Synthesis of TiO_2/Co_3O_4 Core-Shell Nanowire Array and Study on Photo electrochemical Water Splitting

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Abstract: In order to improve the photo electrochemical (PEC) performance, good light absorption capacity and efficient charge transport capacity are essential. In this paper, in order to increase the responsiveness of TiO2 in the visible-light region, we designed a core-shell heterostructure, we coated Co_3O_4 on the surface of TiO_2 nanowire array (NWAs) that can effectively absorb visible light. The photocurrent density of the TiO_2/Co_3O_4 NWAs reached to 0.94 mA/cm^2, which is 27.1% higher than that of pure TiO2 nanowire array. The carrier concentration of the TiO_2/Co_3O_4 NWAs is 3.8×10^{19} cm^{-3}, which is increased by 324% compared to the pure TiO_2 nanowire array. The result shows that the TiO_2/Co_3O_4 core-shell nanowire array can improve the carrier concentration and carrier transport and separation ability, thereby improving its photo electrochemical performance.

1. Introduction

Although solar energy is clean, non-polluting and sustainable, its intermittent characteristics greatly limit its use as a solar thermal and photoelectric conversion as a means of solar energy utilization. Therefore, it is particularly necessary and urgent to use photo electrochemical decomposition of water to produce hydrogen and convert solar energy into chemical energy storage. At the same time, this method of hydrogen production will also become one of the necessary methods for clean and energy-saving hydrogen production. TiO_2 has the characteristics of non-toxicity, stable photochemical performance, low price, and high photocatalytic activity [1,2], which makes TiO_2 have broad application prospects in the field of water decomposition to produce hydrogen and become one of the hottest research contents in this field.

In 1972, Fujishima and Honda reported on Nature [3] that using TiO_2 single crystal photo electrode successfully decomposed water into H_2 and O_2 under light conditions. Since then, the development of efficient and stable photocatalytic water decomposition oxygen production technology has quickly become a research hotspot in the fields of materials, physics, chemistry, etc.[4,5]. TiO_2 has the characteristics of non-toxicity, stable photochemical performance, low price, high photocatalytic activity, etc., making TiO_2 have broad application prospects in the fields of water and air purification, hydrogen decomposition from water, antibacterial disinfection, self-cleaning anti-fog coating, etc. One of the hottest research content in the field of materials. The wide band gap of TiO_2 and the high electron-hole pair recombination rate severely restrict the improvement of its photo electrochemical water splitting efficiency [6,7]. How to greatly increase the utilization of solar energy and explore efficient, stable and economic visible light the responsive photoelectric catalytic material is one of the key topics in the practical use of photo electrochemical decomposition of water to produce hydrogen. It is urgent for the entire scientific community to achieve a revolutionary breakthrough in the development of basic concepts and materials.

At present, the research on TiO_2 photo anode materials mainly focuses on the structural modification and chemical modification of TiO_2. Common methods include nanostructure design [8], ion doping [9], precious metal deposition [10], compound semiconductors Structure [11] etc. This series of modifications can effectively shorten the carrier transmission distance, broaden the absorption spectrum, improve the carrier separation rate, and the energy conversion efficiency of the entire photo electrochemical water splitting system has been significantly improved. In this paper, by using a simple secondary hydrothermal process, we coated Co_3O_4 on the surface of TiO_2 nanowires to form a TiO_2/Co_3O_4 core-shell heterostructure. The Co_3O_4 shell and the TiO_2 core can absorb sunlight at the same time, thereby broadening the light absorption capacity of TiO_2 for water splitting. In addition, the Co_3O_4 shell can promote the charge separation and transportation in the PEC water decomposition.

2. Experiments

According to reports from previous literature [13], on the surface of FTO substrate, we grew TiO_2 nanowires arrays (NWAs) by a hydrothermal process. The steps are as follows: 10 μL 37% HCl and 0.36 g titanium (IV) tetraisopropoxide (TTIP) were added to 5 mL ethanol to form a solution, then the solution were spin-coated on clean FTO substrate to form a dense layer at a rate of 3000 rmp for 30 s. The FTO substrates were annealed at 500℃ in the air for 1 h. Then the TiO_2 NWAs were grown on the dense TiO_2 barrier layer of the FTO substrate using a secondary hydrothermal method.

