Enhanced photoactivity of Cu-deposited titanate nanotubes for removal of bisphenol A

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One-dimensional nanotubes are promising nanostructured materials for a wide variety of environmental applications. In this study, the Cu-deposited titane nanotubes (TNTs) were fabricated using an alkaline hydrothermal method at 150 °C and then 0.5–2 wt% Cu(II) ions were photodeposited onto the calcined TNTs at 500 °C for enhanced photodegradation of bisphenol A (BPA) under illumination of 365 nm UV light. The as-synthesized TNTs showed tubular structures with the outer diameter and inter-layer spacing of 7–10 and 0.8 nm, respectively. The X-ray absorption near-edge spectral results provided a strong support on the partially structural change from layered titinate to anatase TiO2 through the distortion of octahedral TiO6 unit at 500 °C and the production of mixture of CuO and Cu2O after photodeposition of Cu ions, resulting in the formation of Cu-deposited TiO2/TNT nanocomposites to enhance the photocatalytic activity. A nearly complete removal of BPA by the Cu-deposited TiO2/TNTs was observed, and the pseudo-first-order rate constants (kobs) for BPA photodegradation by Cu-deposited TiO2/TNTs at pH 7.0 were 1.8–5.2 and 4.3–12.7 times higher than those of pure Degussa P25 and ST01 TiO2, respectively. In addition, the kobs for BPA photodegradation reached the maximum value of 0.253 ± 0.032 min⁻¹ at 1 wt% Cu(II). The X-ray photoelectron spectra showed that the ratio of Cu2O to total Cu increased from 3.2% in the dark to 35.2% after illumination of 365 nm UV light for 5 min. In addition, electron paramagnetic resonance results indicated that the copper ions could serve as the electron mediators to prolong the retention time of photo-generated radicals, resulting in the enhancement of photodegradation efficiency and rate of BPA by Cu-deposited TiO2/TNTs.

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1. Introduction

The development of efficient photocatalysts for removal of emerging pollutants has received considerable attention for treatment of recalcitrant compounds in water and wastewater. Nanostructured TiO2 is one of the most promising materials widely used in photocatalytic and photovoltaic technologies [1]. In addition to TiO2 nanoparticles, the one-dimensional (1D) titanate nanotubes (TNTs) are promising nanostructured materials for energy and environmental applications [2,3]. The fabrication of TNTs has been extensively studied and alkaline hydrothermal treatment is one of the most often used methods for preparation of TNTs due to the low cost and simplicity [3–5]. However, the TNTs prepared by the alkaline hydrothermal treatment are H-titanate forms and show inferior performance on photodegradation of pollutants when compared with that of Degussa P25 TiO2 [1,6].

Several strategies have been developed for enhancement of photocatalytic ability of TNTs. A suitable and feasible strategy to retain the photocatalytic activity of TNTs is the post-thermal treatment to form well-crystallized TiO2 while still retaining the tubular structures [7]. Several studies have demonstrated the enhanced photocatalytic activity of calcined TNT towards organic dye photodegradation [8–10]. Addition of transition metal ions as dopants to decrease the recombination rate or to shift the adsorption wavelength is another promising method to improve the degradation efficiency and rate of organic pollutants in aqueous solutions. Several studies have depicted that addition of metal ions such as V, Zr, Fe, Ag, Co, and Cu could enhance the photodegradation efficiency of titanium-based materials [11–14]. The Cu(II) ion is one of the effective catalytic species for the enhancement of photocatalytic activity of TiO2 [15,16]. Doong et al. [16] depicted that Cu(II) can be reduced to the low-valent species in the presence of formate and then deposited on the surface of TiO2, resulting in the decrease in electron-hole recombination rate and the acceleration of electron transfer rate to enhance the photodegradation efficiency and rate of methylene blue. Several metal ions including Ag, Pt, and Fe have also been...
employed to enhance the photodegradation efficiency and rate of CO, methylene orange, and acetone by 1D nanostructured titanates [17–19]. However, the effect of Cu ions on the enhanced photocactivity of TNTs towards emerging pollutant degradation remains unclear.

