Composites of Vanadium (III) Oxide (V$_2$O$_3$) Incorporating with Amorphous C as Pt-Free Counter Electrodes for Low-Cost and High-Performance Dye-Sensitized Solar Cells

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ABSTRACT: To replace precious Pt-based counter electrodes (CEs) with a low-cost Pt-free catalyst of CEs is still a motivating hotspot to decrease the fabrication cost of dye-sensitized solar cells (DSSCs). Herein, four different V$_2$O$_3$@C composite catalysts were synthesized by pyrolysis of a precursor under N$_2$ flow at 1100 °C and further served as catalytic materials of CEs for the encapsulation of DSSCs. The precursors of V$_2$O$_3$@C composites have been prepared via a sol–gel method using different proportions of V$_2$O$_3$ with soluble starch in a H$_2$O$_2$ solution. Power conversion efficiencies (PCEs) of 3.59, 4.79, 5.15, and 5.06% were obtained from different V$_2$O$_3$@C composites, with soluble starch-to-V$_2$O$_5$ mass ratios (S/V) of 1:2, 1:1, 2:1, and 4:1, respectively, as CEs to reduce iodide/triiodide in DSSCs. The improvement of electrode performance is due to the combined effects on the increased specific surface area and the enhanced conductivity of V$_2$O$_3$@C composite catalysts.

1. INTRODUCTION

Solar energy, a kind of renewable energy source, is rich in reserves, clean, and environmentally friendly. It is rarely limited by the geographical scope. However, it is also easily affected by natural factors such as season, climate, day and night, altitude, and so on and has intermittent and unstable characteristics. To overcome the above problems, dye-sensitized solar cells (DSSCs) had already been applied to store solar energy through the direct conversion of photoelectrons. The optimization of each component compounds, have been extended as CE materials to replace the high-cost Pt. These materials as CEs in DSSCs have many advantages of abundance, low cost, easy synthesis, and high stability with large electrochemical activity for the regeneration reactions of I$_3^−$/I$^−$.

Among the above catalytic materials of CEs, transition-metal oxides (TMOs) of group VB and VIB, as one of the TMCs, are widely applied to the novel Pt-free CEs due to a similar d-band electron density to that of Pt. In VB group oxides of TMOs, V element of V-based oxides could be diverse in the valence state between V$^{2+}$ and V$^{5+}$, and it exists in various forms from VO$_{2n-1}$ to VO$_{2n+1}$. The extensive interest in V-based oxides as catalysts in various electrochemical devices (batteries, supercapacitors, etc.) is because of their unmatched structural types, multiphase states, and easy modification. As shown in our previous work, V$_2$O$_3$-based CEs had been successfully prepared using VOCl$_3$ as metal precursors with the urea metal route. The DSSCs using V$_2$O$_3$/CEs showed a decent PCE value of 5.40%. Vijayakumar et al. also reported that V$_2$O$_3$ nanofiber CEs yielded an efficiency of 5.0%. To further improve the performance and reduce the costs of DSSCs, researchers have focused on producing single V$_2$O$_3$ catalysts...
better by incorporating with carbon or carbon-derived materials because of the outstanding conductivity, controllable specific surface, and low-cost fabrication of carbonaceous materials. Additional carbonaceous materials as a basic carrier could change the energy band structure and distort the lattice, which result in high-energy activation to improve the electrical conductivity and provide more reaction sites in V-based oxides. Also, in our work, V₂O₃@AC composite catalysts have been fabricated by the pyrolysis of NH₄VO₃ with different mass ratios of activated carbon (AC) at high temperatures. Compared with the 4.54% PCE of Pt and 3.33% of pure V₂O₃, the DSSCs using V₂O₃@AC composite can reach the highest PCE of 5.55% for the regeneration of the I³⁻/I⁻ redox couple. Gnanasekar et al. wrapped monoclinic crystal VO₂ on one-dimensional carbon as a cost-effective CE and achieved a PCE of 6.53%. As a result, it is significant to explore a stabler, cheaper, and simpler assembly and higher activity to improve the performance of Pt-free CEs in DSSCs. Herein, different proportions of V₂O₃@AC composite catalysts were synthesized via pyrolysis of a precursor under N₂ flow by a solid-state reaction at high temperatures. The precursors were obtained by a sol–gel method with soluble starch (denoted as S) as a carbon source and V₂O₅ (denoted as V) as a metal source in H₂O₂. Soluble starch is a kind of common natural biomass material, which has a large specific surface area and shows flammability and network cross-linking; therefore, it is suitable to be used as a carbon source of composite catalysts. The introduction of soluble starch into the precursor can reduce the sintering temperature, accelerate the diffusion rate, and even impel grain growth, which makes it easier to control and optimize the composition and structure of V-based oxides. In this work, four proportions of V₂O₃@AC composites with specific composition, structure, morphology, and properties were obtained by guided pyrolysis from different mass ratios (S/V) of 1:2, 1:1, 2:1, and 4:1. The structural characterization of V₂O₃@AC composites (S/V) was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and N₂ adsorption/desorption analysis, and the corresponding electrochemical performance and basic parameters were determined by different electrochemical testing techniques.

