диаметрі 350 нм полистирол (PS) бөлшектері қалыптаушы шаблондар ретінде пайдаланылып, кеуекті TiO_2 қабықшалары дайындалды және полистирол (PS) бөлшектерінің концентрациясының фототок генерациясына әсері жүйелі түрде зерттелді. Морфологиялық және оптикалық талдаулар жарықты жұту қасиеттері жақсартылған кеуекті құрылымдардың сәтті қалыптасқанын растады. Оптимизацияланған PS-модификацияланған TiO_2 қабықшасы шамамен 118 мкА/см^2 фототок тығыздығын көрсетті, бұл модификацияланбаған TiO_2 қабықшасымен салыстырғанда шамамен 20,5%-ға жоғары. Интегралдаушы сфера көмегімен жүргізілген өлшеулер кеуекті қабықшалардың жалпы жарық жұтуының артқанын көрсетті, бұл фототок тығыздығының жақсаруы кеуекті архитектурадағы жарықтың тиімдірек ұсталуымен байланысты екенін дәлелдейді. Бұл жұмыс кеуектілікті басқарудың маңыздылығын көрсетіп, полистирол (PS) бөлшектерінің көмегімен шаблондау TiO_2 негізіндегі фотоактивті жұқа қабықшалардың тиімділігін арттырудың тиімді тәсілі екенін дәлелдейді.

Түйін сөздер: TiO_2 жұқа қабықшалары, полистирол бөлшектері, кеуектілікті басқару, фототок тығыздығы, жарықты ұстау.

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ПОВЫШЕНИЕ ГЕНЕРАЦИИ ПЛОТНОСТИ ФОТОТОКА С ПОМОЩЬЮ ПОРИСТЫХ ПЛЁНОК TiO_2, МОДИФИЦИРОВАННЫХ ПОЛИСТИРОЛЬНЫМИ ЧАСТИЦАМИ

Аннотация

Разработка пористых тонких пленок TiO_2 представляет большой интерес для фотоэлектрических и фотокаталитических применений благодаря их способности улучшать использование света. В данной работе пористые пленки TiO_2 были получены с использованием полистирольных (PS) частиц диаметром 350 нм в качестве структурообразующих шаблонов, а влияние концентрации PS частиц на генерацию фототока было систематически исследовано. Морфологический и оптический анализы подтвердили успешное формирование пористых структур с улучшенными характеристиками светопоглощения. Оптимизированная плёнка TiO_2, модифицированная полистирольными (PS) частицами, продемонстрировала плотность фототока около 118 мкА/см^2, что соответствует увеличению примерно на 20,5% по сравнению с немодифицированной пленкой TiO_2. Измерения с использованием интегрирующей сферы показали повышение общего поглощения света пористыми пленками, что свидетельствует о том, что улучшение генерации плотности фототока обусловлено более эффективным захватом света в пористой структуре. Данная работа подчеркивает важность управления пористостью и демонстрирует, что структурирование с использованием PS частиц является эффективным подходом для повышения эффективности фотоактивных тонких пленок на основе TiO_2.

Ключевые слова: тонкие пленки TiO_2, полистирольные частицы, управление пористостью, плотность фототока, захват света.