Endocrine disrupting chemicals such as bisphenol A (BPA), estradiol, and estrone are typical emerging pollutants commonly found in the aquatic environments [20,21]. BPA is a known chemical used for manufacturing polycarbonate resins and stabilizing plastics. This compound can be easily released into the environment through the domestic sewages and industrial wastewaters, which may cause endocrine-disruptive effects on human beings and aquatic biota [22]. Various technologies including adsorption [23], chemical oxidation [24], advanced oxidation processes [25,26], and photocatalysis [27–29] have been developed to remove BPA from water and wastewater. Among the technologies developed, photocatalytic oxidation is one of the most effective methods for elimination of BPA in aqueous solutions [28]. Guo et al. [29] used three-dimensional mesoporous TiO2 nanocatalysts to photodegrade BPA and found that the degradation rate of BPA by mesoporous TiO2 was 4 times higher than that by Degussa P25 TiO2. However, the photocatalytic degradation of BPA by 1D Cu-deposited nanomaterials has rarely been reported.

In this study, the Cu-deposited TNTs were fabricated using an alkaline hydrothermal method and calcined at 500 °C for 4 h to form TiO2/TNT nanocomposites. The 0.5–2 wt% Cu ions were then photo-deposited onto the TiO2/TNT surfaces for enhanced photodegradation of BPA. The morphology as well as microstructures of as-synthesized and Cu-deposited TiO2/TNTs including surface area, pore texture, and crystallinity were characterized by scanning/transmission electron microscopy (SEM/TEM), surface area analysis, X-ray diffractometry (XRD), and X-ray absorption near-edge spectroscopy (XANES). The photocatalytic activity of Cu-deposited TiO2/TNTs towards BPA degradation was further evaluated. In addition, the change in photo-generated radicals were also measured to elucidate the possible role of Cu(II) ions in photodegradation of BPA by Cu-deposited TiO2/TNTs.

2. Materials and methods

2.1. Chemicals

All chemicals were used as received without further treatment. ST01 TiO2 powder was obtained from Ishihara Sangyo Ltd. (Tokyo, Japan). Sodium hydroxide pellets (NaOH) and copper(II) nitrate pentahydrate (Cu(NO3)2·5H2O, 98%) were purchased from Riedel-de Haén (Seelze, Germany). Hydrochloric acid (36.5–38.0%) was purchased from J.T. Baker (Phillipsburg, NJ). Bisphenol A (99% purity) was purchased from Aldrich. All solutions were prepared with high-purity bidistilled deionized water (Millipore Co., 18.3 MΩ cm) unless otherwise mentioned.

2.2. Fabrication of Cu-deposited TNTs

The 1D nanostructured TNTs were synthesized by a hydrothermal method using ST-01 TiO2 as the starting material. In general, 1.6 g of ST01 TiO2 powders were dispersed into 20 mL of 10 M NaOH in a 30 mL-Teflon-lined vessel. The suspension was ultrasonicated for 1 h at room temperature and then the hydrothermal reaction was carried out at 150 °C for 24 h. After cooling down to room temperature, the hydrothermal products were washed with 0.1 N HCl and bidistilled water repeatedly until the pH of solution was around 7.0. Ethanol was then used to replace water, and the hydrothermal products were separated from the washing solution by filtration, dried at 60 °C for 10 h in oven. The as-synthesized TNTs were then calcined at 500 °C in air for 4 h to form TiO2/TNT nanocomposites.

The Cu-deposited TiO2/TNTs were prepared by the photodeposition method. Typically, 1 g/L of calcined TiO2/TNT composites were dispersed in distilled water under vigorous stirring, and various amounts of Cu(NO3)2 solution were added into the solution to get the final concentrations of 5–40 mg/L Cu(II). The suspension was irradiated by 365 nm UV light for 4 h at 25 °C, and the obtained Cu-deposited TiO2/TNTs were harvested by filtration, dried at 60 °C for 10 h in oven. The Cu(II) concentrations in filtrates were then determined by inductively coupled plasma optical emission spectroscopy, and the aqueous Cu(II) concentration was 0.25, 9.6 and 18.4 mg/L, when the added Cu(II) concentrations were 5, 20 and 40 mg/L, respectively, which indicates that the deposited amounts of Cu(II) onto the TiO2/TNT nanocomposites were ca. 0.5, 1 and 2 wt%. In addition, the obtained Cu-deposited TiO2/TNTs were stored in the glove box under N2 atmosphere until analysis to minimize the oxidation of copper species.