At a certain concentration of $CoCl_2$ solution, The TiO_2/Co_3O_4 NWAs were grown visa a secondary hydrothermal method at 180℃. The steps are as follows: under strong stirring at 60℃, 0.12g $CoCl_2 \cdot 6H_2O$ powder was added to 5 mL diethylene glycol to make a clear solution. Then, under electromagnetic stirring, 10 mL 2-propanol and 5 mL ethanol were added into the above solution. After that, the above TiO_2 NWAs were immersed in a sealed Teflon-lined stainless-steel autoclave contained with the mixture [14]. The autoclave was then transferred to oven hydrothermally reacted at 180℃ for 120 minutes. The resulting product was washed three times with deionized water and ethanol, then dried in the air, finally were annealed at 500℃ for 1 h in the air.

Under a rate of 8° per minute, crystallinity and phase analysis were obtained by a Rigaku D/max-2500V diffractometry using Cu Kα radiation at 40kV scanning 2θ range from 10° to 80°. Scanning electron microscopy (SEM) was characterized with FE-SEM (SUPRA40, Zeiss GmbH, Germany) microscopes. Using Barium sulfate as the internal absorption baseline, the optical properties of the samples were acquired with a TU-1901 UV-Vis absorption spectrophotometer (PERSEE, China),

3. Results and Discussions

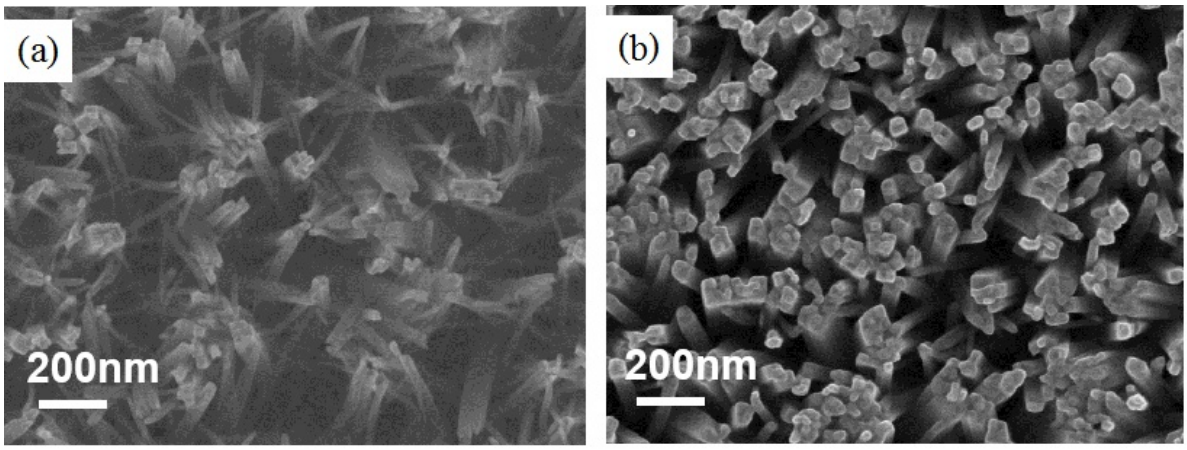

Figure 1. SEM image of TiO_2 NWAs and TiO_2/ Co_3O_4 NWAs

Figure 1(a) is the SEM image of a sample of TiO_2 nanowire array. From the figure, it can be seen that TiO_2 has a nanowire structure and grows along the C-axis direction perpendicular to the substrate, and it can be calculated that the average diameter of the TiO_2 nanowire is about 55 nm. Figure 1(b) is an SEM image of the TiO_2/Co_3O_4 nanowire array sample. It can be seen from the figure that the surface of the TiO_2 core body is thicker than the pure TiO_2 nanowire array sample, forming a TiO_2/Co_3O_4 core-shell structure nano Line structure, it can be calculated that the average diameter of the sample under this condition is about 73 nm.

