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UV Assisted Chemical Gas Sensing of Nanoporous TiO_2 at Low Temperature

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Abstract :

Nanoporous TiO_2 powders were prepared following a two-step method. The highly ordered uniform TiO_2 nanotube arrays were first grown by the electrochemical anodization of a Ti metal sheet and subsequently, mechanically milled to obtain the porous TiO_2. The obtained nanoporous TiO_2 sample contains nanotube-like particles with a length around 400 nm and inner diameter ~100 nm and also some near-spherical TiO_2 single crystals with a diameter around 10 nm. The sensing properties of as-synthesized nanoporous TiO_2 based resistive-type chemical sensor to formaldehyde were demonstrated. The sensor exhibits good sensitivity to formaldehyde at room temperature under UV-irradiation. The response of the sensor increased almost linearly as a function of the concentration of formaldehyde from 10-50 ppm.

Key words: Nanoporous TiO_2; Formaldehyde; Gas sensors; UV Irradiation.

Nanoporous TiO_2 has attracted great attention due to its unique properties in photocatalysis, energy conversion and storage systems, and chemical sensing [1-12]. Among various nanostructured TiO_2, the nanotubes have more attractive features such as more effective separation of photo-generated electron-hole pair to prevent recombination in solar cells [1-4]. Typically, the TiO_2 nanotube was synthesized by the hydrothermal method. However, in the TiO_2 nanotubes synthesized by the hydrothermal method [5, 7], cations or protons always exist in between the zigzag Ti-O double layer during the hydrothermal treatment. Consequently, further high temperature treatment is needed to remove the exchanged protons, which usually lead to undesirable agglomeration of the nanotubes [5, 7].

In this work, the nanoporous TiO_2 with the nanotube-like microstructure were synthesized by a new two-step method. The crystallography and dimensions at nanoscale were firstly achieved by heat-treatment of the rigid TiO_2 nanotube arrays and the final dispersed nanotubes with pre-defined nanostructure were obtained independently by mechanical milling. This combined techniques help bypass further high temperature heat-treatment as is usually done in the widely used hydrothermal method to prepare dispersed nanotubes. Sensing properties of the as-synthesized TiO_2 nanotubes based sensors to formaldehyde, a highly health-threatening gas species substantially present both indoors and outdoors [8-11], were demonstrated at room temperature with the assistance of UV illumination.

1 Experimental Section

1.1 Materials Preparation and Microstructure

During the process for synthesis of the nonporous TiO_2., the highly-ordered uniform TiO_2 nanotube array was grown by conventional electrochemical anodization of a Ti metal sheet [11]. Titanium sheet (99.4% purity, 0.2 mm thickness) was degreased by ultrasonication for 10 min in acetone, ethanol and deionized water in sequence. The anodization solution was prepared with ethylene glycol (EG) containing 0.3 wt% NH_4F and 2 vol% deionized water. Titanium sheet was anodized at 30 V at room temperature. The electrochemical oxidation occurs on both sides of the Ti sheet and the nanotubes grow towards the middle. Therefore, both ends of the oxide nanotubes would eventually meet each other back-to-back. After anodization, TiO_2 nanotubes were annealed at

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400 ^oC for 2 hours. The calcined nanotube arrays were then broken down and ground manually to obtain the TiO_2 nanoparticles with the residual nanotube fragments.

The phase formation of the fabricated samples was analyzed using a powder X-ray diffractometer (XRD: D8 Advance, Bruker- AXS, Germany). The surface morphology of the fabricated nanotubes was examined using a scanning electron microscope (SEM: S-3000N, Hitachi, Japan) on gold-coated specimens. The more close examination of the microstructure of the samples was further carried out by transmission electron microscopy (TEM: JEOL 2100, Japan).

1.2 Sensor Fabrication and Electrical Measurements

The prepared nanotube-based TiO_2 nanopowders were mixed with alpha-terpineol (Aldrich, Shanghai) forming the printable paste. The paste was then deposited on commercial interdigitated gold electrode printed substrate to form a resistive-type gas sensor. The electrical measurements were conducted in a sealed chamber with a total volume of 50 L [8-11]. The electrical resistance in the various concentrations of formaldehyde gas vapor in the background of humid ambient (relative humidity, RH ~ 33%) at room temperature (19±3 ^oC) was measured by an Agilent digital DC electrometer (34401A) with data acquisition capability using the IntuiLink software.