2.3. Photocatalytic activity of BPA by Cu-deposited TiO2/TNTs

The photocatalytic degradation reaction was carried out in a hollow cylindrical photoreactor equipped with a water jacket. The inner wall of the water jacket is made of fused silica and the outer wall is made of Pyrex. Four 8 W black light blue lamps (BLB lamp, ~875, Winstar Lighting Co., Taipei, Taiwan) with 365 nm as the major peak wavelength were used as the light source and positioned within an inner part of the photoreactor encompassing 4 quartz tubes. The reactor was cooled by circulating water through a Pyrex jacket and maintained the temperature at 25 °C. The 1 g/L titanium-based nanomaterials including Cu-deposited TiO2/TNTs and commercial TiO2 nanoparticles were added in a 15 mL of BPA solution. Prior to the illumination, the suspension was magnetically stirred in the dark for 30 min to ensure the adsorption equilibrium of BPA onto the catalysts. After the equilibrium, the UV light was turned on and aliquots (1 mL) were withdrawn from the solution at various time intervals for analysis after removal of catalysts by centrifugation at 14,000 rpm for 5 min. After centrifugation, 0.5 mL of supernatant of each sample was transferred to a 2 mL HPLC vial and the aqueous concentration of BPA was determined by a high-performance liquid chromatograph (HPLC) equipped with C-18 column (LUNA 5u 100A, 4.6 mm × 250 mm, Phenomenex) and a diode array detector (HPLC-DAD, Agilent Technologies, series 1200). The isocratic methanol/acetonitrile/water mixture (50:30:20, v/v) at a flow rate of 0.5 mL/min was used as the elute. In addition, absorbance at 225 nm was used to determine the BPA concentration.

2.4. Reaction kinetics

It is known that the rate of photocatalytic degradation of organic pollutants at liquid-solid interface can be described by the Langmuir–Hinshelwood kinetic model [13,30]:

\[
\frac{dC}{dt} = k_{app} \frac{S_r C}{1 + K_r C}
\]

where \( r_0 \) is the reaction rate of BPA photodegradation, \( C \) is the aqueous concentration of BPA, \( k_{app} \) is the limiting-step rate constant of reaction at maximum coverage under the given conditions, \( S_r \) is the total reaction sites of Ti-based nanomaterials, and \( K_r \) is the
adsorption coefficient of BPA. When the BPA concentration (C) is low, Eq. (1) can be simplified to the pseudo-first-order kinetics:

$$\ln \left( \frac{C}{C_0} \right) = -k_{\text{obs}}t$$

(2)

where $k_{\text{obs}}$ is the pseudo-first-order rate constant for BPA photodegradation (min$^{-1}$).

2.5. Characterization

The surface morphology of as-synthesized and Cu-deposited TiO$_2$/TNTs was characterized by SEM (JEOL JSM-6700F OXFORD INCA ENERGY 400). All the samples were Pt-coated using Ion Sputter e-1030 (Hitachi, Tokyo) to increase the conductivity of the sample surface. After coating with Pt, samples were placed under high vacuum (10$^{-3}$–10$^{-7}$ mbar) conditions. An acceleration electron voltage of 5 kV was applied to obtain the SEM images. In addition, the dimension and morphology of nanostructured titane materials were examined by TEM (JEOL JEM-2010) and high resolution transmission electron microscopy (HRTEM, JEOL, JEM-3000F) at accelerating voltages of 200 and 300 kV, respectively.

The Brunauer–Emmett–Teller (BET) specific surface area and pore size distribution were carried out by nitrogen adsorption and desorption at 77 K using a surface area and porosimetry system (ASAP 2020, Micromeritics). In addition, pore, radii and volumes of the nanostructured materials can be determined using Barrett, Joyner and Halenda’s (BJH) mathematical models. The BJH method for calculating pore size distributions is based on a model of the adsorbent as a collection of cylindrical pores.