2. RESULTS AND DISCUSSION

2.1. Material Characterization. Figure 1 presents the details of diffraction angles of four V₂O₃@C (S/V) and the pure V₂O₃ at 32.9, 36.2, 37.8, 41.1, 43.6, 49.8, 54.0, 58.2, 63.6, 65.1, 71.0, 76.2, 78.3, 80.5, 82.0, and 86.21°, which can be indexed to the crystal facets of the pristine V₂O₃ in (104), (110), (006), (113), (202), (024), (116), (214), (300), (101), (220), (306), (223), (312), and (134), respectively. The XRD peaks of V₂O₃@C (S/V = 1:2, 1:1) were similar to those of pure V₂O₃. With the increase in the proportion of soluble starch in the precursor, the prepared V₂O₃@C (S/V = 2:1, 4:1) showed an additional wide and weak pattern at around 24.9°, which is caused by the (002) facet diffraction of amorphous C, and further demonstrated noncrystalline C incorporating with V₂O₃ as a carrier by soluble starch carbonized at high temperatures without affecting the diffraction patterns of V₂O₃. The strong diffraction patterns of V₂O₃ in the composites almost cover the broad and low diffraction patterns of amorphous C due to the highly ordered crystal structure of V₂O₃ in the composites.

The morphologies of four V₂O₃@C (S/V) and the as-prepared pure V₂O₃ were observed in Figure 2. The special characterization of pure V₂O₃ particles belongs to a solid block material with compact apparent density and less pores in Figure 2e. The shape of pure V₂O₃ was an irregular sphere with particle size in the range of 100–500 nm. The nanostructures of V₂O₃@C (1:2 and 1:1) all presented that the particle shapes were sphere, potato, ellipsoids, etc., with the particle size distribution in a relatively narrow range of 50–150 nm. Also, SEM results show that there is no excess amorphous C on the surface of V₂O₃@C (1:2:1:1), as in Figure 2a,b, indicating that the soluble starch almost completely reacts with V₂O₃ to form V₂O₃ in the precursor. With further increase in the soluble starch mass ratio, V₂O₃@C (2:1, 4:1) obviously composed of two different components, including V₂O₃ and amorphous C, as observed from Figure 2c,d. The smaller floucculate C fills the gaps among V₂O₃ particles with uniform distribution in the analysis of SEM, that is, embodiment of amorphous substances. In particular, the V₂O₃ morphologies in V₂O₃@C (2:1) show low apparent density and open structure as nanoscale jars with a diameter of 50–100 nm and a wall thickness of about 15 nm, as shown in Figure 2c. The surface of V₂O₃@C (2:1) has several uniformly distributed open nanojars that would improve the effective surface area of the material particles, increase the number of catalytic sites, and greatly promote the electrocatalytic performance of CEs. Simultaneously, there is moderate dual connectivity that consists of uninterrupted nanoparticles and interconnected pore channels in V₂O₃@C (2:1), which should be an alternative Pt material with high effective catalytic activity as CEs. However, the excess carbonization of soluble starch in V₂O₃@C (4:1) results in that most of the surface of V₂O₃ was covered by smaller floucculate C particles (Figure 2d). The higher the amount of soluble starch, the smaller the V₂O₃ particle size, and the particle morphology becomes more and more spherical, which shows the isotropic growth with a narrower average particle size of <10 nm. This determination of morphology coincides with amorphous carbon in the V₂O₃@C composites by X-ray diffraction results. Energy-dispersive X-ray (EDX) analysis was further carried out to confirm the elements V, O, and C within V₂O₃@C (2:1), as in Figure 2f. EDX patterns of other CE composite materials showed similar results, but only the content of the elements was different.

