ABSTRACT

A one-pot synthesis of Nb$^{5+}$-doped TiO$_2$ nanoparticles (NPs) with low cost and high efficiency for dye sensitized solar cells (DSSCs) is disclosed in the present invention. The Nb$^{5+}$-doped TiO$_2$ NPs with Nb dopants of 0–5 mol% are prepared by directly mixing TiO$_2$ slurry with Nb$_2$O$_5$ gel obtained by UV treatment of a mixture of NbCl$_5$ powder, ethanol and water in a certain ratio, following by heat treatment without using hydrothermal method. The as-prepared NPs exhibit well-crystallized pure anatase TiO$_2$ phase with uniform particle distribution. The incorporation of Nb$^{5+}$ leads to a stronger and broader light absorption in visible light range and a decrease of band gap with increasing Nb dopant content, which enhances the efficiencies of light-harvesting and electron injection and suppresses the charge recombination. The present method provides a simple and cost-effective mass-production route to synthesize n-type metallic ion doped TiO$_2$ nanoparticles as excellent photoanode materials.

8 Claims, 13 Drawing Sheets
(51) **Int. Cl.**

**C01G 33/00**  (2006.01)

**C09C 1/36**  (2006.01)

**H01G 9/00**  (2006.01)

(52) **U.S. Cl.**

CPC  ..........  **C01P 2002/84** (2013.01);  **C01P 2002/85** (2013.01);  **C01P 2004/03** (2013.01);  **C01P 2004/04** (2013.01);  **C01P 2004/82** (2013.01);  **H01G 9/2059** (2013.01)

(56) **References Cited**

**PUBLICATIONS**


* cited by examiner
Figure 3
Figure 6
Figure 8
Figure 9
Figure 10
Figure 11
ONE-POT SYNTHESIS OF NB2O5-DOPED TiO2 NANO PARTICLES

CROSS-REFERENCE TO RELATED APPLICATION

This application claims benefits from the U.S. provisional patent application No. 61/925,663 filed Jan. 10, 2014, and the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

The present invention relates to a method for one-pot synthesis of Nb2O5-doped TiO2 nanoparticles. The present invention also relates to the use of the Nb2O5-doped TiO2 nanoparticles for fabricating doped sensitized solar cells.

BACKGROUND OF THE INVENTION

With the great increase of global energy consumption, the development of highly efficient and low-cost renewable energy resources becomes extremely important and necessary, in which the most feasible technology is to directly convert solar energy into electronic power by solar cells. As an attractive alternative to conventional silicon-based solar cells for low-cost clean energy, dye sensitized solar cells (DSSCs) have received considerable interests due to their low production cost, simple fabrication processes, environmental friendliness, and relatively high photoelectric conversion efficiency. For DSSCs, achieving high energy conversion efficiency is one of the important keys to the future commercialization in the huge electricity generation market. In the past few decades, the development of DSSCs can be regarded as a process of continuously improving efficiency since nano-crystalline DSSCs were reported by Grits et al. in 1991. The energy conversion efficiencies over 12% has been achieved for DSSCs in the lab size devices; however, it is still far lower than the current multicyrstalline silicon solar cells (~20%), and there is a large space for the improvement of DSSCs performance. Therefore, developing new materials and structure with low-cost fabrication technique for DSSCs, and understanding the intrinsic mechanisms of photo-electron conversion are highly desired.

In general, a typical DSSC comprises a dye-sensitized TiO2 nanocrystalline porous film coating on a transparent conductive oxide (TCO) glass substrate as the photoanode, a liquid redox electrolyte containing an I3/-/I- redox couple, and a platinum (Pt) catalyst as the counter electrode (CE). The photoanode containing porous TiO2 nanoparticles (NPs), one of the most important components in DSSCs, is responsible for adsorbing dye molecules, transferring the photogenerated electrons from the dye to TiO2 and to the conductive substrate, and providing a diffusion path for redox ions, which importantly influences the charge recombination, electron collection and transportation rate, and the light absorption. Therefore, the characteristics of the porous TiO2 NPs, especially the morphology and size, interparticle connectivity, pore structure, and electric structure, are greatly vital in determining the final photovolatic performance of DSSCs. It has been demonstrated that the wide band gap of TiO2 (3.2 eV) and high recombination rate of photogenerated hole-electron pairs are main limitation factors for its performance improvement and widespread application in industry. In order to address these problems, several strategies, such as dye sensitizing, heterostructure, ion doping, etc., have been developed. Among them, the ion doping is believed to be the most economical and facile method to optimize the performance of TiO2 NPs by simply modifying its structure (morphology, size, electronic structure), which has been widely used in the photocatalysis, biological engineering and gas sensors fields, but there are relatively few studies applied in DSSCs. More recently, in order to further improve the efficiency of DSSCs, several efforts has been tried to modify nanostructured TiO2 NPs by metal ions doping such as Er3+ Yb3+ Mg2+ Zn2+ Mn2+ Co2+ and Nb5+, aiming to enhance electron transportation and suppress charge recombination. Of these doping elements, the Nb stands out to show great potential in improving DSSCs performance due to the synergistic advantages of superior electrical conductivity, similar atom radii with Ti, high valence favorably enhancing free carriers, and excellent ability in stabilizing the phase structure and tailoring the optical properties. For example, Liu et al. and Nikolay et al. have synthesized Nb-doped TiO2 particles by a hydrothermal method and used them in high efficiency DSSCs. However, an important limitation for the practical application of the Nb-doped TiO2 NPs applied in DSSCs is that the starting materials either use expensive niobium ethoxide or the preparation method adopts the hydrothermal technique which includes multi steps and long time, thereby leading to high preparation cost and low production efficiency. For example, Nb-doped TiO2 was prepared by a sol-gel method followed by a hydrothermal treatment in Liu et al.; the original sources of TiO2 and Nb in Nikolay et al. were from niobium powder and tetrabutyl titanate, which were added into hydrogen peroxide and ammonia (5:1 v/v) to obtain the precursor and followed a series of procedure. Both of these conventional methods are more complicated and in higher cost to synthesize the TiO2 and precursor.

