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Composite Catalyst of Reduced Black TiO_{2-x}/CNT: Highly Efficient Counter Electrode for ZnO-Based Dye-Sensitized Solar Cells

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A composite catalyst (reduced black TiO_{2-x}/carbon nanotube) was synthesized through a simple sol-gel method and applied as a counter electrode (CE) in ZnO-based dye-sensitized solar cells (DSSCs). This material demonstrated notable electrocatalytic activity for I₃⁻ reduction, and the resultant DSSCs achieved a PCE of 5.71%.

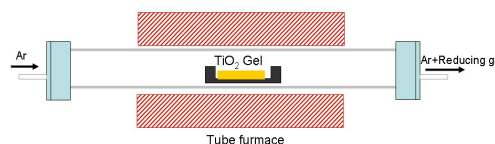
Since the breakthrough achieved by M. Gratzel and his co-workers in 1991,¹ dye-sensitized solar cells (DSSCs), a novel type of photovoltaic device, have received significant research attention as a potential solution to environmental pollution and the energy crisis. Typically, a DSSC comprises a photoanode,²⁻⁶ a counter electrode (CE), and an electrolyte. The CE of a DSSC is usually composed of Pt, which is a rare and expensive element that thus limits the wide and cost-effective application of DSSCs.⁷⁻¹⁷

As photoanode, pure and various doped TiO₂ have been extensively studied because of its abundance, nontoxicity, and stability. In 2010, Feng et al.¹⁸ fabricated reduced TiO₂ by using a facile one-step combustion method and noted that oxygen vacancy extends the photoresponse of TiO₂ from the UV to the visible light region, resulting in a high visible light photocatalytic activity. Reduced black TiO₂ (TiO_{2-x}) with oxygen vacancies (OVs) has been demonstrated to exhibit visible light absorption.¹⁷⁻²⁷ However, as a counter electrode, the study on reduced black TiO₂ has not been reported in the literature.

Black TiO_{2-x} is prepared via several methods, including heating under reducing conditions (e.g., H₂) or vacuum, high-energy particle (electron, laser, or Ar⁺) bombardment, and chemical vapor deposition. In practice, these techniques are limited by a number of factors, such as harsh synthesis conditions, multiple steps, and expensive facilities. Thus, developing an economical and simple method for fabricating a stable, reduced, black TiO₂ electrocatalyst remains a great challenge. Such difficulty is reflected by the limited number of studies that have explored TiO_{2-x} electrocatalytic activity.

In this paper, we report a simple sol-gel method employed to synthesize the reduced black TiO_{2-x}. This reduced material exhibits

extremely high stability and serves as an active CE for ZnO-based DSSCs. To further improve the PCEs of ZnO-based DSSCs, a composite catalyst comprising TiO_{2-x} with notable electrocatalytic activity and carbon nanotubes (CNTs) with excellent hole-transporting property was fabricated and successfully applied as CE. We expect this composite catalyst to exhibit good electrocatalytic activity in the reduction of I₃⁻ to I⁻. The resulting DSSCs with this composite catalyst as CE achieved a high PCE of 5.71%, which is close to the value achieved by a traditional Pt CE.



Scheme 1 Schematic formation of black TiO_{2-x} with oxygen vacancy.

TiO_{2-x} was prepared according to Scheme 1. First, 1 g carbamide and 14 mL tetrabutyl titanate were dissolved in 20 mL ethanol to prepare solution A. Then, 1 mL hydrochloric acid and 5 mL deionized water were combined with 10 mL ethanol to produce solution B. At room temperature, solution B was added to solution A. After the TiO₂ sol was obtained completely, the product was dried in an oven at 80 °C for 5 h. The resulting TiO₂ gel was sintered at 500 °C in an Ar atmosphere for 5 h. Thereafter, black powders (sample) were obtained. During the combustion, the TiO₂ gel decomposed and consequently released CO, CO₂, NO, NO₂, and other products. Ti(IV) could be reduced to Ti(III) by the reducing gases (CO and NO) to obtain the reduced TiO₂ (TiO_{2-x}). By adding CNTs to solution A, we obtained a TiO_{2-x}/CNT composite material after direct sintering under the same conditions. For comparison, TiO₂ was prepared via sintering at 500 °C in ambient air. As-synthesized powders were dispersed in isopropanol. Then, the obtained suspension was sprayed on an FTO glass (0.8 cm × 10 cm). The resulting films were sintered in an Ar atmosphere at 500 °C for 2 h, thereby producing TiO₂-CE, TiO_{2-x}-CE, TiO_{2-x}/CNT-CE, and CNT-CE. The Pt electrode on the FTO glass was fabricated via thermal decomposition. On the basis of the methods presented in published articles, ZnO paste with a 60 nm particle size was prepared through

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a solid-state reaction. The doctor blade technique was used to fabricate ZnO photoanode films.^{4, 5, 28} The photoanode films were heated at 250 °C for 120 min. and then sensitized with 0.5 mM N719 in absolute ethanol solution at 45 °C for 120 min.

