Simultaneous Cu Doping and Growth of TiO2 Nanocrystalline Array Film as a Glucose Biosensor

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Abstract

Doping additional ions into semiconductor is a potential strategy to modify the electronic structure of semiconductor materials. By using a highly reactive colloidal Cu clusters as doping precursor, we present here the successful doping of Cu ions into TiO2 nanocrystalline that simultaneously transformed from amorphous anodic TiO2 nanotubes during a dissolution and recrystallization process. The Cu-doped TiO2 nanoparticles (Cu-TNPs) film was characterized by X-ray diffraction, scanning and transmission electron microscopy and Raman spectroscopy. The Cu-TNPs show a rugby-like shape with exposed active {101}, {001} facets and the long-axis parallel to [001] lattice direction. The substitutional Cu2+ ions dopants in TiO2 nanocrystals caused the swelling of the crystalline unit cell. Such efficient doping design facilitate the improvement of nanostructured TiO2 as a potential biosensor for glucose molecules.

Full Text

Preamble

Doping additional ions into semiconductors represents a promising strategy for modifying the electronic structure of semiconductor materials. Here, we demonstrate the successful doping of Cu ions into TiO nanocrystalline structures that simultaneously transform from amorphous anodic TiO nanotubes during a dissolution and recrystallization process, using highly reactive colloidal Cu clusters as the doping precursor. The resulting Cu-doped TiO nanoparticles (Cu-TNPs) film was characterized by X-ray diffraction, scanning and transmission electron microscopy, and Raman spectroscopy. The Cu-TNPs exhibit a rugby-like morphology with exposed active {101} and {001} facets, with the long axis oriented parallel to the [001] lattice direction. The substitutional Cu^{2} ion dopants in the TiO nanocrystals induce swelling of the crystalline unit cell. This efficient doping design facilitates the enhancement of nanostructured TiO as a potential biosensor for glucose molecules.

Keywords: Cu-doping, TiO nanocrystalline, Array structure, Biosensor, Laser ablation in liquids

Introduction

Titanium dioxide (TiO) is an important biomaterial for biomedical applications such as bone reconstruction, intravascular stents, drug delivery, and biosensing. Since Cosnier and coworkers reported in 1997 that mesoporous TiO films could function as glucose biosensors by immobilizing enzyme molecules under an amperometric approach, various nanostructured TiO materials combined with glucose oxidase have been employed in the fabrication of sensitive and stable biosensors. Although sensitivity and stability can be further improved through novel nanostructure design and/or loading of new chemical substances, challenges related to enzyme immobilization, low-temperature storage, limited shelf life, and device cost reduction remain problematic. Consequently, significant research effort has focused on substituting economical and durable inorganic electrochemical catalysts (metals, alloys, and metal oxides) for fragile enzymes, as these active materials can directly catalyze the electrochemical oxidation of glucose molecules in alkaline media. For example, Yu et al. demonstrated that TiO nanotubes decorated with Ni nanoparticles (NPs) exhibit high catalytic electroactivity for glucose oxidation with a detection limit of 2 M. Li et al. enhanced the sensitivity to 1590.9 A mM^{1} cm^{2} by loading Ni-Cu alloy NPs on TiO nanotubes. Luo et al. reported that CuO nanofibers modified TiO nanotubes for glucose sensing showed low sensitivity (79.79 A mM^{1} cm^{2}) but a good detection limit of 1 M.

Notably, in sensor applications, the actual active catalytic centers are the oxidized species of the catalytic metal, which are typically pre-oxidized before sensing and function as active electron-transfer mediators after adsorbing glucose molecules. Metal-decorated TiO usually requires multiple cyclic voltammetry (CV) sweeps in strong alkaline solution to generate an increasing number of oxidized species as active sites for metal catalysis. However, this pre-treatment step inevitably causes erosion of TiO in strong alkaline solution. Therefore, direct combination of metal oxide with TiO is desirable for fast and simple sensing detection in practical applications. Additionally, electrodes require an extra polymer binder (such as Nafion) to immobilize the TiO sensor, which may reduce catalytic active sites and degrade glucose sensitivity, while the inevitable separation of the TiO sensor from the electrode after prolonged operation can lead to loss of electrochemical activity. Moreover, specimen preparation via chemical approaches can introduce contaminants from other chemicals, impairing the biocompatibility of TiO in the sensing process. Consequently, an alternative and green approach to combine oxidized species of catalytic metal with TiO that is fixed or in-situ grown on a conductive substrate is highly desirable.