Therefore, a facile one-pot synthesis as an economical, simple, and high yield approach for preparing Nb5+-doped TiO2 nanoparticles for use in highly efficient DSSCs with a high energy conversion efficiency is highly demanded.

SUMMARY OF THE INVENTION

To address the demand, the first aspect of the present invention relates to a method for making Nb5+-doped TiO2 nanoparticles (NPs) with low cost and high yield efficiency for use in DSSCs. The Nb5+-doped TiO2 NPs with 0-5 mol% of Nb dopants are prepared by first directly mixing a TiO2 slurry with a functionalized Nb2O5 gel following by heat treatment without using hydrothermal method. The functional Nb2O5 gel is obtained by UV treatment of a mixture of NbCl5 powder, ethanol and water with a certain ratio (0.027% w/v of NbCl5 powder, volume ratio of ethanol to water 1:1). The as-prepared NPs exhibit well-crystallized pure anatase TiO2 phase with uniform particle distribution and average size of about 15-18 nm. The Raman and XPS results demonstrate that the Nb is well doped into the TiO2 lattice and the substitution of Nb5+ on Ti4+ is formed using the presently claimed method. The incorporation of Nb5+ leads to a stronger and broader light absorption in visible light range (red shift) and a decrease of band gap with increasing Nb dopant content, which importantly enhances the efficiencies of light-harvesting and electron injection, and effectively suppresses the charge recombination. In one of the embodiments of the present invention, the best energy conversion efficiency of 8.44% is resulted from 2.0 mol % Nb-doped TiO2, which presents a significant improvement of 18.3% compared with the undoped (0 mol % Nb) TiO2 cell. The presently claimed method provides a simple and cost-effective mass-production
route to synthesis n-type metallic ion doped TiO₂ nanoparticles as excellent photocathode materials.

The second aspect of the present invention relates to the use of the Nb⁺⁺⁺-doped TiO₂ nanoparticles (NPs) prepared by the presently claimed method for fabricating DSSCs. It involves the fabrication of a photocathode which is coated with a film of undoped TiO₂ slurries followed by a film of the Nb⁺⁺⁺-doped TiO₂ nanoparticles thereon. The coated photocathode after sintering is then sandwiched with a counter electrode, an electrolyte and a spacer to form an assembly. The assembly is then hot sealed by covering a thin glass in the presence of a hot- 

**BRIEF DESCRIPTION OF THE DRAWINGS**

The accompanying drawings illustrate embodiments of the present invention and, together with the description, serve to explain the principles of the invention.

**FIG. 1** is a photograph of the sol-gel containing Nb after UV and centrifugation treatment (a) and the Raman spectra of the as-prepared sol-gel sample (b).

**FIG. 2** shows the XRD patterns of undoped and Nb-doped TiO₂ nanoparticles (a) and details of the XRD patterns around 24° to 27° 20 values (b).

**FIG. 3** shows the TEM images of the Nb-doped TiO₂ nanoparticles with different Nb contents: (a) 0 mol %; (b) 0.5 mol %; (c) 1 mol %; (d) 5 mol %. (e) is the electron diffraction pattern of 0.5 mol % Nb-doped TiO₂ nanoparticles. The insets in the images are the corresponding HTREM morphologies for each sample.

**FIG. 4** shows the Raman spectra of the Nb-doped TiO₂ nanoparticles with different Nb contents (a) and the magnified spectra in the range of 450-600 cm⁻¹ (b) and the range of 550-750 cm⁻¹ (c).

**FIG. 5** shows the XPS survey spectra of Nb-doped TiO₂ nanoparticles with different Nb contents: (a) 0 mol %; (b) 2 mol %; (c) 5 mol %.

**FIG. 6** shows the Ti 2p (a), O 1s (b) and Nb 3d (c) high resolution XPS spectra of Nb-doped TiO₂ nanoparticles with different Nb contents; (d) is the fitting result of the 2 mol % Nb-doped TiO₂ sample for the O 1s spectra.

**FIG. 7** shows the UV-vis transmission (a) and absorbance (b) spectra of DSSCs based on the Nb-doped TiO₂ NPs electrodes with different Nb contents. (c) is the magnified absorbance spectra in the wavelength range of 400-500 nm. (d) is the (dηhv)¹/² versus hν plots for the Nb-doped TiO₂ electrodes. The inset in (d) shows the variation of optical band gap with the increase of Nb dopant content.

**FIG. 8** shows the incident photon-to-current conversion efficiency (IPCE) spectra of DSSCs based on the undoped and Nb-doped TiO₂ NPs electrodes.

**FIG. 9** shows the photocurrent density–photovoltage (J–V) curves (a) and dark current-voltage curves (b) for DSSCs based on the undoped and Nb-doped TiO₂ NPs electrodes with different Nb contents.

**FIG. 10** shows the Nyquist plots (a) and Bode plots (b) of the EIS for DSSCs based on the Nb-doped TiO₂ NPs electrodes with different Nb contents. The inset in (a) is the equivalent circuit.

**FIG. 11** is a schematic diagram with photos showing the preparation procedures of the TiO₂-Nb composite slurry.

**FIG. 12** shows the SEM microstructure morphologies of the Nb-doped nanostructured TiO₂ films with different Nb contents: (a) 0 mol %; (b) 0.5 mol %; (c) 1 mol %, (d) is the cross-section microstructure of the 0.5 mol % Nb-doped TiO₂ film on the conductive FTO glass.

**FIG. 13** is a schematic diagram of the two photocatalyst systems for water splitting.

**DESCRIPTION OF THE INVENTION**

The following examples are used to assist the illustration and understanding of the presently claimed invention, but are not intended to limit the scope of the presently claimed invention.