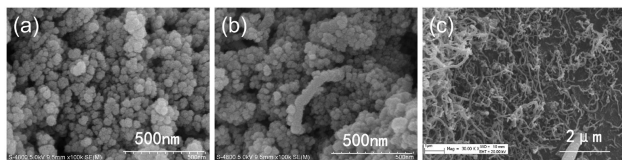


Fig. 1 SEM images of (a) TiO_{2-x}, (b) TiO_{2-x}/CNT composite, and (c) CNT.

The scanning electron microscopy (SEM) image in Fig. 1 shows the morphologies of black TiO_{2-x}, TiO_{2-x}/CNT, and CNT. As indicated by the results, TiO_{2-x} can be well composited with CNT through our synthetic approach.

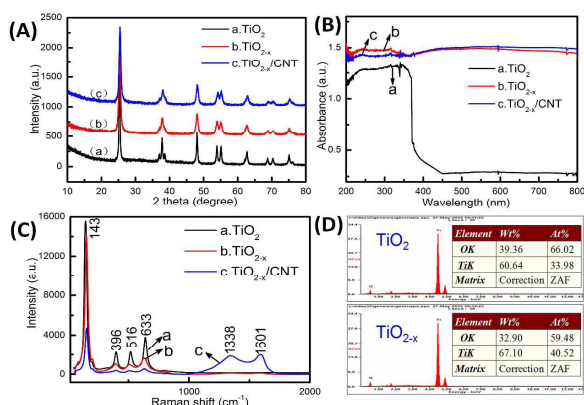


Fig. 2 (A) XRD patterns, (B) UV-vis absorption spectra, and (C) Raman spectrogram of TiO₂, TiO_{2-x} and TiO_{2-x}/CNT; (D) EDS of TiO₂ and TiO_{2-x}.

The X-ray diffraction (XRD) patterns of the three samples (Fig. 2A) indicate that the TiO₂ and TiO_{2-x} are anatase and well crystallized because all the peaks coincided well with JCPDS:21-1272. The UV-vis absorption spectroscopy of the three samples (Fig. 2B) suggests that the OV extended the photoresponse of TiO₂ from the UV to the visible light region. The presence of OV was confirmed with Raman spectroscopy and Energy-dispersive spectrometry (EDS), as shown in Figs. 2C and 2D. Fig. 2C shows Raman spectrogram of TiO₂, TiO_{2-x} and TiO_{2-x}/CNT. Peak of Raman shifting between 100 and 1000 cm⁻¹ indicates the Ti-O bond numbers of TiO₂ is more than that of TiO_{2-x}. Which is consistent with the results of EDS in Fig. 2D. As indicated by the results, TiO_{2-x} with OVs can be well fabricated, which means the OVs extend the photoresponse of TiO₂. OVs are preferential adsorption sites for iodine molecules and demonstrate notable electrocatalytic activity for I₃⁻ reduction.

Fig. 3A shows the J-V curves of the DSSCs based on TiO₂, TiO_{2-x}, TiO_{2-x}/CNT, CNT, and Pt at 1 sun (AM 1.5 G, 100 mW cm⁻²) illumination. The photovoltaic parameters derived from the J-V curves are summarized in Table 1. The DSSCs based on black TiO_{2-x}/CNT achieved a PCE of 5.71%, which is near the value achieved by DSSCs based on Pt (6.07%). The increased J_{sc} and FF should be responsible for the OVs and CNT.

Table 1 Photovoltaic parameters of DSSCs and EIS parameters fabricated with two identical TiO₂, TiO_{2-x}, TiO_{2-x}/CNT, CNT and Pt electrodes.

CE	V _{oc} [V]	J _{sc} [mA/cm ²]	FF [%]	Eff [%]	R _s [Ω]	R _{ct} [Ω]	Z _N [Ω]
TiO ₂	0.42	2.42	5	0.05	235.32	13574.24	16132.88
TiO _{2-x}	0.69	12.45	40	3.43	32.47	12.23	19.84
TiO _{2-x} /CNT	0.70	12.36	66	5.71	8.91	4.84	5.26
CNT	0.63	8.61	53	2.87	4.51	9.73	50.68
Pt	0.68	13.12	68	6.07	3.01	0.75	0.55

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Tafel polarization are common electrochemical methods that are used to determine the inherent relationship between performance and material type in DSSCs. Fig. 3B presents the cyclic voltammograms of the I⁻/I₃⁻ redox couple based on TiO₂, TiO_{2-x}, CNT, TiO_{2-x}/CNT, and Pt. All of the curves exhibited redox peaks, except for those of the I⁻/I₃⁻ redox couple based on CNT and TiO₂. The left redox peak can be assigned to the reaction shown in Equation (1) as follows:



