

NiO-TiO₂ p-n Heterojunction

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NiO is a typical p-type semiconductor and it has widely been combined with TiO₂ to form the p-n heterojunction due to its suitable energy band structure, high charge carrier concentration, high chemical stability and low cost. Decreasing the size of NiO to nanoclusters helps to improve the electron transfer channels on the surface of TiO₂, thus enhance photocatalytic hydrogen production efficiency.

Keywords: hydrogen production ; photocatalysis ; p-n heterojunction ; NiO ; TiO₂

1. Introduction

Over the past decades, environmental pollution and energy depletion have become increasingly critical. Photocatalysis has been realized as a potential strategy to solve these two global issues ^[1]. For a long time, environmental photocatalysis over semiconductors has been widely investigated for environmental remediation such as waste water treatment ^[2]. Since Fujishima and Honda firstly demonstrated the photoelectrolysis of water over crystalline TiO₂, photocatalytic water splitting for hydrogen production and photocatalytic carbon dioxide valorization have also attracted great attention as the environmentally friendly solutions to further overcome energy and environmental crisis ^{[3][4][5]}. Solar-driven water splitting over transition metal oxides ^{[6][7][8]}, composite oxides ^{[9][10]}, carbonitride and chalcogenides ^{[11][12]} have been widely investigated, wherein n-type anatase TiO₂ is the most commonly used photocatalyst due to its nontoxicity, high chemical stability, cost-effectiveness and facile structure modification ^{[13][14]}. However, its limited quantum efficiency because of the high recombination rate of electron-hole pairs and its intrinsic wide band gap still hinder its commercialization. Herein, numerous strategies have been applied to improve the photocatalytic activity of TiO₂ materials, such as forming heterostructure with other semiconductors, doping, dye sensitization, and exposed facets modification ^{[14][15]}. Among them, heterostructures has been revealed to be an efficient method to improve photocatalytic efficiency ^{[16][17][18][19]}. As a typical heterostructure, p-n junction constructed by combining a n-type semiconductor (electron-rich) with a p-type semiconductor (hole-rich) can be a very efficient strategy to realize the separation of photogenerated electrons and holes. The charge separation is spontaneously driven by a formed built-in electric field and then the enhanced photocatalytic performance can be realized ^{[20][21][22]}.

NiO is a typical p-type semiconductor and it has widely been combined with TiO₂ to form the p-n heterojunction due to its suitable energy band structure, high charge carrier concentration, high chemical stability and low cost ^[23]. To date, many methods have already been developed to prepare NiO-TiO₂ nanocomposites, such as hydrothermal, incipient wetness impregnation, sol-gel, and evaporation-induced methods ^{[24][25][26][27]}. Although an inner-built electric field is a very efficient manner to improve the transfer of charge carriers between TiO₂ and NiO, the commonly fabricated nanocomposites usually suffer an untight contact between these two components, leading to a fast charge accumulation at a nanoparticle surface during the photocatalytic process. These accumulated charges become a recombination center to reduce the photocatalytic quantum efficiency.

2. Discussion

Figure 1 illustrates three fabrication processes for NiO-TiO₂ nanoparticles. Strategy 1 (S1) shows a process by using both precursors of NiO and TiO₂ (nickel acetate and tetraisopropyl titanate) directly. A nanocrystal of TiO₂ covered by NiO clusters can be obtained during a sol-gel process and the following thermal treatment endows the nanocrystal with high crystallinity. This method can generate NiO-TiO₂ nanocomposites with low NiO loading according to our previous work ^[28]. However, this method also leads to a crystal transformation of NiO to form NiTiO₃, which has negative effects on photocatalytic hydrogen production ^[29]. To avoid the formation of NiTiO₃, crystalline TiO₂ was used to replace its precursor tetraisopropyl titanate in strategy 2 (S2). During a hydrothermal process, nickel ions are only absorbed on a surface of TiO₂ rather than penetrated into TiO₂ crystal as the high crystallinity of TiO₂ inhibits a crystal transformation. NiO-TiO₂ nanocomposites with a high dispersion of NiO can herein be obtained after calcination. However, the second strategy can

only prepare NiO-TiO₂ nanocomposites with a low NiO loading due to a weak electrostatic adsorption ability of a TiO₂ surface. Herein, to further improve the loading of NiO, strategy 3 (S3) was employed by directly heating the suspension of TiO₂ and nickel acetate followed by calcination. The effects of photocatalyst preparation strategies on NiO loading, a crystal size, a pore size/distribution, and photocatalytic hydrogen production were compared as shown in **Table 1**. It appears that the samples from S1 have almost the same parameters and performance as those from S2. Higher NiO content endows the samples from S1 and S2 with better photocatalytic hydrogen production. However, further increasing NiO content by S3 causes a decrease in hydrogen evolution.