As shown in Figure 2, the figure shows the XRD analysis of FTO samples, TiO_2 nanowire array samples and $TiO_2@Co_3O_4$ nanowire array samples. Comparing the XRD pattern of the TiO_2 nanowire array sample with the XRD pattern of the FTO conductive glass sample, it can be seen that two sets of new characteristic peaks appear at 36.5 ° and 63.2 ° in the XRD pattern of the TiO_2 nanowire array sample. The standard card can be drawn to correspond to the (101) crystal plane and (002) crystal plane of the rutile TiO_2 (JCPDS No.88-1175), in which the diffraction peak of the (002) crystal plane It is stronger than the (101) crystal plane, indicating that TiO_2 grows preferentially along the C axis. Comparing the XRD pattern of the TiO_2/Co_3O_4 nanowire array sample with the XRD pattern of the TiO_2 nanowire array sample, it can be seen that a new set of characteristic peaks appear at 31.3 ° in the XRD pattern of the TiO_2/Co_3O_4 nanowire array sample, compare PDF The standard card can be concluded that it corresponds to the (220) crystal plane of Co_3O_4 (JCPDS No. 43-1003), which shows that there are two components of TiO_2 and Co_3O_4 in the sample. This shows that after the second hydrothermal reaction, the outer layer of TiO_2 nanowire array is wrapped with a layer of Co_3O_4.

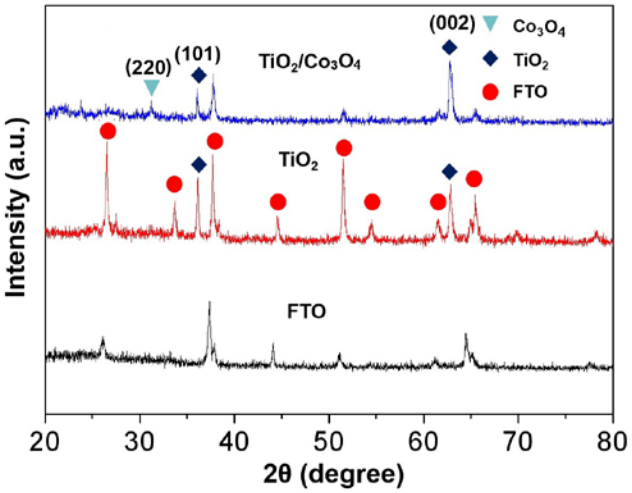

Figure 2. XRD patterns of FTO, TiO_2 NWAs and TiO_2/ Co_3O_4 NWAs

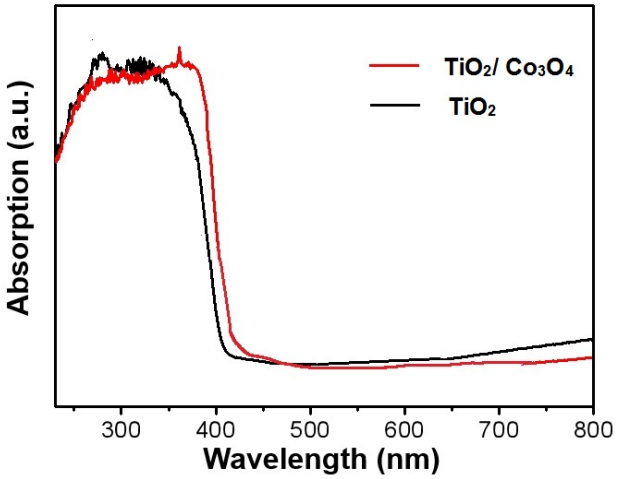

Figure 3. UV absorption of of TiO_2 NWAs and TiO_2/ Co_3O_4 NWAs

Figure 3 is the ultraviolet-visible light absorption diagram of TiO_2 nanowire array and TiO_2/Co_3O_4 nanowire array. The black curve in the figure is the spectral absorption curve of the TiO_2 nanowire array, and its maximum absorption wavelength is about 390 nm. The UV-visible absorption diagram of TiO_2/Co_3O_4 nanowire array shows that the core-shell structure of TiO_2/Co_3O_4 makes the absorption spectrum significantly red-shifted, and the maximum absorption wavelength can reach 420 nm. The appearance of the spectral redshift phenomenon increases the absorption of visible light by the material, and is more conducive to absorbing visible light in sunlight, thereby increasing the efficiency of photoelectrochemical decomposition of water.