This study focused on the first reaction because such reaction evidently occurs in DSSCs under actual working conditions. The CV curves for TiO₂ and CNT (Fig. 2B) did not show any redox peak between -0.2 and 0.9 V, thus indicating the extremely low catalytic activity in these cases. However, the catalysis of TiO_{2-x} and TiO_{2-x}/CNT in this system was remarkable, as illustrated in Fig. 3B. Hence, TiO_{2-x}/CNT can be a suitable alternative to the expensive Pt as a catalytic material for the CEs of DSSCs. In addition, the value of peak to peak separation (E_{pp}) is negatively correlated with the standard electrochemical rate constant of a redox reaction, which is an important parameter for comparing the catalytic activities of different CEs. The E_{pp} value for TiO_{2-x}/CNT (298 mV) is smaller than that for TiO_{2-x} (324 mV), CNT (542 mV) and similar to sputtered Pt (286 mV), further confirming that TiO_{2-x}/CNT is a superior catalyst for the reduction of I₃⁻ to I⁻. Therefore, TiO_{2-x}/CNT is expected to be an alternative to expensive Pt in DSSCs as a promising catalytic material for CEs.

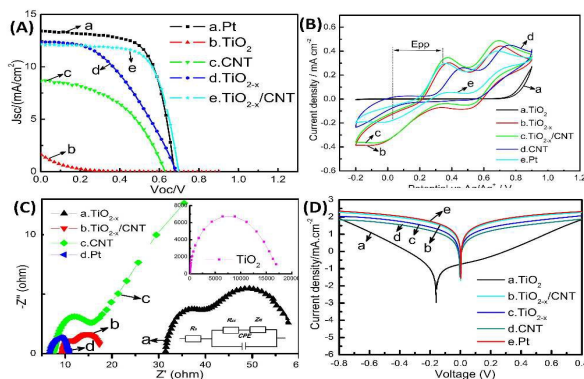


Fig. 3 (A) Photocurrent-voltage (J-V) curves of the DSSCs based on TiO₂, TiO_{2-x}, TiO_{2-x}/CNT, CNT and Pt, (B) CVs of the I⁻/I₃⁻ redox couple, (C) Nyquist plots of EIS for the symmetrical cell, CE/electrolyte/CE, and (D) Tafel polarization curves of symmetrical cells.

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EIS measurements were obtained to further reveal the electrochemical behavior within the system of the CE and electrolyte employed in the symmetrical cells constructed using two identical CEs (CE/electrolyte/CE). Fig. 3C shows the Nyquist plots. Typically, two semicircles indicate the charge-transfer resistance (R_{ct}) at the CE/electrolyte interface (left semicircle) and the Nernst diffusion impedance (Z_N) of the redox couple in the electrolyte (right semicircle). The fitting data are summarized in Table 1. In good accordance with the CV test results, the EIS results revealed that $\text{TiO}_{2-x}/\text{CNT}$ was more effective than TiO_{2-x} and CNT in reducing I_3^- . The differences in R_s , R_{ct} , and Z_N led to the varied efficiencies of the DSSCs based on the three CEs.

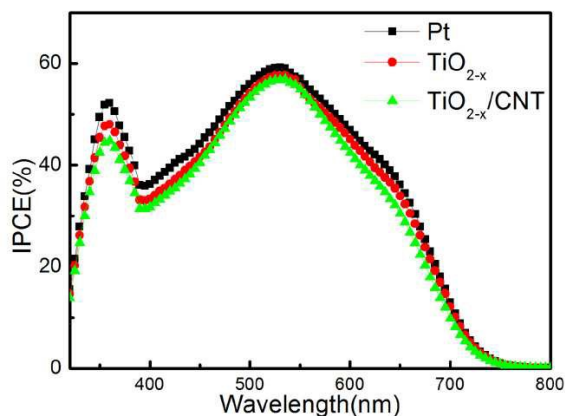


Fig. 4 IPCE spectra of DSSCs based on TiO_{2-x} , $\text{TiO}_{2-x}/\text{CNT}$ and Pt.