The N₂ adsorption–desorption isotherms of V₂O₃@C (S/V) all exhibited narrow loops complying with a type-IV isotherm that indicate that four V₂O₃@C materials are mesoporous, and the pure V₂O₃ can be identified by an
unapparent hysteresis loop belonging to a type-I characteristic of isotherms, as shown in Figure 3. With the increase in the soluble starch mass ratio, the hysteresis loop integral areas of V$_2$O$_3$@C composites gradually increase. Table 1 shows that the $S_{BET}$ values of S/V = 4:1 (350.2 m$^2$/g) and 2:1 (181.7 m$^2$/g) are higher than those of 1:1 (85.1 m$^2$/g), 1:2 (45.5 m$^2$/g), and V$_2$O$_3$ (33.5 m$^2$/g); the $V_p$ values follow an increasing order: 0.171 (2:1) > 0.116 (4:1) > 0.115 (1:1) > 0.040 (1:2) > 0.031 cm$^3$/g (V$_2$O$_3$); the $d_p$ values of 3.368, 3.782, 3.798, 3.795, and 3.361 nm were obtained from S/V = 1:2, 1:1, 2:1, 4:1, and pure V$_2$O$_3$, respectively. These data indicate that the pure V$_2$O$_3$ was a solid bulk material with a lower $V_p$ and a very

Figure 2. (a−d) SEM images of V$_2$O$_3$@C with S/V = 1:2, 1:1, 2:1, 4:1 and (e) pure V$_2$O$_3$. (f) EDX pattern (2:1).

Figure 3. (a) N$_2$ adsorption−desorption isotherms and (b) $d_p$ of V$_2$O$_3$@C (S/V) and pure V$_2$O$_3$. 
Table 1. Textural Properties of V$_2$O$_3$@C (S/V) and Pure V$_2$O$_3$

| materials          | $S_{\text{BET}}$ (m$^2$/g) | $V_p$ (cm$^3$/g) | $d_p$ (nm) |
|--------------------|-----------------------------|------------------|------------|
| S/V = 1:2          | 45.5                        | 0.040            | 3.368      |
| S/V = 1:1          | 85.1                        | 0.115            | 3.782      |
| S/V = 2:1          | 181.7                       | 0.171            | 3.798      |
| S/V = 4:1          | 350.2                       | 0.116            | 3.795      |
| V$_2$O$_3$         | 33.5                        | 0.031            | 3.361      |

![Figure 4](image-url)  
*Figure 4. CV profile of V$_2$O$_3$@C (S/V) and Pt CEs.*

small $S_{\text{BET}}$, and the amorphous C incorporated with V$_2$O$_3$ could offer a larger $V_p$ value for I$_3^-$/I$^-$/I$^-$ diffusion and more active edge sites for the regeneration of I$_3^-$/I$^-$/I$^-$.

Because too much amorphous C covers the surface of the material, $V_p$ and $d_p$ of V$_2$O$_3$@C (4:1) were smaller than those of V$_2$O$_3$@C (2:1). The porous structure of four V$_2$O$_3$@C composites is (S/V) also in good agreement with the SEM (Figure 2) results.

2.2. Electrochemical Properties of Electrodes. The redox reaction of I$_3^- + 2e^- \rightarrow 3I^-$ occurs on the interface between CEs and the electrolyte to recycle and regenerate the I$_3^-$/I$^-$/I$^+$ pairs of DSSCs at a low potential.