Figure 4(a) is the Mott-Schottky curve of the TiO_2 nanowire array; Figure 4(b) the Mott-Schottky curve of the TiO_2/Co_3O_4 nanowire array. According to literature[12], We can calculated that the carrier concentration of TiO_2 nanowire array is 8.95×10^{18} cm^{-3}; the carrier concentration of TiO_2/Co_3O_4 nanowire array is 3.8×10^{19} cm^{-3}. Compared with the carrier of pure TiO_2 nanowire array, the concentration has been increased by 324%. Comparing the carrier concentration of TiO_2 nanowire array and TiO_2/Co_3O_4 nanowire array with their UV-visible absorption spectrum analysis, it can be seen that the core-shell structure TiO_2/Co_3O_4 can effectively expand the spectral

absorption, so compared to pure TiO_2 nanometer, the carrier concentration of the line array is significantly increased.

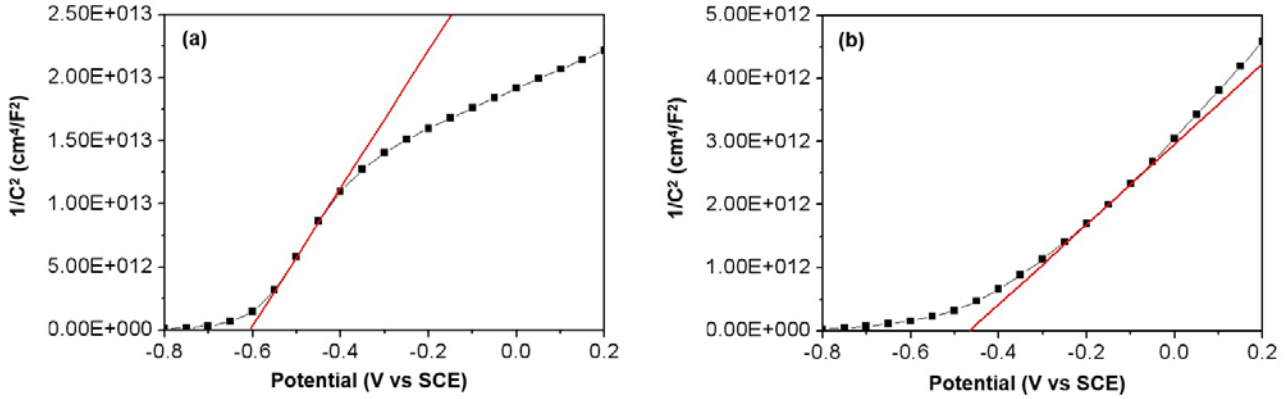

Figure 4. Mott-Schottky curve of TiO_2 NWAs and TiO_2/ Co_3O_4 NWAs

Figure 5 shows the photocurrent density J-V curves of TiO_2 nanowire array and TiO_2/Co_3O_4 nanowire array. The black dotted line in the figure is the Jph curve of the dark current of the sample in the absence of light, and the value is about 0 mA/cm^2. The curve of the solid black line is the Jph curve of the pure TiO_2 nanowire array, and the photocurrent density at a voltage of 1.23 V versus RHE is 0.74 mA/cm^2. The blue curve is the J_{ph} curve of the TiO_2@Co_3O_4 nanowire array sample. The photocurrent density at 1.23 V versus RHE is 0.94 mA/cm^2, which is an increase of 27.1% compared to the TiO_2 nanowire array. Compared with the pure TiO_2 nanowire array, the photocurrent density of the TiO_2/Co_3O_4 nanowire array has a significant gain effect, which may be related to the increase in carrier concentration and carrier separation rate.