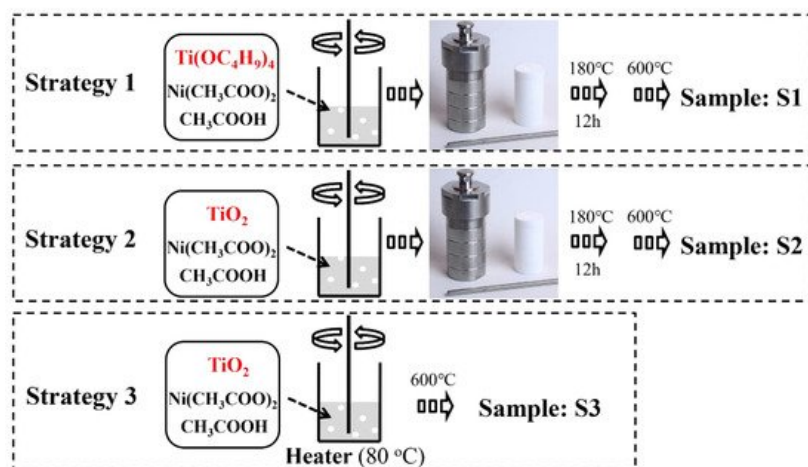


Figure 1. Schematic illustration of three different fabrication processes for NiO-TiO₂ nanoparticles.

Table 1. Structural parameters along with photocatalytic hydrogen evolution of each sample.

Sample	NiO Content (wt%)	Crystallite Size XRD (nm)	Crystallite Size SEM (nm)	S_{BET}/m^2g^{-1}	Pore Size (nm)	H ₂ Evolution rate/ $mmolh^{-1}g^{-1}$
NiO	-	55	40–80	9.5	N/A	2.1 ± 0.2
TiO ₂	-	25	20–30	31.9	5–50	6.6 ± 0.7
S1-10%	1.7	20	20–40	38.0	5–50	17.7 ± 0.9
S1-20%	3.3	30	20–40	39.5	5–50	23.5 ± 1.2
S2-10%	1.5	35	25–45	36.4	5–40	16.3 ± 0.8
S2-20%	3.1	35	25–45	35.6	5–40	20.4 ± 1.0
S3-10%	9.8	40	30–50	50.7	5–40	8.9 ± 0.7
S3-20%	19.4	45	30–50	52.7	5–40	8.8 ± 0.7

The morphology of NiO-TiO₂ composites prepared by strategy 1 was firstly investigated by scanning electron microscopy (SEM). Nanocrystals with a size of around 20 nm can be clearly observed for S1-10% (**Figure 2a**). Further increasing the loading of NiO, the size increased to around 30 nm for S2-20% (**Figure 2b**). The XRD patterns demonstrated that both S1-10% and S1-20% were mainly composed by anatase TiO₂ with high crystallinity, indicating the presence of NiO with extremely low content in the as-fabricated composites (**Figure 2c**). The presence and distribution of NiO can be revealed by transmission electron microscopy (TEM). NiO nanocrystals with a size of around 30 nm were observed, with high crystallinity as evidenced by the distinguishable lattice fringe (**Figure 3d**). Numerous bright dots can be clearly observed on the surface of a TiO₂ nanocrystal, which were ascribed to the loaded NiO, indicating that the presence of NiO was in the form of an ultrafine nanocluster and its distribution was uniform on the surface of TiO₂. The even dispersion of NiO increases the photocatalytic performance due to the formation of numerous p-n heterojunction channels. However, the content of NiO by this method was limited to <3.33% as further increasing NiO loading would introduce the formation of NiTiO₃ [28].