**EXAMPLE 1**

One-Pot Preparation Of Nb-Doped TiO₂ Nanoparticles

All chemical materials are purchased commercially, and used without further purification. Because the preparation process of TiO₂ NPs have been mature at present, the commercial TiO₂ slurry (Eternal Chemical Co., Ltd.) containing uniform NPs (concentration 18.6%) can be directly used as the starting base materials to provide the Ti source in the present invention, aiming to simplify the doping preparation process and improve the preparation efficiency. Niobium chloride (NbCl₅) is used as the starting material to provide the Nb dopant source. The one-pot synthesis of Nb⁺⁺⁺-doped TiO₂ NPs is described as follows: 0.08 g NbCl₅ (99%, Aldrich) powder is dissolved in 1.5 mL ethanol and then 1.5 mL deionized H₂O is added and stirred to obtain a transparent precursor solution. After that, the transparent precursor solution is sequentially treated by the processes of UV irradiation for 20 min, high speed centrifugation (4000 rpm, 10 min), and removing the residual H₂O to obtain a polymeric gel containing Nb. Then, the polymeric gel is prepared in different weights corresponding to the molar ratios of Nb/(Nb+TiO₂) varying from 0.5–5.0 mol % by respectively adding 2 g commercially available TiO₂ slurry into the polymeric gel containing corresponding amount of niobium compound (please refer Table 1), followed by a high-speed mixing (2200 rpm, 2 min) and defoaming (2000 rpm, 2 min) using a condenser mixer (Are-250, Thinky) to obtain several homogenously mixed TiO₂-Nb composite slurries with different molar ratios of Nb/(Nb+TiO₂). It is possible to scale up the amount of commercially available TiO₂ slurry to a maximum of about 5,000 g depending on the capacity of the mixer. The whole preparation procedure is shown in **FIG. 11**. The Nb⁺⁺⁺-doped TiO₂ NPs with different dopant contents (0–5 mol %) are finally obtained by a heat treatment of each of the respective homogenously mixed TiO₂-Nb composite slurries at 500°C for 30 min.

<table>
<thead>
<tr>
<th>Ratio: H₂O:C₃H₆OH</th>
<th>STD</th>
<th>Nb 0.5 mol %</th>
<th>Nb 1 mol %</th>
<th>Nb 2 mol %</th>
<th>Nb 5 mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NA</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
</tr>
</tbody>
</table>
TABLE 1—continued

<table>
<thead>
<tr>
<th></th>
<th>STD</th>
<th>Nb 0.5 mol %</th>
<th>Nb 1 mol %</th>
<th>Nb 2 mol %</th>
<th>Nb 5 mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total volume of solvent</td>
<td>NA</td>
<td>3 ml</td>
<td>3 ml</td>
<td>3 ml</td>
<td>3 ml</td>
</tr>
<tr>
<td>Original Weight of NbCl₃</td>
<td>NA</td>
<td>0.08 g</td>
<td>0.08 g</td>
<td>0.08 g</td>
<td>0.08 g</td>
</tr>
<tr>
<td>UV irradiation time</td>
<td>NA</td>
<td>20 min</td>
<td>20 min</td>
<td>20 min</td>
<td>20 min</td>
</tr>
<tr>
<td>Residual Weight of Sol-gel after centrifugation</td>
<td>NA</td>
<td>1.184 g</td>
<td>1.184 g</td>
<td>1.184 g</td>
<td>1.144 g</td>
</tr>
<tr>
<td>Weight of Added Nb Sol-gel into 2 g TiO₂ slurry</td>
<td>0</td>
<td>92.21 mg</td>
<td>184.82 mg</td>
<td>373.97 mg</td>
<td>964.28 mg</td>
</tr>
</tbody>
</table>

EXAMPLE 2

Fabrication of DSSCs

The fluorine-doped SnO₂ conducting glasses (FTO, 10Ω/□, 3.1 mm thick, Nippon Sheet Glass) are ultrasonically cleaned in 4% glass cleaner (PK-LCG545, Parker) at 50°C for 30 min, followed by rinsing with deionized water. To fabricate the photoanode, a two-film electrode is used. A first film which is a three-layer film of commercially available undoped TiO₂ slurry is firstly coated onto the cleaned FTO glass by screen printing technique and then further coated by a second film which is a bi-layer film of the TiO₂—Nb composite slurry prepared according to Example 1. The thickness of the obtained TiO₂ bi-layer film is about 10 μm. The bi-layer film of the TiO₂—Nb composite slurry coated on the three-layer film of commercially available undoped TiO₂ slurry is then sintered at 450°C for 30 min to remove the organics and then slowly cooled to room temperature to form a sintered photoanode. Subsequently, the sintered photoanode is immersed in a 0.4 mM N719 dye solution (Solaronix) at room temperature for 12 h to make the porous Nb-doped TiO₂ nanoparticles sufficiently absorb dye molecules, followed by rinsing with ethanol and drying in air. The tin-doped indium oxide glass (ITO, 7Ω/□, 1.1 mm thick, Gen Tech.) coated by platinum nanoparticles (Pt NPs) catalyst by a dip-coating process is used as the counter electrode (CE).[28] The DSSCs are assembled by sandwiching a dye-covered TiO₂ photoanode and a Pt NPs-coated CE with an electrolyte (0.2M 1-propyl-3-methylimidazolium iodide or called PMII, 0.05 M LiI, 0.1M LiI, 0.2M tetrabutylammonium iodide or called TBAI, 0.5M 4-tert-butylpyridine or called TBP in acetonitrile:valeronitrile (75:25) solvent (AN:VN)) in the presence of a 25-μm thick thermal-plastic Surlyn® spacer (SX1170-25, Solaronix). The active area of the cells is about 0.16 cm². Finally, the DSSCs are hot sealed using a piece of thin cover glass with a hot-melt film underneath as an adhesive.