Fig. 3D shows the Tafel polarization curves. These curves display the logarithmic current density ($\log J$) as a function of voltage. Theoretically, the Tafel curve can be divided into three zones. The low-potential curve ($|U| \leq 120$ mV) corresponds to the polarization zone. The zone in the middle-potential range is produced by charge transfer and is called the Tafel zone. The high-potential curve ($|U| > 120$ mV) is designated as the diffusion zone. By comparing the curves for TiO_2 , TiO_{2-x} and CNT, we noted that the $\text{TiO}_{2-x}/\text{CNT}$ curve showed a large exchange current density on the electrode surfaces. This finding implied that $\text{TiO}_{2-x}/\text{CNT}$ achieved high catalytic activity similar to Pt. The exchange current density (J_0) can be expressed using Equation (2), where R , T , n , and F are constants. R_{ct} could be obtained from the EIS measurements. J_0 varied inversely with R_{ct} . The diffusion current density (J_{lim}) was determined with the diffusion of the redox couple in the electrolyte. In the diffusion zone, $\text{TiO}_{2-x}/\text{CNT}$ and Pt showed higher J_{lim} values than TiO_2 , TiO_{2-x} and CNT, as demonstrated in Equation (3). A large diffusion coefficient D was obtained, thus proving that $\text{TiO}_{2-x}/\text{CNT}$ held a large diffusion velocity for the redox couple in the electrolyte.

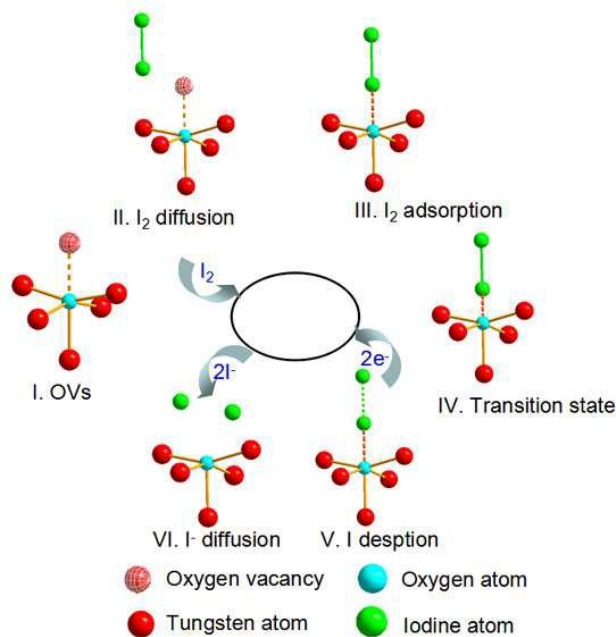
$$J_0 = RT/nFR_{ct} \quad (2)$$

$$J_{lim} = 2ne_0DcN_A/l \quad (3)$$

where N_A is the Avogadro constant; l is the spacer thickness; and D , n , e , and c are usual meanings.

The IPCE spectra of DSSCs are collected in Fig. 4. The IPCE of the N719-sensitized cells are maximized at around 530 nm.³² The

$\text{TiO}_{2-x}/\text{CNT}$ CE and TiO_{2-x} CE based DSSCs exhibit similar IPCE to the cell with a Pt CE between 350 and 650 nm, which is in good agreement with the difference of J_{sc} values.



Scheme 2 Schematic mechanism of oxygen vacancies as an important catalytic site for electrocatalysis.

In this work, the long-term stability of the DSSCs using $\text{TiO}_{2-x}/\text{CNT}$ CE under light was checked. After half a year, Voc, Jsc, FF, and PCE retained 90.2%, 94.2%, 87.8%, and 82.7% of their highest values, respectively. The result shows that $\text{TiO}_{2-x}/\text{CNT}$ is a stable CE catalyst in the iodide electrolyte.

All the electrocatalytic results revealed that the activity of the iodide reduction reaction was notably dependent on the OVs of the titanium oxide catalyst, which serve as important catalytic site descriptors. The mechanism comprises six important steps, as shown in Scheme 2. The diffusion of an iodine molecule is typically rapid and in equilibrium. As for the iodine reduction reaction, the exact mechanism is unclear. Previous studies have shown that the iodine molecule is preferentially adsorbed in the presence of metal atoms in an inorganic complex instead of in the presence of nonmetallic atoms.^{17, 29-31} Thus, iodine molecules should be on top of Ti atoms. OVs are preferential adsorption sites for iodine molecules. Upon adsorption on Ti atoms, the iodine molecule can readily dissociate into two iodine atoms.

Conclusions

The OVs of TiO_{2-x} extended the photoresponse of TiO_2 from the UV to the visible light region and showed the catalytic activity for I_3^- reduction. And the composite material $\text{TiO}_{2-x}/\text{CNT}$ can be used as an effective alternative to the traditional Pt. The composite material showed a suitable morphology and good catalytic performance for I_3^- reduction. A high PCE of 5.71% was successfully achieved by the $\text{TiO}_{2-x}/\text{CNT}$ CE. This value is superior to that achieved by pure CNT (2.87%) and pure TiO_{2-x} (3.43%). The composite material in this

work shows great promise as an alternative to the rare and expensive Pt. Its use could lead to the development of highly efficient yet cost-effective DSSCs.

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