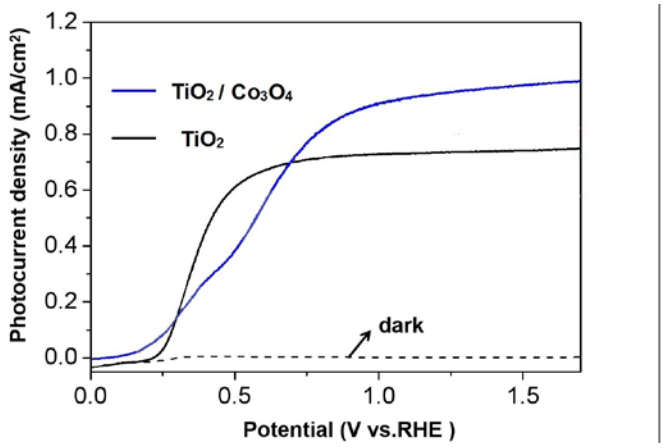

Figure 5. Linear sweep voltammagrams of TiO_2 NWAs and TiO_2/ Co_3O_4 NWAs

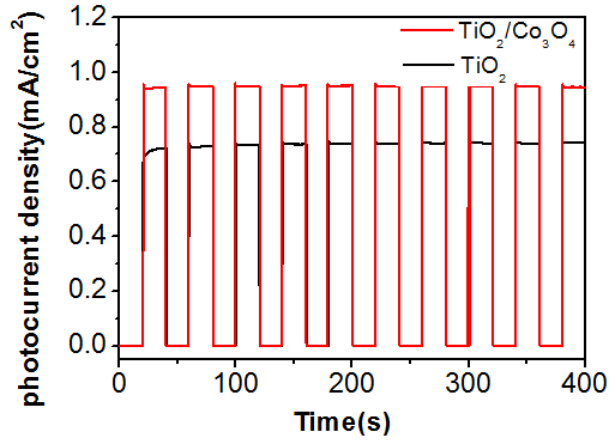

Figure 6. J-t curves for the TiO_2 NWAs and TiO_2/ Co_3O_4 NWAs

Figure 6 shows the J-T curves of TiO_2 nanowire array and TiO_2/Co_3O_4 nanowire array. The black and blue curves in the figure are the changes of photocurrent density of TiO_2 nanowire array and TiO_2/Co_3O_4 nanowire array with the test time. It can be seen from the figure that the dark current density of all samples is basically stable at 0 mA/cm^2 under dark conditions, which is consistent with the value measured in the J-V curve, indicating that the samples have good stability under no light and bias conditions. The photocurrent density of TiO_2 nanowire array and TiO_2/Co_3O_4 nanowire array under illumination in the picture is about 0.74 mA/cm^2 and 0.94mA/cm^2, which is basically consistent with the value tested in the J-V curve, indicating that the sample is biased under illumination good stability under pressure.

Conclusions

A simple two-step hydrothermal reaction was successfully used to synthesize the TiO_2/Co_3O_4 core-shell nanowire array. Compared with the TiO_2 nanowire array, the photo electrochemical catalytic performance of the TiO_2/Co_3O_4 nanowire array has been significantly improved, and the photocurrent density has reached 0.94 mA/cm^2. Compared with pure TiO_2 nanowire array, is improved by 27.1%, and there is no obvious fluctuation of photocurrent and dark current in alkaline test solution (1 mol/L NaOH solution), showing good stability. The improvement of the photo electrochemical performance of the TiO_2/Co_3O_4 nanowire array is related to its unique core-shell nanowire structure. The external Co_3O_4 material can effectively expand the absorption spectrum to increase the carrier concentration, and the internal TiO_2/Co_3O_4 heterojunction interface can accelerate Carrier transport speed promotes carrier separation.

Acknowledgements

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