EXAMPLE 3

Characterization Methods

The chemical structure of the gel is analyzed by Raman spectroscopy (inVia Reflex, Renishaw) with a laser wavelength of 514 nm. The crystal structure and phase identification of the prepared TiO₂ NPs are performed by X-ray diffractometer (XRD, D8 Advance, Bruker). The morphology, size, crystallinity, and lattice structure of the NPs are investigated by field-emission transmission electron microscope (FE-TEM, Tecnai G2 F20 S-TWIN, FEI) as well as high resolution TEM (HRTEM). The binding state of chemical bond is studied by Raman spectra. The electronic structure and binding energy are determined by means of X-ray photoelectron spectroscopy (XPS, PHI-5400, PE). The surface morphology and microstructure of the TiO₂ films are observed by scanning electron microscope (SEM, S-4800, Hitachi). The optical transmittance spectra of the films are performed by UV-vis spectrophotometer (HP 8453). The incident photon-to-current conversion efficiency (IPCE) spectra of DSSCs are obtained by IPCE Kit equipment in wavelength range of 400-800 nm. The photocurrent-voltage (J-V) curves of DSSCs are recorded with a computer-controlled digital source meter (Keithley 2400) under exposure of a standard solar simulator (PEC-L101, Pecell) under 1 sun illumination (AM 1.5 G, 100 mW/cm²). The electrochemical impedance spectroscopy (EIS) is measured on DSSCs under 1.5 AM illumination by a computer-controlled electrochemical workstation (Reference 3600, Gamry) in the frequency range of 0.1-10⁵ Hz and AC amplitude of 10 mV at open-circuit conditions.

EXAMPLE 4

Structural Characterization of Nb-Doped TiO₂ NPs

During the one-pot preparation of Nb-doped TiO₂ NPs, the homogenous mixing of the Nb gel with the commercially available TiO₂ slurry are very important, in which the gel with suitable viscosity is the key. Homogenous, transparent and stable sols are preferred to obtain at the volume ratio of 1:1 for ethanol/H₂O, as shown in FIG. 11. The UV treatment can accelerate the hydrolysis and condensation of the sol to form a polymeric gel, as shown in FIG. 1a. The Raman analysis of the dehydrated gel is shown in FIG. 1b. Two obvious peaks can be found. One is emerged at 883 cm⁻¹, which is commonly corresponding to the stretching mode of terminal Nb=O bonds typical appeared in amorphous Nb₂O₅.[20,29] The other is at 2979 cm⁻¹, which is usually assigned to the stretching O—H bond.[30] It indicates that the dehydrated gel is mainly composed of amorphous Nb₂O₅, and O—H functional group, which favors its mixing with TiO₂ slurry to form new dehydrated metal oxide molecular structures.[29] The viscosity of TiO₂—Nb composite slurry is decreased with increasing Nb dopant content by increasing Nb gel weight, which influences the film printing quality.

FIG. 2 shows the XRD patterns of the undoped and Nb-doped TiO₂ NPs with different Nb contents. It can be seen that samples consist of only anatase phase with body-centered tetragonal crystal structure, which is similar to the result of Li et al.[26] but different from that of Nikolay et al.[22] whose
result shows that there is also TiO2 rutile phase found in the Nb-doped TiO2 NPs and Nb can suppress the formation of rutile phase. No other peaks such as Nb, Nb2O3, NbCl4 or rutile phase are detected, revealing that the anatase TiO2 nanostructure is well retained after doping and Nb has been successfully incorporated into the TiO2 lattice. Moreover, it is found that the (101) diffraction peaks of anatase phase gradually shift to lower diffraction angle with increasing Nb dopant content (Fig. 2b), which may be caused by the substitution of Ti4+ with Nb5+ because the Nb5+ radius (0.64 Å) is larger than Ti4+ radius (0.61 Å). According to the Debye-Scherrer equation (2d sinθ = λ, d, crystal plane spacing, λ, wavelength), the crystallite size of 0.5 mol% Nb-doped TiO2 NPs is calculated to be about 16.7 nm. Furthermore, the slightly increased full width at half maximum (FWHM) for (101) peaks from 0.5-5 mol% Nb suggests that the crystallite size decreases with increasing Nb content, which is well consistent with the TEM images shown in Fig. 3 and Table 2. As clearly seen, all Nb-doped TiO2 NPs show high crystallinity and uniform crystallite size distribution with tetragonal shapes, rather than the mixed nanocrystals with rhombic and rod-like shapes reported previously by Nikolay et al.[22] The mean size exhibits a slight decrease from 17.7 nm to 14.7 nm but the shape does not change with the increase of Nb dopant content. It is different from the report of Trizio et al.[20] in which the shape of TiO2 NPs changes from tetragonal platelets to peanutlike rods. The decrease of the crystallite size indicates the introduction of Nb can effectively inhibit the growth of anatase TiO2 NPs, which is favorable to electron transport and collection.[15] As compared with the (101) lattice planes in the HRTEM images for the undoped TiO2 and 1 mol% Nb-doped TiO2 NPs, the tiny increase in d-spacing directly correlated with the lattice distortion further verifies that the Nb5+ is homogeneously filled into the cation sites that are usually occupied by Ti4+.

**TABLE 2**

<table>
<thead>
<tr>
<th>Particles</th>
<th>Nb 0 mol %</th>
<th>Nb 0.5 mol %</th>
<th>Nb 1.0 mol %</th>
<th>Nb 2.0 mol %</th>
<th>Nb 5.0 mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean size (longest dimension)</td>
<td>17.7 nm</td>
<td>16.5 nm</td>
<td>15.4 nm</td>
<td>15.1 nm</td>
<td>14.7 nm</td>
</tr>
</tbody>
</table>

Fig. 4 shows the Raman spectra of the undoped and Nb-doped TiO2 NPs with different Nb contents. Being different from the Raman spectra (Fig. 1b) of the gel containing amorphous Nb2O3, all TiO2 NPs present single anatase phase active modes without any impurity phase, in well agreement with the XRD results (Fig. 2). The appearance of the amorphous Nb2O3 means that the incorporated Nb atoms have been fully doped into the TiO2 lattice because the Nb2O3 generally has higher crystallization temperature than TiO2.[31] The study of Trizio et al.[20] shows that the amorphous Nb2O3 will possibly appear when excess Nb dopant is added (>10%). Four main characteristic peaks of TiO2 are centered at 146, 396, 518, 639 cm⁻¹, which are corresponding to Eg (v6), B1g, A1g and Eg (v1) vibrational modes, respectively. The Raman peaks at 146 cm⁻¹ usually assigned to Ti–O bond are observed to broaden with increasing the Nb content, which implies the formation of Nb–O–Ti bond.[20][29] The intensity of Raman peaks for the Nb-doped TiO2 NPs show an increase in comparison with the undoped TiO2, suggesting an improved crystallinity degree caused by the decreased crystallization temperature due to Nb doping. Additionally, the peaks at 518 cm⁻¹ and 639 cm⁻¹ exhibit a slight shift to smaller wavenumber (Figs. 4b and c), which may result in a decreased band gap energy and improved photocatalysis property.[14]