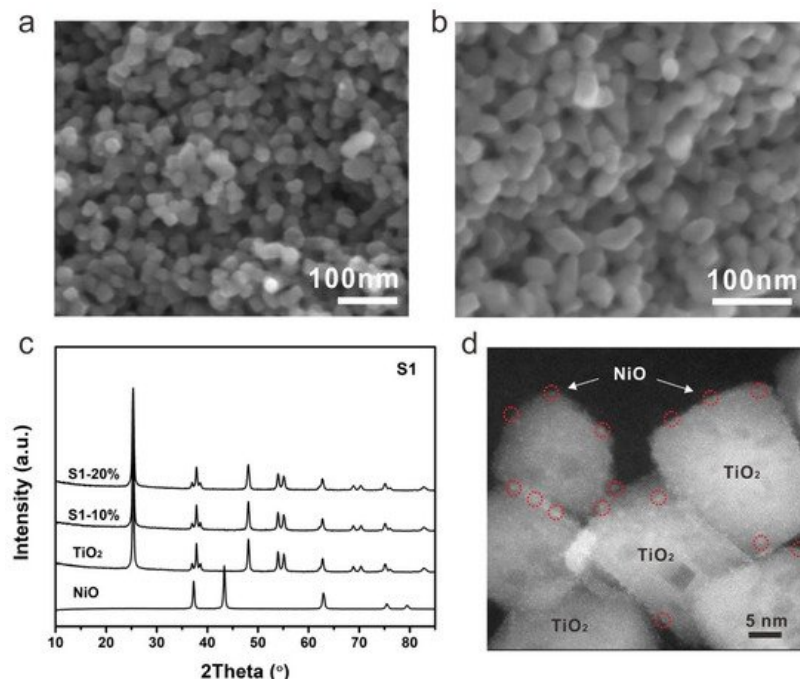


Figure 2. SEM images of (a) S1-10% and (b) S1-20%, (c) XRD patterns and (d) HR-TEM image of S1-20%.

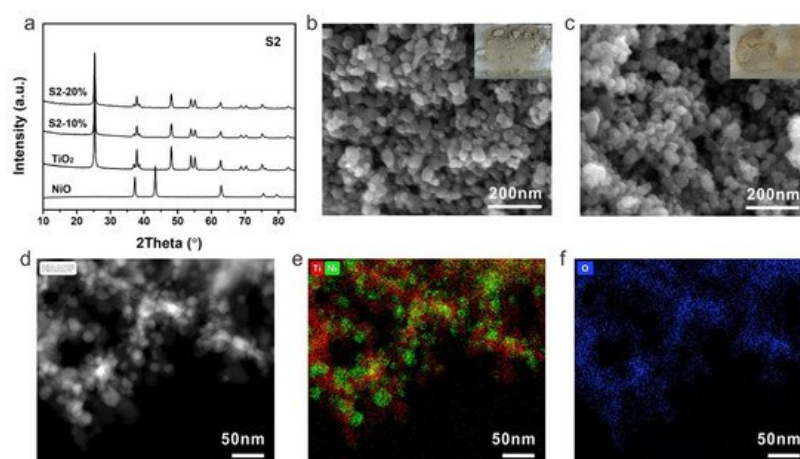


Figure 3. (a) XRD patterns, SEM images of (b) S2-10%, (c) S2-20%, (d) HAADF-STEM image of S2-20% and the corresponding elemental mapping (e) Ti (red), Ni (green) and (f) O (blue). Insets are the corresponding photographs of S2-10% and S2-20%.

The samples prepared by strategy 2 were then investigated by XRD to firstly check their components. Similar to the samples from strategy 1, typical TiO₂ with an anatase phase was detected and no peak of NiO was observed due to a low content of NiO (**Figure 3a**). Nanocrystals can be identified from SEM images for both S2-10% and S2-20% (**Figure 3b,c**). Because of the low content of NiO, the obtained photocatalysts exhibited a light grey color. As crystalline TiO₂ was used to prepare the composites, NiTiO₃ can be avoided even at a high concentration of a nickel precursor. The dispersion and interaction between TiO₂ and NiO were then investigated by TEM. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) showed a distinguishable nanocrystal of S2-20% (**Figure 3d**). The corresponding elemental mapping of Ti and Ni demonstrated a uniform distribution of NiO on TiO₂, indicating the formation of uniform p-n heterojunction within the photocatalyst by strategy 2 (**Figure 3e,f**).