Two key parameters $\Delta E_p$ (peak-to-peak separation) and $I_p$ (current density of cathodic peak) can be determined from the CV profile to evaluate the electrocatalytic activity of the electrode. Figure 4 shows $\Delta E_p$ values of 0.150 (1:2), 0.205 (1:1), 0.202 (2:1), and 0.229V (4:1) and $I_p$ values of 1.092 (1:2), 1.238 (1:1), 1.724 (2:1), and 1.636 (4:1) in V$_2$O$_3$@C (S/V) CEs. The smaller the $\Delta E_p$ value, the larger the electrocatalytic ability and reversibility of the I$_3^-$/I$^-$ regeneration reactions, which would be beneficial to the enhancement of DSSC performance.

In theory, $\Delta E_p \propto 1/k_f$, where $k_f$ is the rate constant of electrochemical reaction. Thus, smaller $\Delta E_p$ values indicate that the reaction of I$_3^- + 2e^- \rightarrow 3I^-$ can be carried out at a rapid rate on CEs. The larger $I_p$ can also demonstrate the catalytic material on CEs to more effectively catalyze the reduction of I$_3^-$ to I$^-$. Comparing the $\Delta E_p$ and $I_p$ values of four kinds of V$_2$O$_3$@C (S/V) with Pt, the corresponding values of V$_2$O$_3$@C (2:1 and 4:1) are better than those of Pt CEs (0.151V, 0.534 mA/cm$^2$). Therein, in the V$_2$O$_3$@C composite (2:1), the open nanojar V$_2$O$_3$ incorporated with amorphous C and activated by high temperature and N-doping provided suitable dual connectivity and more vacancies and defects, which result in lower $\Delta E_p$ and higher $I_p$ values.

The V$_2$O$_3$@C composite (2:1) as a Pt-free efficient CE would be favorable to enhance the electrocatalytic activity in DSSCs. For the expected catalyst, it is important to evaluate the long-term stability of the catalytic property. Herein, the V$_2$O$_3$@C (2:1) material as a CE catalyst was assessed by 30 consecutive CV cycles. There are minor $I_p$ attenuation and little redox peak position shift of I$_3^- + 2e^- \rightarrow 3I^-$, which demonstrate that V$_2$O$_3$@C CEs possess stability as well as increased catalytic activity against I$_3^-$/I$^-$ redox couples.

The characteristic electrochemical impedance spectroscopy (EIS) parameter values of $R_{\text{ct}}$ (charge transfer resistance), $R_s$ (solution resistance), and $Z_w$ (Warburg impedance) were collected from the Nyquist plots of the symmetric cells with different V$_2$O$_3$@C (S/V) and Pt CEs in Figure 5. The increasing order of value of $R_{\text{ct}}$ is 28.81 Ω (1:2) > 14.8 Ω (Pt) > 10.72 Ω (1:1) > 7.10 Ω (4:1) > 6.08 Ω (2:1). $R_s$ values of 41.71, 45.82, 46.38, 48.01, and 37.66 Ω and $Z_w$ values of 0.064, 0.050, 0.114, 0.103, and 0.126 Ω were obtained from S/V = 1:2, 1:1, 2:1, 4:1, and Pt CEs, respectively. The $R_{\text{ct}}$ values of V$_2$O$_3$@C (4:1, 2:1) are much smaller than those of other V$_2$O$_3$@C (S/V) and Pt. In the preparation process of CE composite catalyst materials, the carbonization of soluble starch with cross-linking and natural adhesion can result in the improvement of the dispersion uniformity of flocculate amorphous C in the precursor. Hence, V$_2$O$_3$ incorporating with amorphous C can very meaningfully provide that the continuous conductive layers in between the interface of V$_2$O$_3$@C composites transfer electrons and the interconnective pore channels permeate and diffuse I$_3^-$/I$^-$ electric pairs in the electrolyte.

