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Abstract

We present a novel strategy for simultaneous doping of Cu ions into TiO2 nanocrystals and transforming amorphous anodic TiO2 nanotubes (TNTs) into anatase nanoparticle (NP) array film. Highly reactive colloidal Cu clusters derived by laser ablation in liquids were used as doping precursor, which can react with amorphous TiO2 nanotubes to form doped anatase NPs by dissolution and recrystallization processes. The Cu-doped TiO2 NPs (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, red shift of the absorption edge, and enhanced absorption in the visible-light region. The green and efficient doping design would facilliate the ongoing effort toward improving nanostructured TiO2 as a practical biosensor for glucose molecules.

Full Text

Preamble

Simultaneous Cu Doping and Growth of TiO_2 Nanocrystalline Array Film as a Glucose Biosensor

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Abstract: We present a novel strategy for simultaneous doping of Cu ions into TiO_2 nanocrystals and transforming amorphous anodic TiO_2 nanotubes (TNTs) into anatase nanoparticle (NP) array film. Highly reactive colloidal

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Keywords: Cu-doping, TiO_2, Nanocrystalline, Array, Biosensor

Introduction

Titanium dioxide (TiO_2) is a potential biomaterial of great interest in biomedical fields such as bone reconstruction, intravascular stents, drug delivery, and biosensing, due to its high stability, nontoxicity, low cost, and other favorable properties. Since Cosnier and coworkers reported that mesoporous TiO_2 films could work as glucose biosensors by immobilizing enzyme molecules under an amperometric approach in 1997, the application of various nanostructured TiO_2 to combine with glucose oxidase has been the main aspect in fabricating sensitive and stable biosensors. Although sensitivity and stability have been further improved through designing new nanostructures and/or loading new chemical substances, difficulties arising from immobilizing enzymes, storing at low temperature, prolonging validity, and lowering device cost remain troublesome. Consequently, it has become an important endeavor to substitute economical and durable inorganic electrochemical catalysts (metals, alloys, and metal oxides) for fragile enzymes, as these active materials could directly catalyze the electrochemical oxidation of glucose molecules in alkaline media. For example, Yu et al. proved that TiO_2 nanotubes decorated with Ni nanoparticles displayed high catalytic electroactivity for glucose oxidation with a detection limit of 2 M, while Li and coworkers enhanced the sensitivity to 1590.9 A mM^{-1} cm^{-2} by loading Ni-Cu alloy nanoparticles on TiO_2 nanotubes. Meanwhile, Luo et al. reported that CuO nanofibers modified TiO_2 nanotubes in glucose sensing exhibited a low sensitivity of 79.79 A mM^{-1} cm^{-2} but a good detection limit of 1 M. Even though these catalysts displayed satisfactory performance by combining with nanostructured TiO_2 whose large specific surface areas could facilitate improved sensitivity and stability of the device, new challenges are still ensuing.

On the one hand, note that the real active catalytic centers are the oxidized species of catalytic metal, which are usually oxidized before sensing and function as active electron-transfer mediators after absorbing glucose molecules. The metal decorated on TiO_2 usually undergoes multiple cyclic voltammetry (CV) sweeping in strong alkali solution to incite an increasing number of oxidized species as active sites for metal catalysis. However, this pre-treatment step compels TiO_2 to venture erosion in strong alkali solution. Herein, directly combining the metal oxide with TiO_2 is desirable for fast and simple sensing detection in application. On the other hand, the electrode needs an extra polymer binder (such as Nafion) to immobilize the TiO_2 sensor. This may reduce catalytic active sites and degrade glucose sensitivity, and the inevitable separation of the TiO_2 sensor from the electrode after persistent operation can lead to loss in electrochemical activity. Moreover, synthesis of specimens via common chemical approaches could introduce contaminations from other chemicals, which would impair the biocompatibility of TiO_2 in the sensing process. Under overall analysis, an approach to combine oxidized species of catalytic metal with TiO_2 fixed or in-situ grown on a conductive substrate through a green and convenient method is thus desirable.