The chemical state and electronic structure of the Nb-doped NPs are investigated by XPS measurement which is sensitive to the tiny differences in metal oxidation states, as shown in Figs. 5 and 6. Fig. 5 shows the typical XPS survey spectra of pure TiO2, 2 mol% Nb and 5 mol% Nb-doped TiO2 NPs. The peaks for Ti, O, and Nb are clearly observed in the Nb-doped NPs, and the peak intensity of Nb increases with the increase of Nb dopant, confirming the presence of niobium element. The C peaks observed are probably due to incomplete decomposition of the carbon in the starting material and air absorbents. The atomic concentration of Nb obtained from the XPS data of 2 mol% Nb-doped TiO2 NPs suggests that the molar ratio of Nb to TiO2 is 1.9%, which is close to the theoretical value. Fig. 6 shows the high resolution XPS spectra of Ti 2p (a), O 1s (b and d) and Nb 3d (c) for pure and doped NPs. In Fig. 6a, the binding energies (BE) of Ti 2p1/2 and Ti 2p3/2, typically corresponding to Ti4+ oxidation state, appear approximately at 458.6 eV and 464.4 eV, respectively, showing a separation of 5.8 eV. No Ti2+ Ti5+ peaks are observed, which indicates that only stoichiometric TiO2 is formed. Moreover, a little shift of the Ti 2p spectra to higher BE value is observed after Nb doping as compared to pure TiO2, which is likely attributed to the isovalent substitution effect of Ti atoms by Nb atoms. The O 1s spectra (Fig. 6b) at about 529.7 eV comes from Ti4+–O bonds, displaying a similar shift toward a higher energy levels with increasing the Nb dopants due to the increasing contribution by the lattice oxygen in TiO2.[32] It shows a two-band structure (Fig. 6d), namely, the main peak for the O1s electron binding energy for TiO2 (O2-) and the other peak at 530.5 eV which may be attributed to the adsorbed OH groups (Ti–OH) come from the gel.[34] The XPS spectra for the Nb region (Fig. 6c) exhibit the Nb 3d5/2 peak at 209.9 eV and Nb 3d3/2 at 207.3 eV, respectively, with a spin-orbit splitting of 2.4 eV. The area/intensity of the Nb 3d peaks increases with the increase of Nb contents. Usually, the BE of Nb5+ and Nb4+ appears at 204 and 205 eV[111] respectively. Therefore, it confirms that the Nb element in the doped TiO2 NPs only exists in Nb5+ to form the Nb–O–Ti bonds and it has been doped into TiO2 lattice, which would lead to an increase of the BE since the electronegativity of Nb (1.6) is larger than that of Ti (1.54) and to extra electrons for charge compensation.[103] The XRD, Raman and XPS data all point to the conclusion that only metal ions of Nb5+ and Ti4+ produced in the Nb-doped NPs by using this cost-effective method.

The microstructure morphologies of the Nb-doped TiO2 films show a uniform distribution of NPs in size and shape, as illustrated by Figs. 12a and c. The film thickness is about 10 μm with dense structure (Fig. 12f). No particle agglomerations are found, indicating that a homogenous mixing and doping of Nb with the pure TiO2. Moreover, as compared to the undoped films (Fig. 12a), the density of Nb doped TiO2 films (Figs. 12b and c) is obviously improved with increasing the Nb dopants, suggesting the Nb doping effectively enhances the crystallite of TiO2 NPs.

**EXAMPLE 5**

Optical Properties of Nb-Doped TiO2 NPs

Fig. 7a shows the transmission spectra of the pure TiO2 and Nb5+-doped TiO2 NPs films measured by UV-vis in the wavelength range of 300-800 nm. The corresponding absorbance spectra are shown in Fig. 7b. As seen, all films exhibit
10-35% transmission in visible region and a strong absorption below 400 nm. With increasing the Nb dopants, the absorbance intensity of visible light increases and the absorption edge displays a shift toward the longer wavelength (visible light region), as shown in FIGS. 7b and c. The light absorption covers the UV and whole visible range of 200-900 nm. The red shift phenomenon can be attributed to the charge transfer from O\textsuperscript{2-} \textsuperscript{2} level to Nb\textsuperscript{4+} \textsuperscript{4} d\textsuperscript{4} level instead of Ti\textsuperscript{3+} \textsuperscript{3}d\textsuperscript{3} due to Nb doping.\cite{ref15} When Nb is doped, some unoccupied Nb\textsuperscript{5+} \textsuperscript{4}d energy level below the conduction band (CB) of TiO\textsubscript{2} would be formed, which will transfer the electron from the valence band (VB) of TiO\textsubscript{2} to this doped Nb energy level to achieve the visible absorption. It also indicates the Nb doping decreases the band gap of TiO\textsubscript{2}, consequently, leading to a modification of the light absorption characteristic and the expansion of the absorption range of visible light. Based on the UV-vis spectra, the optical band gap (E\textsubscript{g}) is calculated according to the following equation:

\begin{equation}
\alpha h\nu = A(h\nu-E\textsubscript{g})^n
\end{equation}

where \(\alpha\) is the optical absorption coefficient, \(h\nu\) is photo energy, \(E\textsubscript{g}\) is the absorption band gap, \(A\) and \(n\) are constants. For the indirect semiconductor of anatase TiO\textsubscript{2}, \(n\) is equal to \(\frac{1}{2}\). The \((\alpha h\nu)^{-2}\) versus \(h\nu\) plots are shown in FIG. 7d. The tangent intercept represents the band gap, showing an obvious red shift. The variant of the \(E\textsubscript{g}\) with increasing the Nb dopant is given in the inset of FIG. 7d, which exhibits an overall narrow after Nb doping. Similar tendency is also reported by Li et al.\cite{ref26} and Kim et al.\cite{ref127} The smaller band gap means the CB of TiO\textsubscript{2} decreases with increasing Nb dopant through the mixing of Nb 4d and Ti 3d states,\cite{ref125} which favors the enhancements of the electron-injection efficiency and short-current when it is applied in DSSCs. The Honda-Fujishima effect\cite{ref128} found that when a TiO\textsubscript{2} electrode was irradiated with UV light, the electrons and holes were generated and caused water splitting directly on semiconductor/liquid contact. The heterogeneous reaction occurs at the surface needs to supply sufficient potentials for water splitting\cite{ref129}. The essential points are the difference in the band gap and the levels of the conduction band (CB) and valence band (VB) level. Due to the redox potential of H\textsuperscript{+}/H\textsubscript{2} (0V vs. NHE), the CB level has to be more negative than that. On the other hand, the top of VB level needs to be more positive than the redox potential of O\textsubscript{2}/O\textsubscript{2-}(1.23V) as shown in FIG. 13. The Nb-doping leads to a smaller band gap of TiO\textsubscript{2}, which implies that there is a potential for a more effective utilization in photocatalyst for water splitting under UV light irradiation. For further application, it could be photocatalyst for O\textsubscript{2} evolution and H\textsubscript{2} evolution with suitable mediator.

FIG. 8 shows incident photon-to-current conversion efficiency (IPCE) spectra of the undoped and Nb-doped TiO\textsubscript{2} NPs as the photoanode applied in DSSCs, which is defined as the number of electrons generated by light in the external circuit divided by the number of incident photons. Apparently, the IPCE at all wavelengths displays an important enhancement with increasing the Nb dopant from 0.5–2 mol % as compared to the undoped TiO\textsubscript{2}. Moreover, an enhanced IPCE spectra at longer wavelengths in visible region is observed, which mainly results from the expanded visible light absorption due to Nb doping (FIG. 7). The IPCE is determined by the amount of dye loading influencing light-harvesting, the charge collection efficiency and charge-injection efficiency.\cite{ref130} For this case, the intrinsic improvement of IPCE can be mainly attributed to the enhanced electron-injection due to the decreased band-gap and the improved electron-transfer capacity caused by the increased conductivity verified previously when Nb was doped into TiO\textsubscript{2}.\cite{ref126} Moreover, from XRD and surface analysis, the film density and crystallinity increase with increasing Nb content from 0.5–2.0 mol %, which prefers to produce higher specific surface areas.\cite{ref132} It may result in a higher dye molecule loading and also provides a slight increase in the ability to convert more photons to electrons. However, the IPCE exhibits an obvious decrease when the Nb content is increased to 5 mol %, which is primarily caused by the poor quality of Nb-doped film. It is found that the composite slurry viscosity is very low when the Nb dopant content is increased to 5 mol % by increasing the gel weight, which makes it difficult to print on previous undoped TiO\textsubscript{2} film layer. As a result, a poor Nb-doped film layer with inhomogeneous TiO\textsubscript{2} distribution and thickness is formed, consequently, leading to less dye molecule loading and low IPCE. It further indicates the Nb-doped NPs film layer plays an important role in the photon-to-current conversion process for the highly efficient DSSCs.

**EXAMPLE 6**

**Photovoltaic Performance of DSSCs**

FIG. 9a shows the photovoltaic performance of DSSCs based on the undoped and Nb-doped TiO\textsubscript{2} NPs electrodes with different Nb contents under one sun illumination (AM 1.5 G, 100 mW/cm\textsuperscript{2}). The obtained photovoltaic parameters are listed in Table 3. It can be seen that the photovoltaic performance of DSSCs based on Nb-doped TiO\textsubscript{2} NPs exhibits a pronounced increase with increasing the Nb contents from 0.5 to 2.0 mol % as compared to the DSSCs based on the undoped TiO\textsubscript{2} NPs. The DSSCs based on the 2.0 mol % Nb-doped NPs present the maximum short-circuit photocurrent density (J\textsubscript{sc}) of 16.17 mA cm\textsuperscript{-2} and the highest energy conversion efficiency (\(\eta\)) of 8.44% with an open circuit voltage (V\textsubscript{oc}) of 0.73 V and a fill factor (FF) of 0.71. In comparison with the undoped TiO\textsubscript{2}, the J\textsubscript{sc} and \(\eta\) of the 2.0 mol % Nb-doped TiO\textsubscript{2} DSSCs are increased by 22.7% and 18.9%, respectively, which are superior to previous results of DSSCs based on Nb-doped TiO\textsubscript{2} NPs synthesized by hydrothermal method.\cite{ref22, ref26} It further indicates that the DSSCs based on the presently claimed one-pot synthesized Nb-doped TiO\textsubscript{2} NPs are not only superior in the low-cost but also in the photovoltaic performance. In the DSSCs prepared by the presently claimed method, the J\textsubscript{sc} is dependent on the electron-injection, charge-transfer, and charge-recombination processes.\cite{ref11} FIG. 7 indicates that the Nb doping leads to an enhanced light-harvesting from visible range and a decreased band-gap. For the n-type semiconductor of Nb-doped TiO\textsubscript{2}, the decrease of band gap means that a positive shift of the CB. As a result, the driving force of electron injection, namely the difference between the dye lowest unoccupied molecular orbital (LUMO) level and the CB of TiO\textsubscript{2} is increased, consequently, leading to an important improvement of the J\textsubscript{sc}. On the other hand, the XPS and UV-vis verities that the Nb\textsuperscript{5+} doping can also induce some intraband states such as the Nb 4d level, which can enhance the overall mobility and transportation of the excited electrons.\cite{ref22} Additionally, the Nb element has higher conductivity (6.93×10\textsuperscript{4} (cm-U)) than Ti (2.34×10\textsuperscript{4} (cm-U)), and the tightly bound Nb to TiO\textsubscript{2} NPs assists to promote more rapid electron transfer from CB of TiO\textsubscript{2} to the conductive substrate, effectively suppressing the recombination of injected electrons with the \(V\textsuperscript{-}\) ions. Therefore, the J\textsubscript{sc} is largely improved. Furthermore, it can be seen that the \(V\textsuperscript{-}\) is also slightly improved after Nb doping (Table 3). The \(V\textsuperscript{-}\) is determined by the energy difference between the quasi-Fermi level (E\textsubscript{qf}) of the illuminated semiconductor electrode and the
potential of the redox couple in the electrolyte.\textsuperscript{113} Considering TiO\textsubscript{2} as a n-type semiconductor, the incorporation of Nb is a donor doping, which would promote the E\textsubscript{p} to shift toward the TiO\textsubscript{2} CB, consequently, leading to an increase of V\textsubscript{oc}. Therefore, the introduction of Nb doping not only increases the photocurrent via expanded light absorption and enhanced electron-injection, but also improves the photovoltage by n-type doping effect. This double-function is very significant for enhancing the photovoltaic performance of the DSSCs.