The crystalline structures were identified by XRD using X-ray diffractometer (Bruker NEW D8 ADVANCE, Germany) with a Lynx eye high-speed strip detector and Ni-filtered Cu Kα radiation ($\lambda = 1.5406 \text{Å}$) operating at a generator voltage and an emission current of 40 kV and 40 mA, respectively. The X-ray diffraction patterns were acquired over the 2θ ranging from 20° to 90° with sampling step width of 0.05° (step time = 0.5 s).

The X-ray adsorption near-edge structure (XANES) spectra of Ti K-edge and Cu L$_{2,3}$-edge were measured using BL-16A and BL-20A, respectively, at National Synchrotron Radiation Research Center (NSRRC, Hsinchu, Taiwan) in which the electron storage ring was operated at 1.5 GeV with a beam current of 300 mA. The Ti K-edge absorption spectra were measured in a total X-ray fluorescence yield mode at room temperature using a Lytle detector with powder sample dispersed onto Kapton tape. X-rays were monochromated by using a Si(1 1 1) double monochromator before reflecting off a higher-order harmonic light reflection mirror. The photon energies were calibrated using the L$_3$-edge of a Mo foil at 2520 eV. Energy steps as small as 0.2 eV were employed near the absorption edges with an accounting time of 2 s per step. In addition, the Cu L$_{2,3}$-edge absorption spectra were detected using high-energy spherical grating monochromator beam-line with a micro-channel-plate detector system. The photon energy was calibrated with 0.1 eV using the Cu L$_3$ white line at 931.2 eV of a CuO reference.

The photo-generated free radicals from the photodegradation of BPA by Cu-deposited TiO$_2$/TNTs in the presence of 4.4 mM 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was examined using an electron paramagnetic resonance (EPR) spectrometer (Bruker, EMX-10, Germany) working at X-band frequency of 9.49–9.88 GHz with power of 8.02 mW. A 250 W Xe lamp (Ushio Inc.) at major output wavelength of 365 nm was equipped to the sample cavity by lined optical fiber. Oxygen-saturated Cu-deposited TiO$_2$/TNT suspensions containing DMPO and BPA were irradiated with UV light at room temperature. After irradiated for 5–30 min, the spectra of trapped charges in solutions were recorded at room temperature. The instrumental conditions were set at a center field of 3400–3510 G and a sweep width of 200 G.

3. Results and discussion

3.1. Characterization of as-synthesized and calcined TNTs

Fig. 1 and Fig. S1 show the SEM and TEM images of as-synthesized TNTs and Cu-deposited TiO$_2$/TNTs. The as-synthesized TNTs showed tubular structures with lengths of few μm (Fig. 1a and Fig. S1a). In addition, the TEM and HRTEM images of the as-synthesized TNTs exhibited uniform diameters along with the length (Fig. 1b). The open-ended and multi-layered tubular structures of as-synthesized TNTs shown in TEM images indicated that the inner and outer diameters were 4–6 and 7–10 nm, respectively, with interlayer spacing was about 0.8 nm, which are in good agreement with the previous report [4]. After post-thermal treatment at 500°C for 4 h and deposition of Cu ions, an obvious change in surface morphology was observed in which the tubular structures and nanoparticles coexisted (Fig. S1b). The TEM images of Cu-deposited TiO$_2$/TNTs showed the production of well-crystallized nanoparticles on the tube walls (Fig. 1c). In addition, the EDS analysis indicated that the nanocomposites contained Ti, O and Cu (Fig. 1d), which means that the Cu species has deposited onto the surface of TNTs.