Doping represents an effective method for introducing metallic ions or oxidized species into compounds. Various methods such as sol-gel, magnetron sputtering, and solution impregnation have been proposed for doping TiO for photocatalysis and biosensing applications. However, achieving green and uniform doping in the TiO crystalline lattice while simultaneously immobilizing the as-formed doped composite on a fixed substrate remains a significant challenge. Particularly for doping in nanoscale crystals, the self-purification effect of nanoscale crystalline structures can result in segregation or accumulation of impurities on surfaces or grain boundaries. Many reports have demonstrated that TiO nanotube (TNTs) array films can be in-situ anodized on Ti substrates to form a Schottky-type contact that benefits rapid electron transport to the Ti substrate during biosensing. An appropriate and green doping strategy to achieve uniform distribution of impurities in TiO array structures together with immobilization on a Ti substrate is favorable for practical sensor applications.

Laser ablation in liquids (LAL) is a powerful technique for obtaining high-purity nanocrystals with unique physicochemical properties. LAL employs the high temperature and high pressure characteristics of laser-induced plasma plumes, which lead to unsaturated valences and defects on the surface of resulting nanocrystals due to nonequilibrium growth processes. Here, using the array structure of TNTs as an immobilized substrate, we intentionally select LAL-derived reactive Cu colloid as the dopant precursor. We demonstrate efficient in-situ doping of Cu^{2} ions through a dissolution-recrystallization process under hydrothermal treatment. The Cu^{2} ion dopants in anatase nanocrystals cause swelling of the crystal unit cell.

Experimental

Preparation of TNTs by Anodic Oxidation of Ti A 0.25 mm thick Ti foil (99.99%) was sequentially cleaned in acetone, ethyl alcohol, and water under sonication, then dried in air at room temperature. All chemical solvents and reagents were analytical grade. The anodizing electrolyte consisted of ethylene glycol containing 0.25 wt% NH F and 2 vol% H O. One side of the Ti foil contacted the electrolyte through a 15 cm diameter O-ring. Graphite served as the counter electrode in a two-electrode cell. Anodic oxidation was conducted at room temperature for 90 min at a DC voltage of 60 V. After repeated washing with deionized water and drying, some pieces of the as-formed TNTs films were annealed at 450 °C for comparative experiments, while other films were kept amorphous for the hydrothermal procedure.

Hydrothermal Treatment of LAL-Derived Cu Colloid and TNTs Colloidal Cu solution was prepared by LAL technique (Fig. S1 in ESI†). Briefly, a Cu target (99.99%) was immobilized on a support in a vessel filled with 15 mL deionized water. The Cu target was irradiated for 10 min by an Nd/YAG pulsed laser with 1064 nm wavelength, 10 Hz frequency, 10 ns pulse duration, and 100 mJ/pulse energy. The fresh colloid (15 mL) was sealed in an autoclave containing a piece of amorphous TNTs film. The hydrothermal reaction proceeded for 15 h at 200 °C. After reaction, the film was obtained and repeatedly washed in deionized water, then dried for further investigations.

Structural Characterization and Properties of Cu-Doped TiO NP Film An FEI Sirion 200 field-emission scanning electron microscopy (FESEM) was used to evaluate the morphology of the film product. Crystalline structure was investigated by high-resolution transmission electron microscopy (HRTEM) (JEM, JEOL-2010). For TEM sample preparation, a small amount of product was stripped from the Ti metal substrate and ultrasonically dispersed; the obtained suspensions were then dropped onto a holey-carbon coated molybdenum grid. Phase structure was investigated by X-ray diffraction (XRD) using a Philips diffractometer (X' pert Pro) with Cu-K radiation (= 1.5419 Å). Electrochemical CV spectra, amperometric curves, and impedance spectra of the Cu-doped TiO nanoparticles (Cu-TNPs) and blank anatase TNTs were obtained through a Zahner IM6e Electrochemical Workstation to investigate the response as nonenzymatic glucose biosensors. Zeta potential of the Cu colloid was measured by a Zetasizer 3000 HSa.