Furthermore, the Warburg impedance ($Z_w$) of V$_2$O$_3$@C (S/V) shows a similar 45° straight line, indicating that the reaction of I$_3^- + 2e^- \rightarrow 3I^-$ indicates the charge transfer process rather than the mass transport process.

The exchange current density ($j_0$) of Tafel polarization was determined as four different V$_2$O$_3$@C (S/V) and Pt CEs in the reduction of I$_3^- + 2e^- \rightarrow 3I^-$, as shown in Figure 6. A larger $j_0$
value means that a small applied potential results in an appreciable increase in current. Tafel polarization results show \( J_\text{d} \) values of four different \( \text{V}_2\text{O}_3@\text{C} \) and Pt CEs in the following order: 2:1 (0.669 mA/cm\(^2\)) > 4:1 (0.529 mA/cm\(^2\)) > Pt (0.501 mA/cm\(^2\)) > 1:1 (0.482 mA/cm\(^2\)) > 1:2 (0.294 mA/cm\(^2\)). Particularly, \( \text{V}_2\text{O}_3@\text{C} \) (2:1) CEs show the largest slope of extrapolated straight lines in the Tafel zone of anodic and cathodic branches, which revealed the largest \( J_\text{d} \) compared to other \( \text{V}_2\text{O}_3@\text{C} \) (S/V) and Pt CEs. The Tafel polarization results indicate that \( \text{V}_2\text{O}_3@\text{C} \) composites (2:1, 4:1) possess a lower polarization potential and a quicker charge exchange rate on the interface between \( \text{I}_3^- \) and \( \text{V}_2\text{O}_3@\text{C} \) than that of Pt CEs in DSSCs. In conclusion, the excellent performance of \( \text{V}_2\text{O}_3@\text{C} \) composites (2:1) CEs can be attributed to the moderate dual connectivity with continuous nanoparticles and interconnected pore channels compared to other CEs.