The microstructures of as-synthesized TNTs and Cu-deposited TiO$_2$/TNTs including crystallinity, surface area, and pore structure were further examined. The XRD patterns of the as-synthesized TNTs showed peaks centered at 9.5°, 24.1°, 28.3°, and 48.2° 2θ (Fig. 2). No anatase peak appeared, which indicates the complete conversion of STO1 TiO$_2$ to 1D layered trititanate nanomaterials after hydrothermal treatment [31,32]. The EDS analysis showed that the as-synthesized TNTs contained 72.5% Ti, 25.7% O and a small amount of Na (1.8%), suggesting that the chemical structure of as-synthesized TNTs was Na$_2$Ti$_3$O$_7$·H$_2$O. After calcination at 500°C and photo-deposition of Cu, a new peak at 25.3° 2θ, which can be assigned as the (101) orientation of anatase TiO$_2$ (JCPDS 21-1272), was found. In addition, several new small peaks centered at 24.6°, 29.7°, 32.9°, and 44.3° 2θ appeared in XRD patterns of Cu-deposited TiO$_2$/TNTs, presumably attributed to the formation of TiO$_2$(B) [33]. However, no peak of Cu-based nanoparticles was observed because of the low added amount of Cu(II) ions (0.5–2 wt%). The XPS was further used to confirm the species of Cu ions in Cu-deposited TiO$_2$/TNTs. After deconvolution of Cu 2p$_{1/2}$ XPS spectra shown in Fig. 2b, peaks centered at 933.6 and 932.7 eV, which can be assigned as CuO and Cu$_2$O, respectively, were clearly obtained, indicating the formation of mixture of Cu$_2$O and CuO (Cu$_2$O). It is noteworthy that both CuO and Cu$_2$O can absorb visible light. Therefore, the diffuse reflectance UV–vis spectrometry was used to characterize the optical property of Cu-deposited TiO$_2$/TNTs. Fig. S2 shows the UV–vis spectra of Cu-deposited TiO$_2$/TNT nanocomposites. The absorbance of Cu-deposited TiO$_2$/TNTs started to increase at 600–620 nm and the intensity increase upon increasing Cu amounts from 0.5 to 2 wt%, indicating that Cu(II) ions were photo-deposited onto the surface of TiO$_2$/TNTs to form Cu$_2$O for UV and visible light absorbance.

Fig. 3 shows the nitrogen adsorption–desorption isotherms and pore size distribution of the as-synthesized TNTs and Cu-deposited TiO$_2$/TNTs. The adsorption isotherm of as-synthesized TNTs showed a typical type IV isotherm with H3 hysteresis loop in the relative pressure ($P/P_0$) range of 0.5–0.8, indicating the characteristics of mesoporous materials. The calculation of as-synthesized TNTs increased the pore diameter, and resulted in
the shift in hysteresis loops to the high relative pressure region of 0.8–0.95. The pore size distribution of as-synthesized and Cu-deposited TiO$_2$/TNTs, derived from the BJH method, showed that the average pore diameters were 4.6 and 5.2 nm, respectively. It is noteworthy that the surface area and pore size of ST01 TiO$_2$ were 305 m$^2$/g and 12.7 nm, respectively. When TiO$_2$ nanoparticles were transformed to the tubular structures during the hydrothermal processes, the specific surface area increased to 420 m$^2$/g. After calcination at 500°C and deposition of Cu ions, however, the specific surface area decreased dramatically to 98 m$^2$/g because of the collapse of tubular structures and production of crystalline phase of anatase TiO$_2$ and mixture of CuO and Cu$_2$O, which is in good agreement with the TEM images.

XANES was used to understand the local symmetry of titanium and copper ions of the hydrothermal products. Fig. 4 shows the Ti K-edge and Cu L$_{2,3}$-edge XANES spectra for the as-synthesized TNTs and Cu-deposited TiO$_2$/TNTs. For Ti K-edge spectra, the characteristic peaks in the pre-edge region of 4965–4976 eV, denoted as P$_1$, P$_2$, P$_3$, and P$_4$, corresponded to the transitions from core 1s level to unoccupied 3d states (Fig. 4a) [34–36]. The origin of peak P$_1$ was assigned as an excited band or a transition from 1s → t$_{1g}$, and is believed to be associated with Ti 3d–4p hybridized states. Peaks P$_2$ and P$_4$ were attributed to the 1s → 3d transition and were designated as 1s → t$_{2g}$ and 1s → 3e$_g$ transitions, respectively [35,36]. The pre-edge spectrum of as-synthesized TNTs contained three major features, peaks P$_1$, P$_2$ and P$_4$, with the strong peak located at 4970.7 eV (peak P$_2$), which was the transition of 1s → t$_{2g}$ for tetrahedral symmetry [35]. On the contrary, the pre-edge spectrum of Cu-deposited TiO$_2$/TNTs contained peaks P$_1$, P$_3$, and P$_4$ with a notable blue shift from peak P$_2$ to peak P$_3$, reflecting the distortion of the octahedral TiO$_6$ unit. In addition, the peak P$_4$ was a pure dipolar component and provided a sensitive probe for the degree of distortion [34]. The increase in peak P$_4$ intensity in Cu-deposited TiO$_2$/TNTs also indicated the distortion around the TiO$_6$ octahedral sites.