The structural features of Cu-TNPs and annealed anatase TNTs without hydrothermal treatment were further analyzed by X-ray absorption fine structure (XAFS) spectrometry, including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). XAFS spectra for Cu-K edge of the Cu-TNPs and Ti-K edge of the two anatase TNTs samples (annealed at 450 °C and hydrothermally treated) were obtained using beamline BL14W1 at the Shanghai Synchrotron Radiation Facility, administered by the Shanghai Institute of Applied Physics (Shanghai, China). Transmission (standard Cu foil, Cu O, and CuO) and fluorescence yield (Cu-TNPs and TNTs) spectra were obtained using a double-crystal Si (111) monochromator, ion chambers, and a Ge solid-state detector equipped with a Ni filter. XAFS data were analyzed using Athena software. Cu foil, Cu O, and CuO were used to extract experimental XANES features of Cu metal, Cu , and Cu^{2} ions, respectively.

Results and Discussion

Figs. 1a and 1b show top and side view images (inset) of the anodized TNTs before and after hydrothermal treatment. The original TNT-like morphology disappeared, leaving only accumulated NPs forming a Cu-TNPs film array on the Ti substrate. Fig. 1b [Figure 1: see original paper] shows the compact assembly array of these NPs, with an average particle size of <100 nm on the upper surface of the Cu-TNPs film. As seen in the inset of Fig. 1b, the NPs accumulated one by one along the direction of the original TNTs. The original thickness of the TNTs array film was approximately 4.6 m, which decreased to about 400 nm after the hydrothermal process.

Fig. 1 Top and side views (inset) of the amorphous TNTs (a) and Cu-doped TNPs (b).

HRTEM investigation provides more detailed structural and phase information. Fig. 2a [Figure 2: see original paper] shows a single particle with a rugby-like shape. The region within the white rectangle was magnified in Fig. 2b, and the corresponding selected area electron diffraction (SAED) pattern is shown in Fig. 2c. Lattice spacings of 4.74 and 3.53 Å correspond to the (002) and (101) crystalline planes of anatase TiO , with an interplanar angle of 68.3° consistent with standard data. The crystals grew along the long axis of the ellipsoid, which is parallel to the [001] lattice direction, with exposed active {100} and {101} facets. Corresponding to the assembled NPs in Fig. 2d, elemental mapping images in Figs. 2e, 2f, and 2g show the distribution of O, Ti, and Cu, respectively, in the accumulated NPs. The Cu content was significantly lower than the other two elements. Energy-dispersive X-ray spectroscopy results show atomic weight percentages of 16.35% for Ti and 0.4% for Cu (Fig. S2 in ESI†).

Fig. 2 (a) TEM image of a single Cu-TNP; (b) magnified image of the NP in (a); (c) corresponding SAED pattern of the NP in (b); and (d) TEM image of accumulated NPs. (e-g) Elemental mapping images of O, Ti, and Cu corresponding to (d).

The XRD pattern reveals composition and structural information of the products. For comparison, TNTs samples were also annealed at 450 °C for 2 h to form pure anatase phase. XRD results (Fig. 3) [Figure 3: see original paper] indicated no significant difference between anatase TNTs (red curve) and Cu-TNPs (blue curve). All peaks are consistent with standard cards [JCPDS card No. 21-1272 (anatase TiO) and JCPDS card No. 44-1294 (hexagonal Ti)]. The observed phases were consistent with HRTEM analysis. However, three peaks at 25.4° (101), 48.0° (200), and 63.0° (204) for the anatase TNTs film shifted slightly to lower angles, leading to increased d-spacings for the (101), (200), and (204) planes from 3.520, 1.892, and 1.480 Å to 3.532, 1.901, and 1.487 Å, respectively. According to Equation (S1) in ESI for tetragonal-system compounds, the changes in unit cell parameters (a, b, c) could be deduced. In this study, the a and c values increased from 3.785 and 9.513 Å to 3.803 and 9.543 Å in the anatase structure. This distortion of the anatase lattice could be attributed to doping of Cu species into the interior sites of the original lattice.

Fig. 3 XRD patterns of Cu-TNPs, anatase TNTs, and metal Ti foil.

Figure 4 [Figure 4: see original paper] shows the Raman spectra of annealed TNTs (black curve) and Cu-TNPs (red curve). Four typical Raman peaks of the anatase phase were observed at 147 cm ^{1} (E_g mode), 399 cm ^{1} (B_1g mode), 517 cm ^{1} (both A_1g and B_1g modes), and 637 cm ^{1} (E_g mode) for the TNTs sample. The dominant phase of Cu-TNPs is also anatase TiO structure, as confirmed by XRD results. Similar to many reports on metal ion introduction into TiO lattice via substitutional strategy, Raman active modes of Cu-TNPs shifted slightly to lower frequencies, appearing at 145 cm ^{1}, 397 cm ^{1}, 515 cm ^{1}, and 627 cm ^{1}. Based on extensive energetic computation results, transition metals more readily substitute Ti sites than form interstitial defects. We propose that the Raman peak shift resulted from anatase lattice enlargement due to substitutional doping of Cu ions.