The resistance variation of the nanoporous TiO_2 with a change in gas concentration was measured as the sensor signal. The response (R_s) of the sensor is defined as the relative change of the resistance in the ambient background and that in the various analytes: $R_s = (R_a - R_g)/R_a \times 100$, where R_a and R_g are the resistances of the sensor in ambient air and the analyte, respectively. The UV irradiation was conducted by placing a LED light source as close as possible to the top surface of the sensor. The power density of the LED was ~4 mW and the wavelength range was 360-365 nm. This was enough to activate the anatase TiO_2 which has a band gap ~3.2 eV corresponding to a threshold absorption wavelength at 387.5 nm.

2 Results and Discussion

2.1 Characterization of the naoporous TiO_2

The surface microstructure of the electrochemically anodized TiO_2 nanotube array is shown in Fig.2. The nanotubes were uniformly formed and loosely connected to each other. The contact between the nanotubes is weak and brittle. This allows formation of dispersed nanotubes during the mechanical milling process. The tube diameter in the array is ~ 120 nm and the wall thickness is ~10-20 nm. After heat treatment of the nanotube arrays at 400 ^oC for 2 hours, the nanotubes had a cleavage in the middle of the nanotubes grown on both sides back-to-back. Subsequently, these nanotube arrays were broken down and milled manually for about one hour to achieve the final product.

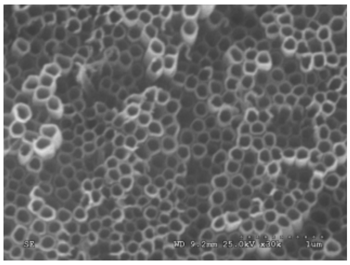

Fig.2 SEM micrograph of the surface of as-fabricated TiO_2 nanotube array

The powder XRD （data not shown）reveals that the final product was an anatase phase. The SEM of the as-prepared TiO_2 nanotube is shown in Fig.3(a). The sample consists of a mixture of the larger rod-like particles and small aggregates. Therefore, TEM was further conducted to investigate the details of both microstructures. Fig. 3(b) shows the microstructure of the larger porous TiO_2 particles. The clear contrast within a large particle indicates a residual nanotube array fragment, which was not completely pulverized during manual grinding.

Figures 3(c-d) show the detailed features of the small aggregates observed in Fig.3(a). The small aggregates in reality consist of two types of particles: the residual broken nanotubes and some nearly-spherical nanoparticles. Obviously, one of the two nanotubes in Fig.3(a) was partly destroyed and left with a half-open tube structure. The other one has an overall tube feature with a length around 400 nm and opening diameter ~100 nm consistent with the SEM result shown in Fig.2. Figure 3(d) shows that the wall of the nanotubes is “piled-up” with tiny TiO_2 crystals indicating a hierarchical feature of the nanotubes. The hierarchical nanotubes survived the milling process leading to the final nanotube based TiO_2 powders. The loosely bonded hierarchical nanostructure is completely dependent upon the mechanical milling process and bypasses further high temperature heat-treatment as is usually done in the widely used hydrothermal method.

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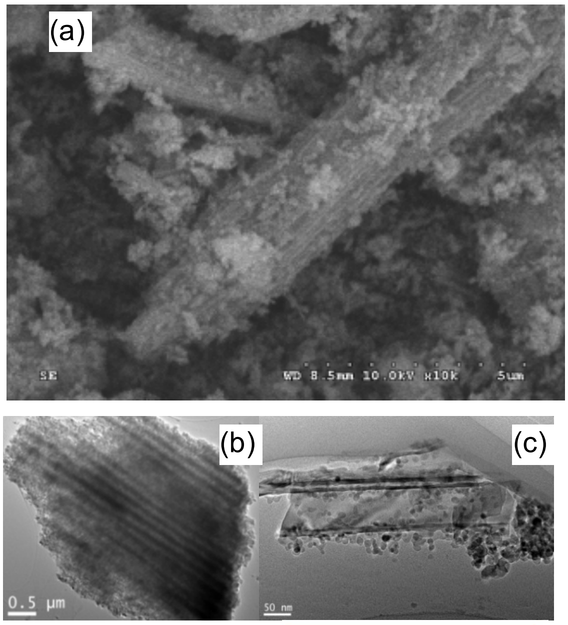
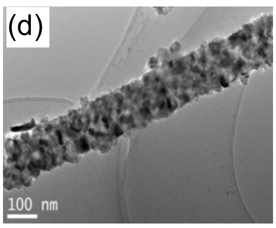
The tiny spherical particles residing along the nanotubes shown in Fig.3(c) have an average diameter ~ 10 nm. These nanoparticles came from the broken wall of the nanotubes and are loosely bonded together. Electron diffraction (ED) pattern of these nanoparticles shows that they are single crystals. BET specific surface area of as-prepared TiO_2 as shown in Fig.3(e) is comparable to that of the commercial Deguess P25 with an average particle ~20-25 nm. These combined hierarchical porous nanostructures are desirable in practical applications [12-13].