In the main-edge region of 4976–4995 eV, three spectral features (denoted as A, B and C) corresponding to the dipole-allowed 1s → 4p transitions were clearly observed [34,36]. The main-edge of as-synthesized TNTs showed small signals of peaks B and C, which was in good agreement with that of layered titanate nanohybrids doped with metal oxides [36,37]. In contrast, the main-edge spectral feature for the Cu-deposited TiO$_2$/TNTs changed and peak B at 4986.5 eV became obvious after the thermal treatment at 500°C, which was similar to that of anatase TiO$_2$. This observation provides a strong support on the local structural change from layered titanate to anatase TiO$_2$ through the distortion of TiO$_6$ units after calcination at 500°C and photodeposition of Cu ions [32].

The Cu L$_{2,3}$-edge absorption spectra for Cu-deposited TiO$_2$/TNTs before and after UV light illumination are displayed in Fig. 4b. The strong peaks in the L$_2$ and L$_3$ areas centered at about 931 and 952 eV were mainly attributed to the inherent divalent copper states, which can be interpreted as the transition of Cu(2p$_{3/2}$)3d$^9$ ground state to Cu(2p$_{3/2}$)$^{-1}$3d$^{10}$ excited state [38]. After illumination with UV light to photo-deposit Cu ions, an additional small peak shown at about 934 eV was the Cu(I) L$_3$-edge resulting from the transition of Cu(2p$_{3/2}$)3d$^{10}$ ground state to Cu(2p$_{3/2}$)$^{-1}$3d$^{10}$4s,
which was originally from the level of oxygen-depleted Cu$_2$O after photo-induced conversion.

### 3.2. Photocatalytic activity of Cu-deposited TiO$_2$/TNTs

The photocatalytic activity of as-synthesized and Cu-deposited TiO$_2$/TNTs was evaluated using BPA as the target compound. Fig. 5 shows the photocatalytic degradation of BPA by various titanium-based nanomaterials under the illumination of 365 nm UV light at pH 7.0. No obvious photodegradation of BPA was observed after illumination of UV light for 90 min in the absence of TNTs (direct photolysis). Similar to the direct photolysis, less than 10% of BPA was photodegraded by as-synthesized TNTs. After post-thermal treatment at 500°C, 40% of the original BPA was photodegraded within 90 min, depicting the increase in photocatalytic activity of TNTs after calcination. The commercial TiO$_2$ nanoparticles also showed good photocatalytic activity towards BPA degradation, and the removal efficiencies of 92% and 70% were observed within 90 min when Degussa P25 and ST01 TiO$_2$, respectively, were added.

The deposition of Cu(II) significantly enhanced the photocatalytic activity of TiO$_2$/TNT towards BPA degradation, and the photodegradation efficiency of BPA increased to >99.9% when 0.5-2 wt% Cu(II) was deposited. The $k_{obs}$ for BPA photodegradation increased from 0.0074 min$^{-1}$ in the absence of Cu(II) to 0.083 ± 0.004 min$^{-1}$ at 0.5 wt% Cu(II) and then reached the maximum value of 0.253 ± 0.032 min$^{-1}$ at 1 wt% Cu(II). After increasing the Cu(II) amount to 2 wt%, the $k_{obs}$ values for BPA photodegradation slightly decreased to 0.137 ± 0.017 min$^{-1}$. It is noted that the $k_{obs}$ for BPA photodegradation by P25 and ST01 TiO$_2$ were 0.049 and 0.02 min$^{-1}$, respectively. This means that the $k_{obs}$ values for BPA photodegradation by Cu-deposited TiO$_2$/TNTs are 1.7-5.2 and 4.3-12.7 times higher than those of pure Degussa P25 and ST01 TiO$_2$, respectively, clearly showing the superior photoactivity of Cu-deposited TiO$_2$/TNTs towards photodegradation of BPA. In addition, 35% of TOC were removed after illumination of 120 min when 10 mg/L BPA was photodegraded by Cu-deposited TiO$_2$/TNT, which is higher than that by pure Degussa P25 TiO$_2$ (21%). These results clearly indicate that Cu-deposited TiO$_2$/TNTs is a promising nanomaterial which can effectively enhance the photo-mineralization efficiency of BPA under the illumination of 365 nm UV light.