Fig. 4 Raman spectra of Cu-TNPs and anatase TNTs.

Figure 5a [Figure 5: see original paper] shows Cu K-edge XAFS spectra of Cu foil, Cu O, CuO, and as-prepared Cu-TNPs, while Fig. 5b shows the corresponding XANES spectra in the pre-edge region. In the XAFS spectrum, the dominant main peak and shoulder peaks in the post-edge region of Cu-TNPs most closely resemble those of CuO. In XANES spectra, pre-edge peaks are intrinsic to various Cu ion species. Characteristic peaks of Cu^{2} ions appear at (i) approximately 8976–8979 eV (a very weak absorption caused by dipole-forbidden 1s → 3d electronic transition), and (ii) at approximately 8985–8988 eV as a shoulder peak, as well as at approximately 8995–8998 eV as an intense peak (both attributed to 1s → 4p transition). Cu ions are normally distinguished by a single peak at 8983–8984 eV. In Fig. 5b, peak A at 8978 eV and peak B at 8986 eV were observed for CuO, whereas peaks C and D at 8983 and 8982 eV correspond to pre-edge absorption of Cu ions in Cu O and Cu atoms in Cu foil. For Cu-TNPs, weak pre-edge absorption at 8978 eV (peak A) and an intense peak between 8995 and 8998 eV, both characteristic of Cu^{2} ions, were observed. However, pre-edge shoulder peak B was not observed, likely due to low dopant concentration. Therefore, the oxidation state of Cu species in the Cu-TNPs sample is Cu^{2} ions.

The post-edge region of the XAFS spectrum (EXAFS) can be presented in energy space, as in Figs. 5a and 5b. EXAFS can also be shown in wave-vector space (k-space) using k^{3}-weighted Fourier transform in Athena software. Fig. S3a in ESI shows EXAFS spectra of Ti K-edge absorption for the annealed TNT sample without hydrothermal treatment and the Cu-TNPs sample, while Fig. S3b compares Cu K-edge EXAFS spectra of Cu foil, Cu O, CuO, and Cu-TNPs in k-space. The Ti K-edge curves for annealed TNTs (black) and Cu-TNPs (red) were almost identical, indicating no significant variation in coordination environments for Ti ions in anatase TiO with and without hydrothermal treatment.

For the Cu-TNPs Cu K-edge in Fig. S3b, the oscillation trend in k-space clearly departed from the other three curves of Cu foil, Cu O, and CuO. This phenomenon further confirms that the coordination circumstances of dopants in the anatase lattice differ from those of Cu species in metallic Cu or oxides. We can thus assume that the dopants did not substantially alter the anatase lattice environment, consistent with the above data analysis.

Fig. 5 (a) XAFS spectra of Cu foil, Cu O, CuO, and Cu-TNPs; (b) XANES spectra of Cu foil, Cu O, CuO, and Cu-TNPs in (a).

Figure 6 [Figure 6: see original paper] presents a general schematic of Cu-TNPs array film formation from TNTs array film via simultaneous doping. Amorphous TNTs could dissolve in situ as TiO octahedral units in water under hydrothermal conditions, then recrystallize as anatase NPs that deposit on undissolved TNTs surfaces. These NPs accumulate along the direction of the original array after complete dissolution of the TNT film. For anatase TiO , each octahedral TiO unit connects with four other units via edge-sharing and with another four via corner-sharing. The TiO surface was negatively charged due to excess O^2 ions, whereas the zeta potential of the as-formed colloid was approximately +23.5 mV, indicating that LAL-generated colloidal Cu cluster surfaces were positively charged. Electrostatic attraction facilitates Cu doping during the recrystallization process. As substitutional dopants in the lattice, Cu^2 ions can occupy Ti ion sites in TiO octahedra. Although less bonding of substitutional species with nearest O^2 ions cannot be completely neglected, the primary effect of larger Cu^2 ions was to swell the unit cell, consistent with enlarged a and c lattice parameters according to XRD, Raman, and XAFS analysis.

Fig. 6 Schematic illustration of Cu-TNPs array film formation.