Doping is an effective way to introduce ions or oxidized species of metal into compounds. Various methods such as sol-gel, magnetron sputtering, and solution impregnation have been proposed for doping metal ions in TiO_2 for photocatalysis and biosensing. However, achieving green and uniform doping in the TiO_2 crystalline lattice while simultaneously immobilizing the as-formed doped composite on a fixed substrate remains a challenge. Particularly for doping in nanoscale crystals, the self-purification effect of nanoscale crystalline even results in segregation or accumulation of impurities on surfaces or grain boundaries. Many reports have proved that TiO_2 nanotubes (TNTs) array film could be in-situ anodized on Ti substrate to form a Schottky-type contact which enhanced rapid transport of surface reaction electrons to Ti substrate in biosensing, but reserving the array structure after doping is difficult. An appropriate and green doping strategy to obtain uniform distribution of impurities in TiO_2 array structure together with immobilized Ti substrate is favorable for practical film applications.

Laser ablation in liquid (LAL) is a facile and green technique to obtain high purity nanocrystals with unique physicochemical properties. LAL employs the high temperature and high pressure characteristics in laser-induced plasma plume, which lead to unsaturated valences and defects on the surface of the resultant nanocrystals because of the nonequilibrium growth processes. Here, to use the array structure of TNTs as an immobilized substrate, we intentionally selected LAL-derived reactive Cu colloid as the precursor of dopants. We demonstrated the efficiency of in-situ doping of Cu^{2+} ions in TiO_2 in a dissolution–recrystallization process under hydrothermal treatment. The doped TiO_2 nanoparticles (NPs)-assembled array structure was characterized using field-emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and Raman spectrometry. The Cu^{2+} ion dopants in anatase nanocrystals increased swelling of the crystal unit cell, as well as redshift of the absorption edge, and enhanced absorption in the visible-light region.

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, and then dried in air at room temperature. All chemical solvents and reagents were analytical grade. The anodizing electrolyte was ethylene glycol solvent containing 0.25 wt% NH_4F and 2 vol% H_2O. One side of the metal Ti foil contacted the electrolyte through a 15 cm diameter O-ring. Graphite was used 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 2 h for subsequent comparative experiments, while some films were kept amorphous for the hydrothermal procedure.

Hydrothermal Treatment of LAL-Derived Cu Colloid and TNTs Film

Colloidal Cu solution was prepared by LAL technique. Briefly, a Cu target (99.99%) was immobilized on a supporter in a vessel filled with 15 mL deionized water. The Cu target was then 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 was sealed in an autoclave containing a piece of amorphous TNTs film. The hydrothermal reaction proceeded for 15 h at 200 °C. After the reaction, the film was obtained and repeatedly washed in deionized water, and finally dried for further investigations.

Structural Characterization and Properties of Cu-Doped TiO_2 NP Film

An FEI Sirion 200 FESEM was used to evaluate the morphology of the film product. The crystalline structure was investigated by HRTEM (JEM, JEOL-2010). For TEM sample preparation, a small amount of the product was stripped from the Ti metal substrate and then ultrasonically dispersed in ethanol, and the obtained suspensions were then dropped onto a holey-carbon coated tungsten grid. The phase structure was investigated using XRD with a Philips diffractometer (X' pert Pro) with Cu-Kα radiation ($\lambda = 1.5419$ Å). Electrochemical CV spectra, amperometric curves, and impedance spectra of the Cu-doped TiO_2 NPs (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 through X-ray absorption fine structure (XAFS) spectrometry, including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The XAFS spectra for Cu-K edge of the Cu-TNPs and Ti-K edge of the two anatase

TNTs samples (sample annealed at 450 °C and hydrothermally treated sample) were obtained using beamline BL14W1 at the Shanghai Synchrotron Radiation Facility, administered by Shanghai Institute of Applied Physics (Shanghai, China). Transmission (standard Cu foil, Cu_2O, 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 Ni filter. The XAFS data were analyzed using Athena software. Cu foil, Cu_2O, and CuO were used to extract the experimental XANES features of Cu metal, Cu^+, and Cu^{2+} ions, respectively.

Results and Discussion

Figs. 1a and 1b show the top and side view images (inserted plot) of the anodized TNTs before and after hydrothermal treatment. The original TNTs-like shape disappeared and only NPs accumulated, depicted as a Cu-TNPs film array on the Ti substrate. Fig. 1b [Figure 1: see original paper] shows the compact assembly array of irregular NPs, with an average particle size of <100 nm standing on the upper surface of the Cu-TNPs film. As seen from the inserted plot in Fig. 1b, the NPs accumulated one by one along the direction of the original TNTs.