Due to the low content of NiO in S1 and S2, XRD did not show the typical peaks of NiO. To further demonstrate the chemical state of nickel in S1 and S2, X-ray photoelectron spectroscopy (XPS) was performed on samples S1-20% and S2-20%. The high-resolution XPS signal of Ni 2p was shown in **Figure 4**. It is clear that the Ni 2p spectrum of S1-20% has the same peak positions compared with that of S2-20%, indicating the chemical state of nickel in S1-20% and S2-20% is the same. Typical peaks at 855.5 eV and 873.1 eV corresponds to Ni 2p_{3/2} and Ni 2p_{1/2} respectively. The corresponding satellite peaks were also detected. The splitting energy of Ni 2p_{3/2} and Ni 2p_{1/2} is 17.6 eV, indicating the presence of nickel species is NiO rather than metallic nickel.

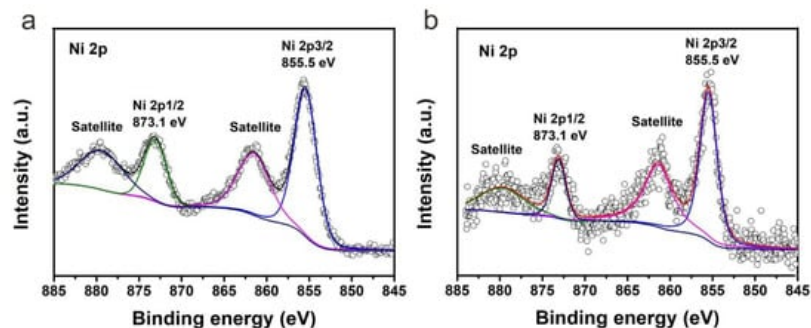


Figure 4. High-resolution XPS signal of Ni 2p of (a) S1-20% and (b) S2-20%.

The samples prepared by strategy 3 were then investigated by XRD to check their components and crystallinity. Different from previous photocatalysts, the S3-10% and S3-20% showed typical diffraction peaks of NiO apart from the anatase TiO₂ (Figure 5a). The intensities of NiO peaks were much higher of S3-20% than that of S3-10%, indicating a higher content of NiO in S3-20%. With high NiO loading, the color of NiO-TiO₂ composites turned to black, which helps to improve the utilization of incident light. The morphology of S3-10% was quite different to that of the previous samples. A smooth surface of TiO₂ nanocrystal changed to a rough surface due to the coverage of NiO on TiO₂ and stick-like NiO can also be identified among the TiO₂ nanocrystals (Figure 5b). The aggregation was more obvious with a higher NiO content (Figure 5c). Even though high NiO loading can be obtained by this method, the dispersion of NiO in the composite was revealed to be uneven. The NiO aggregation can clearly be observed by the HAADF-STEM and corresponding elemental mapping results (Figure 5d–f).

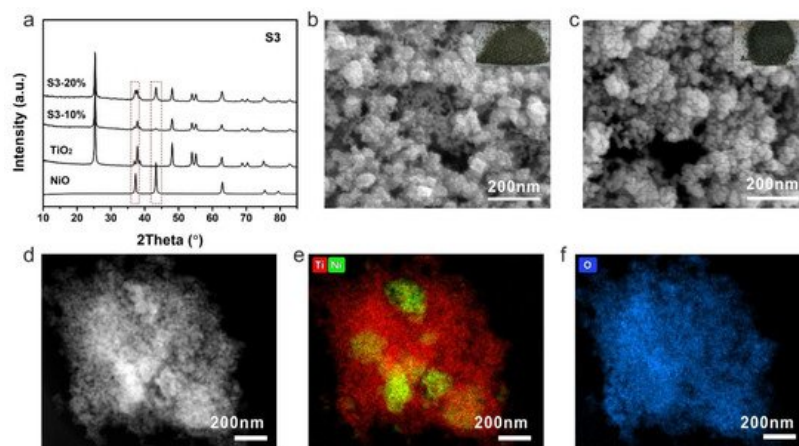


Figure 5. (a) XRD patterns, SEM images of (b) S3-10%, (c) S3-20%, (d) HAADF-STEM image of S3-20% and the corresponding elemental mapping (e) Ti (red), Ni (green) and (f) O (blue). Insets are the corresponding photographs of S3-10% and S3-20%.

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