The Cu(II) ions have different effects on commercial TiO$_2$ nanoparticles. As shown in Fig. 5, addition of 1 wt% Cu(II) slightly lowered the photodegradation efficiency and rate of BPA by Degussa P25 TiO$_2$ after 60 min of UV illumination. However, the photodegradation efficiency and rate of BPA by ST01 increased when 1 wt% Cu(II) was added. This discrepancy is mainly attributed to the different compositions of TiO$_2$ between P25 and ST01. The P25 TiO$_2$ contains 80% anatase and 20% rutile, which could form interparticle electron transfer (IPET) to enhance the photocatalytic activity of TiO$_2$. The addition of Cu(II) has little effect on IPET and may block the photoreactive sites of P25 TiO$_2$, resulting in the decrease in the photodegradation efficiency and rate of BPA. In contrast, ST01 contains 100% anatase TiO$_2$ and the formation of Cu$_2$O enhances the electron–hole separation efficiency. It is noteworthy that the $k_{obs}$ for BPA photodegradation was 0.041 min$^{-1}$ for P25-Cu$_2$O and 0.023 min$^{-1}$ for ST01-Cu$_2$O, which were 6.3–11 times lowered than that of 1 wt% Cu-deposited TiO$_2$/TNTs, clearly
showing that addition of Cu(II) ions has a significant effect on the enhanced photocatalytic activity of TiO₂/TNT nanocomposites towards BPA photodegradation compared with those of commercial TiO₂ nanoparticles.

3.3. Possible reaction mechanism for photodegradation

In this study, we have found that the photocatalytic activity of 1D TNTs towards BPA photodegradation can be significantly enhanced after photodeposition of copper ions. It is believed that the photodegradation of BPA may involve several steps initiated from the photo-generation of electrophilic hydroxyl radicals and/or O-centered radical adducts [27,29,39]. Fig. 6 shows the EPR spectra of free radicals and XPS spectrum of Cu species after the illumination of Cu-deposited TiO₂/TNTs. As illustrated in Fig. 6a, no EPR signal was produced in solutions containing DMPO and Cu-deposited TiO₂/TNTs in the presence of 10 mg/L BPA in the dark. After illumination of Cu-deposited TiO₂/TNTs with UV light for 5 min, the six-line EPR spectra were clearly observed, indicating the generation of O-centered radical adducts such as *OH, *OOH, and ROO* [40,41]. In addition, the EPR intensity increased upon increasing the Cu amount from 0.5 to 1 wt% and then slightly decrease at 2 wt% Cu, clearly showing that addition of copper ion is conducive to the production of radicals. The deconvolution of Cu 2p3/2 XPS spectrum clearly indicated the formation of CuO (933.6 eV) and Cu₂O (932.7 eV) after the illumination of Cu-deposited TiO₂/TNTs for 5 min (Fig. 6b). The ratio of Cu₂O to total Cu species (CuO + Cu₂O), determined by the peak areas of Cu₂O and total Cu2p3/2 species, increased from 3.2% in the dark (Fig. 2b) to 35.2% after the illumination of UV light. This result clearly indicates that Cu species can be reduced to low-valent Cu species during photocatalytic reaction, and subsequently enhances the separation efficiency of holes and electrons. It is noteworthy that Cu₂O can easily be oxidized to form a layer of CuO once exposed to the ambience and the XPS data can only represent the surface information, which indicates that the real content of Cu₂O in the nanocomposites remains unclear. The use of HRTEM with selected area electron diffraction would be conductive to characterize the nanoparticles of Cu-deposited...
that addition of copper ions could serve as the electron mediators to prolong to retention time of photo-generated radicals, resulting in the enhancement of photodegradation efficiency and rate of BPA by Cu-deposited TiO$_2$/TNTs. Results obtained in this study open an avenue to apply 1D nanostructured titanates for effective photodegradation of toxic chemicals in the aqueous solutions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2012.09.011.

References