Samples	BET Area (m^2/g)
Degussa P25	35-45
Nanotube Array	27.9
As-grounded	44.5

(e)

Fig.3 (a) SEM image of the TiO_2 nanotubes after manually pulverized, (b) and (c) TEM images of the detailed features of the particles in (a), and (d) TEM image of a single TiO_2 nanotube obtained.(e)the table gives the BET specific areas of nanopowders.

2.2 Sensing performance of the nanoporous TiO_2 nanotubes based formaldehyde sensor

Figure 5 shows the response of the hierarchical TiO_2 nanotube-based sensor to different concentrations of formaldehyde from 10-50 ppm at ~19 °C and RH~33% under the UV irradiation. As seen in Fig.5 (a), the sensor indicates almost a linear increase as the vapor concentration increased. The sensitivity of the sensor defined as the slope of the line is ~2.4. The sensor also shows good stability and reproducibility of the response to 50 ppm formaldehyde as shown in Fig.5 (b).

Anatase TiO_2 is an n-type semiconductor due to the generated oxygen vacancies at the surface releasing the confined electrons. Under UV irradiation, it has been well documented that UV irradiation on nanostructured TiO_2 can excite the electron-hole pair according to the following scheme [1-3,14-18]:

$$TiO_2 + h\nu \longrightarrow e^- + h^+ \quad (1)$$

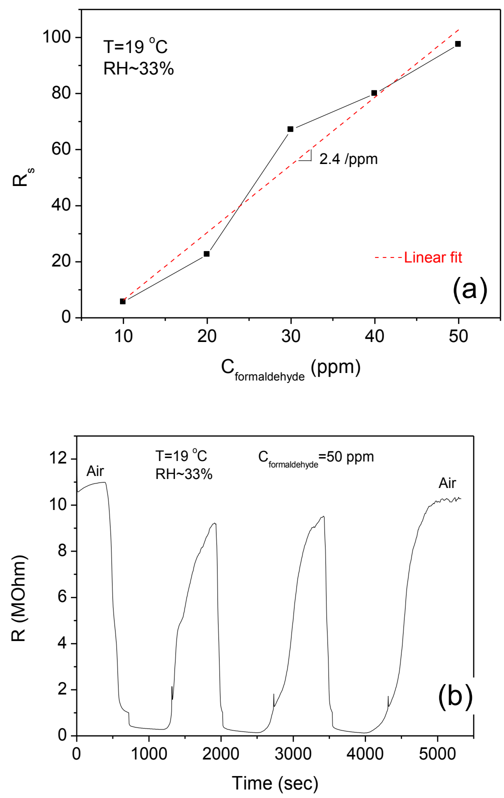


Fig.5 (a) Sensitivity of the TiO_2 nanotube-based sensor to different concentrations of formaldehyde from 10-50 ppm and (b) reproducibility of the sensor response to 50 ppm formaldehyde at ~19 °C and RH ~33% with UV irradiation.

The generated electrons would transfer into the conduction band leading to a decrease in the resistance of the bulk [25]. On the other hand, the holes would be extracted to the oxide surface and participate in the chemical oxidative reaction. They split water into the hydroxyl radicals (OH·) according to the following reaction [1-3, 14-18].

$$H_2O_{(ads)} + h^+ \rightarrow H^+ + \bullet OH \quad (2)$$

These highly active radicals can lead to more active oxidation reaction with formaldehyde according to the following reactions [14-18]:

$$HCHO + 2 \bullet OH \rightarrow CO_2 + H_2O + 2H^+ + 2e^- \quad (3)$$

$$2O^{2-}{}_{(adsorbed)} + 4H^{+} \rightarrow 2H_2O \qquad (4)$$

Thus, the generated electrons according to reaction (3) lead to the strong sensor response in Fig.5 (b). Further work will be proposed to investigate the humidity influence and selectivity of the sensor to other possible interferents such as alcohols and ammonia and testify the sensing mechanism proposed.

3 Conclusions

The nanotube-based nanoporous TiO_2 were prepared by a two-step method: the rigid highly-ordered pure TiO_2 nanotube array was first obtained by using the conventional electrochemical anodization process, followed by mechanical grinding. The sample contains the tube-like porous nanostructure which yields a high specific surface area. The as-synthesized TiO_2 based sensor showed almost linear response as a function of the concentration of formaldehyde from 10-50 ppm under UV irradiation and also a good stability and reproducibility.

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