Fig. 1 Top and side views (inserted plot) 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 in a rugby-like shape. The partial zone in the white rectangle was magnified in Fig. 2b, and the corresponding selected area electron diffraction (SAED) pattern is shown in Fig. 2c. The lattice spacings of 4.74 and 3.53 Å correspond to (002) and (101) crystalline planes of anatase TiO_2, and the angle between the two planes (68.3°) is consistent with standard data. The crystals grew along the long-axis of the ellipsoid that is parallel to the [001] lattice direction with exposed active {100} and {101} facets. Corresponding to the assembled NPs in Fig. 2d, the elemental mapping images in Figs. 2e, 2f, and 2g display the dispersion of O, Ti, and Cu, respectively, in the accumulated NPs. The amount of Cu was significantly less than the other two elements. Energy-dispersive X-ray spectroscopy shows that the atomic ratio of Ti to Cu was 16.35 to 0.4 (Fig. S1 in ESI†).

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

The XRD pattern shows the 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. The XRD results (Fig. 3 [Figure 3: see original paper]) indicated no significant difference between the anatase TNTs (red curve) and the Cu-TNPs (blue curve). All peaks are consistent with standard card data

[JCPDS card No. 21-1272 (anatase TiO_2) 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) of the anatase TNTs film shifted slightly to lower angles, thereby leading to increased d-spacings of (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 change 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. The distortion of the anatase lattice could be due to doping of Cu species in the inner sites of original lattices.

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

Figure 4 [Figure 4: see original paper] shows the Raman spectra of the annealed TNTs (black curve) and Cu-TNPs (red curve). The four typical Raman peaks of the anatase phase were found 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 the anatase TiO_2 structure as confirmed by XRD results. Similar to many reports about introducing metal ions into TiO_2 lattice by substitutional strategy, Raman active modes of Cu-TNPs slightly shifted to lower frequency zones, respectively at 145 cm^{-1}, 397 cm^{-1}, 515 cm^{-1}, and 627 cm^{-1}. Based on extensive computational results, it is especially easier for transition metals to substitute Ti sites than to form interstitial defects. Here, we propose that the shift of Raman peaks was due to enlargement of the anatase lattice by substitutional doping of Cu ions.

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

Fig. 5a [Figure 5: see original paper] shows the Cu K-edge XAFS spectra of Cu foil, Cu_2O, CuO, and the as-prepared Cu-TNPs, and Fig. 5b shows the corresponding XANES spectra of these samples in the pre-edge region. In the XAFS spectrum, it is obvious that the dominant main peak and shoulder peaks in the post-edge region of Cu-TNPs most closely resemble those of CuO. In the XANES spectra, pre-edge peaks are always intrinsic for various Cu ion species. The characteristic peaks of Cu^{2+} ions are found at (i) approximately 8976 eV to 8979 eV (a very weak absorption caused by the dipole-forbidden 1s → 3d electronic transition), and (ii) at approximately 8985 eV to 8988 eV as a shoulder peak, as well as at approximately 8995 eV to 8998 eV as an intense peak (both attributed to the 1s → 4p transition). Cu^{+} ions are normally discriminated by a single peak at 8983 eV to 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 were found at 8983 and 8982 eV, respectively, corresponding to pre-edge absorption of Cu^{+} ions in Cu_2O and Cu atoms in Cu foil.

For Cu-TNPs, weak pre-edge absorption at 8978 eV (peak A) and an intense peak between 8995 eV and 8998 eV, both belonging to Cu^{2+} ions, were observed. However, the pre-edge shoulder peak B wasn’ t observed, probably due to low dopant concentration. Therefore, the oxidation state of Cu species in the Cu-

TNPs sample was 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. S2a in ESI shows the EXAFS spectra of Ti K-edge absorption of the annealed TNT sample without hydrothermal treatment and the Cu-TNPs sample, while Fig. S2b compares the Cu K-edge EXAFS spectra of Cu foil, Cu_2O, CuO, and Cu-TNPs in k-space. The Ti K-edge curves for the annealed TNTs (black) and Cu-TNPs (red) were almost identical. Therefore, the coordination environments show no significant variation for Ti^{4+} ions in anatase TiO_2 with and without hydrothermal treatment. For the Cu-TNPs Cu K-edge in Fig. S2b, the oscillation trend in k-space apparently departed from the other three curves of Cu foil, Cu_2O, and CuO, respectively. This phenomenon further proves that the coordination circumstances of dopants in the anatase lattice varied from Cu species in metallic Cu or oxides. We could thus assume that the dopants did not change the anatase lattice environment significantly, which was consistent with the above data analysis.