### 2.3. Application of \( \text{V}_2\text{O}_3@\text{C} \) Composites in DSSCs

To make a direct comparison of performance with different \( \text{V}_2\text{O}_3@\text{C} \) (S/V) and Pt CEs in encapsulated DSSCs, the \( J-V \) (photocurrent—photovoltaic) curves were characterized under \( I = 100 \text{ mW/cm}^2 \) of a solar simulator (Figure 7). Four different \( \text{V}_2\text{O}_3@\text{C} \) CEs presented \( V_{\text{oc}} \) (open-circuit voltage) values of 665, 736, 738, and 747 mV, \( J_{\text{sc}} \) (short-circuit current density) values of 7.88, 10.31, 11.31, and 10.56 mA/cm\(^2\), fill factor (FF) values of 0.62, 0.63, 0.62, and 0.64, and PCE values of 3.59, 4.79, 5.15, and 5.06, which were, respectively, obtained from S/V = 1:2, 1:1, 2:1, and 4:1, as shown in Table 2. Because of the same dye-sensitized commercial \( \text{TiO}_2 \) photoanode used in the process of assembling DSSC devices, the performances of DSSCs only depend on the electrocatalytic reduction of redox couples at CEs, and different CEs also affect the photocurrent generation at the photoanode through dye regeneration. Under the encapsulation of DSSC in the same way, the \( J_{\text{sc}} \) value of \( \text{V}_2\text{O}_3@\text{C} \) (2:1) is the largest and the four FF values are close to 0.63 ± 0.01. The enhanced \( J_{\text{sc}} \) value of \( \text{V}_2\text{O}_3@\text{C} \) (2:1) can be attributed to its open nanoscale jar morphology with the larger number of catalytic activity sites, continuity channel, and low \( R_{\text{ct}} \). \( V_{\text{oc}} \) is the difference between the Fermi level of the semiconducting material and the potential energy level of the redox potential in the liquid electrolyte. It should be noted that the \( V_{\text{oc}} \) values of \( \text{V}_2\text{O}_3@\text{C} \) (S/V) have a little enhancement with the increase in amorphous C. The variation of \( V_{\text{oc}} \) in the different CEs for DSSCs can be influenced by the surface area of CEs. Despite the exposed geometric area of all \( \text{V}_2\text{O}_3@\text{C} \) composite CEs being 0.5 cm × 0.5 cm, the actual electrochemical active area is different due to the existence of amorphous C in different proportions. The highest value of \( V_{\text{oc}} \) for \( \text{V}_2\text{O}_3@\text{C} \) composite (4:1) CE may be attributed to its much rougher surface with the maximum \( S_{\text{SET}} \) compared to other CEs. FF is the ratio of the maximum power of DSSCs to the product of \( V_{\text{oc}} \) and \( J_{\text{sc}} \). In the \( J-V \) curve of DSSCs, the more rectangular the output characteristics representing the level of PCE, the higher the FF. The FF value is closely related to the concentration gradients in DSSCs. It can be seen that the PCEs of \( \text{V}_2\text{O}_3@\text{C} \) (1:1, 2:1, and 4:1) CEs are higher than 4.54% of Pt CEs (\( J_{\text{sc}} = 11.63 \text{ mA/cm}^2 \), \( V_{\text{oc}} = 779 \text{ mV} \), and FF = 0.50). Although \( \text{V}_2\text{O}_3@\text{C} \) (2:1) CE has a lower \( V_{\text{oc}} \) than \( \text{V}_2\text{O}_3@\text{C} \) (4:1), its overall efficiency is higher than that of \( \text{V}_2\text{O}_3@\text{C} \) (4:1) due to various combined factors. Therein, \( \text{V}_2\text{O}_3@\text{C} \) (2:1) CEs yielded the highest PCE (5.15%) in DSSCs. The remarkably enhanced \( J_{\text{sc}} \) value of \( \text{V}_2\text{O}_3@\text{C} \) (2:1) may have a great contribution to the highest PCE of \( \text{V}_2\text{O}_3@\text{C} \) (2:1) as CEs. With the change of mass ratio (S/V) from 1:2 to 2:1, the PCE of the \( \text{V}_2\text{O}_3@\text{C} \) composites (S/V) gradually increases. However, on further increasing the S/V from 2:1 to 4:1, the PCE of \( \text{V}_2\text{O}_3@\text{C} \) (2:1) was lower than that of \( \text{V}_2\text{O}_3@\text{C} \) (4:1). The possible reason is that too much amorphous C in the \( \text{V}_2\text{O}_3@\text{C} \) (4:1) could lead to the decrease of the electron transfer rate in theuffy materials, and the \( \text{O}_3^- \) in the electrolyte could show a dark current between the photogenerated electrons and dye holes as well as \( \text{V}_2\text{O}_3@\text{C} \) (4:1) CEs with lower \( J_{\text{sc}} \) values. The dark \( J-V \) curves revealed that DSSCs using \( \text{V}_2\text{O}_3@\text{C} \) (2:1) CEs present much lower dark current than those of DSSCs using other CEs, as in Figure 7b. That is to say, different degrees of current leakage occurred in DSSCs using \( \text{V}_2\text{O}_3@\text{C} \) composites. This result not only alludes to the excellent electrocatalytic activity of \( \text{V}_2\text{O}_3@\text{C} \) composite catalysts by \( \text{V}_2\text{O}_3 \) incorporating an appropriate amount of amorphous C.

![Figure 7](https://doi.org/10.1021/acsomega.0c05880) **Figure 7.** \( J-V \) characteristics of DSSC assembled with various CEs: (a) \( I = 100 \text{ mW/cm}^2 \) and (b) in the dark.