Table 3

<table>
<thead>
<tr>
<th>DSSCs</th>
<th>J\textsubscript{sc} (mA cm\textsuperscript{-2})</th>
<th>V\textsubscript{oc} (V)</th>
<th>FF</th>
<th>\eta (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb 0 mol %</td>
<td>13.29</td>
<td>0.72</td>
<td>0.74</td>
<td>7.10</td>
</tr>
<tr>
<td>Nb 0.5 mol %</td>
<td>14.34</td>
<td>0.75</td>
<td>0.72</td>
<td>7.66</td>
</tr>
<tr>
<td>Nb 1.0 mol %</td>
<td>14.61</td>
<td>0.76</td>
<td>0.72</td>
<td>8.01</td>
</tr>
<tr>
<td>Nb 2.0 mol %</td>
<td>16.17</td>
<td>0.73</td>
<td>0.71</td>
<td>8.44</td>
</tr>
<tr>
<td>Nb 5.0 mol %</td>
<td>11.13</td>
<td>0.73</td>
<td>0.73</td>
<td>6.05</td>
</tr>
</tbody>
</table>

Fig. 9b shows the photocurrent density-voltage (J-V) curves from 0 V to 0.8 V in the dark. In DSSCs, a higher dark current density means more serious recombination reaction happening at the interface between TiO\textsubscript{2} NPs photoanode and electrolyte. As seen, the dark current of the DSSCs based on the 2.0 mol % Nb-doped TiO\textsubscript{2} NPs presents an obvious decrease and the onset voltage (see the arrows) displays a slight shift toward about 0.1 V than that of the undoped one. The increase of the onset voltage and the reduction of the dark current further demonstrate that the suitable Nb-doping into TiO\textsubscript{2} NPs successfully reduces the recombination of $^\text{114,115}$.

To further confirm the effect of Nb doping in transporting the electrons and restraining the recombination in the nanostructure, the EIS, a powerful tool to clarify the electronic and ionic transport processes, was measured under the illumination of one sun at open-circuit potential conditions. Fig. 10a shows the Nyquist plots obtained from the DSSCs based on Nb-doped TiO\textsubscript{2} NPs and undoped ones at frequencies ranging from 1 MHz to 0.1 Hz. The equivalent circuit is depicted in the inset of Fig. 10a. The response of the impedance $Z(\omega)$ for the photoanode can be expressed as the following equation:

$$Z(\omega) = \left(\frac{R_s R_k}{1 + i\omega R_k C_{eq}}\right) + \frac{i\omega C_{eq} R_k}{1 + i\omega R_k C_{eq} W_e^{(s-1)} W_e^{(s-1)} W_e^{(s-1)}}$$

$$Z(\omega) = \left(\frac{R_s R_k}{1 + i\omega R_k C_{eq}}\right) + \frac{i\omega C_{eq} R_k}{1 + i\omega R_k C_{eq} W_e^{(s-1)} W_e^{(s-1)} W_e^{(s-1)}}$$

where $R_s$, $R_k$, $W_e$, and $C_{eq}$ represent the electron transport resistance in TiO\textsubscript{2}, the charge-recombination resistance, the rate constant for recombination, and the characteristic angular frequency for electron diffusion in a finite layer, respectively. The detailed electrical parameters obtained are summarized in Table 4:

Table 4

<table>
<thead>
<tr>
<th>DSSCs</th>
<th>$R_s$ (\Omega)</th>
<th>$C_{eq}$ (\textmu F)</th>
<th>$R_p$ (\Omega)</th>
<th>\textit{W_e} (s\textsuperscript{-1})</th>
<th>$R_k$ (\Omega)</th>
<th>\textit{W_e} (s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb 0 mol %</td>
<td>16.3</td>
<td>1.10E-05</td>
<td>3.81</td>
<td>97.42</td>
<td>545.9</td>
<td>3.21</td>
</tr>
</tbody>
</table>

| TABLE 4-continued

<table>
<thead>
<tr>
<th>DSSCs</th>
<th>$R_s$ (\Omega)</th>
<th>$C_{eq}$ (\textmu F)</th>
<th>$R_p$ (\Omega)</th>
<th>$W_e (s^{-1})$</th>
<th>$W_e (s^{-1})$</th>
<th>$R_k$ (\Omega)</th>
<th>$W_e (s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>16.3</td>
<td>1.10E-05</td>
<td>3.81</td>
<td>97.42</td>
<td>545.9</td>
<td>3.21</td>
<td>17.96</td>
</tr>
<tr>
<td>Nb</td>
<td>2.0 mol %</td>
<td>16.3</td>
<td>1.10E-05</td>
<td>4.76</td>
<td>89.62</td>
<td>575.1</td>
<td>2.49</td>
</tr>
<tr>
<td>Nb</td>
<td>5.0 mol %</td>
<td>16.3</td>
<td>1.10E-05</td>
<td>3.57</td>
<td>94.30</td>
<td>607.7</td>
<td>2.37</td>
</tr>
</tbody>
</table>