Cu is well-known for oxidizing carbohydrates without surface poisoning in biosensing applications. Glucose is a typical biosensing target as it is essential to organisms, and electrochemical technology is a popular technique for biosensing assessment. All tests were conducted using saturated Ag/AgCl as the reference electrode and Pt foil as the counter electrode. Both anatase TNTs and Cu-TNPs were used as working electrodes and sealed with epoxy resin, leaving an exposed area of 7 cm^2 on the top surface.

Fig. 7a [Figure 7: see original paper] shows CV sweeps of the two samples in 0.1 M NaOH aqueous solutions with and without 10 mM glucose. Scanning at 50 mV/s proceeded from 0 V to +0.8 V and back to 0 V. Curves A and B for anatase TNTs are nearly rectangular and show no response triggered by absorbed molecules on the electrode surface. Curve C also displays no oxidation or reduction peaks. Only curve D shows a clear current response at approximately +0.65 V, attributed to the oxidation peak of glucose on active Cu^2 /Cu^3 electron-transfer mediators. This demonstrates that the Cu-TNPs electrode can sensitively discriminate glucose molecules but does not significantly respond to interfering molecules.

Fig. 7 (a) CV sweeps of anatase TNTs in 0.1 M NaOH solution (curve A) and in 0.1 M NaOH with 10 mM glucose (curve B); Cu-TNPs in 0.1 M NaOH solution (curve C) and in 0.1 M NaOH with 10 mM glucose (curve D). (b) 30 CV sweeps of Cu-TNPs in 0.1 M NaOH with 10 mM glucose. (c) Amperometric response of Cu-TNPs and anatase TNTs at +0.65 V with successive addition of 7.5 µL glucose solution (100 mM) at 5 min intervals in 15 mL NaOH solution (0.1 M). (d) Linear relationship between oxidation current of Cu-TNPs and glucose concentration.

The reaction processes are described by Equations (1), (2), and (3). Without electrode pre-oxidation, Cu^2 ions in the TiO NPs can directly function as active sites for glucose oxidation. Thirty successive sweeps in NaOH solution with glucose (Fig. 7b) confirmed that the doped electrode remained stable under CV conditions. Fig. 7c shows amperometric responses of anatase TNTs and Cu-TNPs with addition of 7.5 µL pure glucose aqueous solution (100 mM) at 5 min intervals in 15 mL NaOH solution (0.1 M) under +0.65 V oxidation potential. No significant current response was observed for anatase TNTs, whereas current increased significantly with each glucose addition for Cu-TNPs. The initial current response of anatase TNTs was higher than that of Cu-TNPs, possibly due to enhanced interfacial impedance of the accumulated NPs (Fig. S4, see ESI). Fig. 7d shows the linear relationship between response current of Cu-TNPs and glucose concentration in NaOH solution, directly reflecting fast and stable sensor behavior of Cu-TNPs in response to glucose molecules.

To estimate the kinetics of the Cu-TNPs electrode, CV curves (Fig. S5(a)) of the specimen were measured in 0.1 M NaOH solution at different scan rates (10–150 mV/s). Response currents were read at +0.65 V. Fig. S5(b) shows the nearly linear relationship between response currents and square roots of scan rates, indicating that the electrocatalytic process on the Cu-TNPs surface was diffusion-controlled. Based on standard deviation derived from Fig. 7(d), the glucose detection limit was approximately 40 M. Fig. S6 examines Cu-TNPs selectivity by adding interfering species during amperometric response tests. Ascorbic acid, fructose, and uric acid were selected as interfering molecules.

2+3+Cu Cu+ e 3+2+Cu+ glucose Cu+ intermediate 3+2+Cu+ intermediate Cu+ product

Conclusions

In summary, we developed an efficient doping and in-situ phase modification route to obtain Cu-doped TiO nanocrystalline film via hydrothermal treatment using anodic TNTs and LAL-derived colloidal Cu clusters as precursors. The Cu-doped anatase NPs accumulated one by one along the original direction of the initial amorphous TNTs, resulting in a new TiO NPs film on the immobilized Ti substrate. The unique array morphology was preserved even after TNTs dissolution and in-situ phase transition from amorphous TiO to rugby-shaped single-crystal TiO NPs with preferred [001] long-axis growth direction and exposed active {001}, {101} facets. Substitutional Cu dopants in the anatase nanocrystals caused swelling of the crystal unit cell. The film demonstrated excellent biosensing performance in electrochemical tests using glucose molecules as targets. This experimental design for fabricating doped-TiO NPs film on immobilized substrates could be extended to construct similar structures for devices in other applications.

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