Fig. 5 (a) XAFS spectra of Cu foil, Cu_2O, CuO, and Cu-TNPs; (b) XANES spectra of Cu foil, Cu_2O, CuO, and Cu-TNPs in (a).

Figure 6 [Figure 6: see original paper] shows the general schematic view of Cu-TNPs array film formation from TNTs array film with a simultaneous doping process. Amorphous TNTs could dissolve in situ as TiO_6 octahedral units in water under hydrothermal conditions and then recrystallize as anatase NPs, which are inclined to deposit at the undissolved surfaces of TNTs. These NPs accumulate along the direction of the original array after complete dissolution of the TNT film. For the anatase phase of TiO_2, each octahedral TiO_6 unit is connected with four other units by edge-sharing and with another four by corner-sharing. In addition, the surface of TiO_6 was negatively charged because of the surplus of O^{2-} ions, whereas the zeta potential of the as-formed colloid was approximately +23.5 mV, thereby indicating that the surfaces of LAL-generated colloidal Cu clusters were positively charged. Electrostatic attraction results in Cu doping during the recrystallization process. As substitutional dopants in the lattice, Cu^{2+} ions can occupy the site of Ti^{4+} ions in TiO_6 octahedrons. Although less bonding of the substitutional species with the nearest O^{2-} ions cannot be neglected entirely, the major role of larger Cu^{2+} ions was to swell the unit cell in accordance with the enlarged a and c lattice parameters according to XRD, Raman, and XAFS analysis.

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

Cu is well known for oxidizing carbohydrates without surface poisoning in biosensing. Glucose is a typical biosensing target because 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 the 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 the CV sweeps of the two samples in 0.1 M NaOH aqueous solutions with and without 10 mM glucose solute. The sweep at 50 mV/s was from 0 V to +0.8 V and then back to 0 V. Curves A and B, which are for the anatase TNTs, are close to rectangles and did not show any response triggered by absorbed molecules on the electrode surface. Curve C also did not display any oxidation or reduction peaks. Only curve D showed an apparent current response at approximately +0.65 V, which was attributed to the oxidation peak of glucose on active Cu^{2+}/Cu^{3+} electron-transfer mediators. The reaction processes are described using Equations (1), (2), and (3). Without pre-oxidation of the electrode, the Cu^{2+} ions in the TiO_2 NPs could directly function as active sites for glucose oxidation. The 30 successive sweeps in NaOH solution with glucose (Fig. 7b) confirmed that the doped electrode was stable under CV. Fig. 7c shows the amperometric responses of the anatase TNTs and Cu-TNPs with added 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 found for the anatase TNTs, whereas the current increased significantly at each glucose addition for Cu-TNPs. The initial current response of the anatase TNTs was higher than that of Cu-TNPs, possibly due to enhanced interfacial impedance of the accumulated NPs (Fig. S3, see ESI). Fig. 7d shows the linear relationship between the response current of Cu-TNPs and glucose concentration in NaOH solution. This relationship directly reflects the fast and stable sensor behaviors of Cu-TNPs in response to glucose molecules.

Fig. 7 (a) CV sweeping of anatase TNTs in 0.1 M NaOH solution (curve A) and in 0.1 M NaOH solution with 10 mM glucose (curve B); Cu-TNPs in 0.1 M NaOH solution (curve C) and in 0.1 M NaOH solution with 10 mM glucose (curve D). (b) 30 times CV sweeping of Cu-TNPs in 0.1 M NaOH solution 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 the oxidation current of Cu-TNPs and glucose concentration.

Conclusions

In summary, we developed an efficient doping and in-situ phase modification route to obtain Cu-doped TiO_2 nanocrystalline film by 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_2 NPs film on the immobilized Ti substrate. The unique array morphology was observed even after TNTs dissolution and in-situ phase transition from amorphous TiO_2 to rugby-shaped single-crystal TiO_2 NPs with preferred [001] long-axis growth direction and exposed active {001}, {101} facets. The substitutional Cu dopants in the anatase nanocrystals caused swelling of the crystal unit cell, obvious red shift of the absorption edge, and enhanced absorption in the visible-light region. The film showed excellent biosensing performance in electrochemical tests using glucose molecules as targets. The present experimental design for fabricating doped-TiO_2 NPs film on immobilized substrate could be extended to construct similar structures for devices in other applications.

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

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