where $R_s$, $C_{eq}$, and $R_p$ represent the series resistance, the capacitance at the Pt surface and the resistance at the Pt surface, respectively. In Fig. 10a, the biggest semicircles in the medium frequency (1–100 Hz) correspond to the photo-injected electron transport and recombination competition at the TiO\textsubscript{2}/dye/electrolyte interface. As shown, the semicircles at the intermediate frequency regions are decreased with increasing Nb dopant content from 0 to 2 mol %, which implies that the photogenerated electrons transfer faster in the working electrode interface. It is consistent with the increased $W_e$ values in Table 3 and $J_{sc}$ in Fig. 9. The $W_e$ is inversely proportional to electron transportation time ($t$) and $W_e$ is inversely proportional to electron lifetime ($\tau$).\textsuperscript{125} Larger $W_e$ value means faster electron transportation rate within TiO\textsubscript{2} films and larger $J_{sc}$ and smaller $W_e$ means longer electron lifetime and larger $V_{oc}$ (Table 4). The low $W_e$ in 5 mol % Nb is also in accordance with its low $J_{sc}$ data. These results are also supported by the Bode plots (Fig. 10b). It has been verified that the value of electron recombination rate, $k_{er}$ (s\textsuperscript{-1}), is equal to value of the maximum peak frequency ($\omega_{max}$) in the middle frequency region.\textsuperscript{38} As shown, the middle frequency peaks are gradually shifted to lower frequency with increasing Nb content from 0 to 2 mol %, which of decrease in $\omega_{max}$ confirms that a slower electron recombination process in the Nb-doped DSSCs. Furthermore, as mentioned before, the dark J-V curves of Nb-doped cells (Fig. 9b) also show a lower dark current than that for undoped one; this is in agreement with the fewer back reactions and slower recombination for Nb-doped based cells. All these results sufficiently indicate that the suitable incorporation of Nb into the TiO\textsubscript{2} NPs can prominently increase the electron transport rate and effectively suppress the charge recombination process in DSSCs, and consequently, leading to an important improvement in the photovoltaic conversion efficiency.

Uniform Nb\textsuperscript{4+}-doped anatase TiO\textsubscript{2} nanoparticles with different doping contents from 0.5 to 5.0 mol % for use in highly efficient DSSCs are successfully prepared by rapid one-pot synthesis through directly mixing commercial TiO\textsubscript{2} slurry with a functionalized Nb\textsubscript{2}O\textsubscript{5} gel following by heat treatment. The Nb\textsubscript{2}O\textsubscript{5} gel, obtained by UV treatment of a mixture of NbCl\textsubscript{5}, ethanol and water with a certain ratio, is confirmed to contain amorphous Nb\textsubscript{2}O\textsubscript{5} and O—H functional group by Raman spectra. The XRD, Raman and XPS reveals that Nb can be well doped into the TiO\textsubscript{2} lattice and Ti\textsuperscript{4+} is substituted by Nb\textsuperscript{4+} to preferentially generate free carriers using this cost-effective method. The red-shift of the UV-vis absorbance peak and improved IPCE demonstrate that the Nb\textsuperscript{4+} ion doping significantly broadens the spectral absorption of TiO\textsubscript{2} into visible light region and effectively enhances
light-harvesting. The band gap is narrowed with increasing the Nb dopants. The best cell efficiency of 8.44% for DSSCs is obtained based on 2.0 mol % Nb-doped TiO₂, which is improved by 18.9% compared to the undoped TiO₂ DSSC. The improvement of energy conversion efficiency is mainly ascribed to the extended light absorption, faster electron injection and decreased recombination of electron-hole pair by introducing Nb²⁺ doping. This method offers a facile and potential mass-production way to synthesize low-cost n-type metallic ion doped TiO₂ nanoparticles for energy or environmental applications.

While embodiments of the present invention have been illustrated and described, it is not intended that these embodiments illustrate and describe all possible forms of the invention. Rather, the words used in the specification are words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention.

REFERENCES CITED

The disclosure of the following cited references is also incorporated herein by reference in its entirety:


What is claimed is:

1. A method of preparing a Nb₂O₅-doped TiO₂ nanoparticles-containing solution comprising:
    (a) preparing a transparent precursor solution containing niobium chloride (NbCl₅);
    (b) treating the transparent precursor solution with UV;
    (c) centrifuging the UV-treated transparent precursor solution and removing the residual water to obtain a polymeric gel containing niobium (Nb) as the dopant source;
    (d) adding a TiO₂ slurry into the polymeric gel containing corresponding amount of niobium compound followed by a high-speed mixing and deforming to obtain different homogeneously mixed TiO₂-Nb composite slurries in different molar ratio of Nb/(Nb+TiO₂) ranging from 0.5–5.0 mol %; and
    (e) heat treating the homogeneously mixed TiO₂-Nb composite slurries for a period of time in order to obtain the Nb₂O₅-doped TiO₂ nanoparticles-containing solution.
3. The method of claim 2, wherein said NbCl₅ powder is 0.027% w/v in said ethanol and deionized water, and wherein said ethanol to said deionized water is in a volume ratio of 1:1.

4. The method of claim 1, wherein said UV treatment in (b) is for about 20 minutes.

5. The method of claim 1, wherein said centrifuging in (c) is at 4,000 rpm for 10 minutes.

6. The method of claim 1, wherein the TiO₂ slurry in (d) is about 2 g and said corresponding amount of niobium compound is about 92 to 964 mg per about 2 g of said TiO₂ slurry.

7. The method of claim 1, wherein the high-speed mixing in (d) is carried out at 2200 rpm for 2 minutes and the defoaming is carried out at 2000 rpm for 2 minutes by using a conditioner mixer.

8. The method of claim 1, wherein said homogeneously mixed TiO₂—Nb composite slurries in (e) is heat treated at about 500°C. for 30 minutes.

* * * * *