| CEs     | \( V_{\text{oc}} \) (mV) | \( J_{\text{sc}} \) (mA/cm\(^2\)) | FF  | PCE (%) |
|---------|--------------------------|-------------------------------|-----|---------|
| S/V = 1:2 | 665                      | 7.88                          | 0.62| 3.59    |
| S/V = 1:1 | 736                      | 10.31                         | 0.63| 4.79    |
| S/V = 2:1 | 738                      | 11.31                         | 0.62| 5.15    |
| S/V = 4:1 | 747                      | 10.56                         | 0.64| 5.06    |
| Pt       | 779                      | 11.63                         | 0.50| 4.54    |
respectively, obtained PCEs of 4.79, 5.15, and 5.06% from composite (S/V) CEs with S/V = 1:1, 2:1, and 4:1, and 3.33% for Pt and pure V2O3 CEs, respectively, for the vanadate (NH4VO3, purity >99%) were purchased from Shanghai Reagent Factory. The soluble starch and ammonium conductivity and catalysis. The DSSCs using V2O3@C composites can cause various volume defects, enhance the surface energy and adsorption, shorten the time of electron and hole migration to the particle surface, and improve the mechanical stability. The excellent stability of V2O3@C composite CEs as their intrinsic features makes them more suitable as Pt-free materials for low-cost and long-term-stable DSSCs.

3. CONCLUSIONS

In various syntheses of V-based oxides, the choice of reactants and reaction process will directly affect the difference in the material properties. Thus, in this work, eco-friendly soluble starch was carbonized to amorphous C at high temperatures; the amorphous C incorporating with V2O3 to prepare V2O3@C composites can cause various volume defects, enhance the surface energy and adsorption, shorten the time of electron and hole migration to the particle surface, and improve the conductivity and catalysis. The DSSCs using V2O3@C composite (S/V) CEs with S/V = 1:1, 2:1, and 4:1, respectively, obtained PCEs of 4.79, 5.15, and 5.06% from J−V measurements, which were higher than the PCEs of 4.54% and 3.33% for Pt and pure V2O3 CEs, respectively, for the regeneration of I3−/I− redox couple. The corresponding electrochemical performance and basic parameters were determined by CV, EIS, Tafel, and J−V characterizations revealing that V2O3@C composite (S/V) CEs can catalyze the regeneration of I3−/I− higher than Pt CEs. Pt-free CEs are expected to be highly efficient and stable in the practical application of DSSCs as well as to expand the range of CE catalyst selection in the future.

4. EXPERIMENTAL SECTION

4.1. Materials. Vanadium pentoxide (V2O5, purity >99%) and hydrogen peroxide (H2O2, 10 wt %) were purchased from Shanghai Reagent Factory. The soluble starch and ammonium vanadate (NH4VO3, purity >99%) were purchased from Aladdin, Shanghai. All chemicals are of analytical reagent (AR) grade and used as received without purification. Deionized water was obtained from an electrothermal distiller and was used in all experiments.

4.2. Synthesis of V2O3@C Composites. V2O3 was directly prepared by the pyrolysis of NH4VO3 under high-purity N2 flow (50 sccm) at 1100 °C for 1 h. The precursor of V2O3@C composites (S/V) was prepared via a sol−gel method. First, 0.4 g of V2O3 was slowly dissolved in 30 mL of 10 wt % H2O2 solution and stirred evenly. With the violent reaction in the solution, a large number of bubbles emerge. After standing for 10 h, 0.2, 0.4, 0.8, and 1.6 g of the soluble starch were, respectively, added into the homogeneous mixed solution with vigorous stirring. The same four solutions were heated from ambient temperature to 80 °C until the soluble starch in each solution was completely dissolved. All of the four solutions gradually became a red flocculent sol with the volatilization of the solvent and finally turned into a dark green gel. After drying in a vacuum oven at 50 °C for 4 h, the as-precursor was milled for 0.5 h and further formed an 11.5 mm diameter and 10 mm thick tablet by a hydraulic tablet-press at 4 MPa. Then, the four proportions of V2O3@C composite (S/V) catalysts were synthesized via pyrolysis of the precursor under N2 flow (50 sccm) at 1100 °C for 1 h.

4.3. Assembly of DSSCs. The assembly of DSSCs is shown in the Supporting Information.

4.4. Characterization and Electrochemical Measurements. The characterization and electrochemical measurements of CEs are shown in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05880.

Assembly of dye-sensitized solar cells (DSSCs) and characterization and electrochemical measurements of counter electrodes (CEs) (PDF)

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