Cite this: *Nanoscale*, 2015, 7, 16695

Synthesis of rare earth doped TiO₂ nanorods as photocatalysts for lignin degradation†

 Liang Song,^{*a,b} Xueyuan Zhao,^a Lixin Cao,^c Ji-Won Moon,^b Baohua Gu^b and Wei Wang^{*b,c}

A two-step process is developed to synthesize rare earth doped titania nanorods (RE–TiO₂ NRs) as photocatalysts for efficient degradation of lignin under simulated sunlight irradiation. In this approach, protonated titanate nanotubes with layered structures were first prepared by a hydrothermal approach, and rare earth metal ions were subsequently bound to the negatively charged surface of the synthesized titanate via electrostatic incorporation. The as-synthesized RE–TiO₂ NRs after calcination generally showed much higher photocatalytic efficiencies than those of undoped TiO₂ NRs or the commercial P25 TiO₂ photocatalyst. Using methyl orange (MO) as a probing molecule, we demonstrate that Eu–TiO₂ NRs are among the best for degrading MO, with an observed rate constant of $4.2 \times 10^{-3} \text{ s}^{-1}$. The La³⁺, Sm³⁺, Eu³⁺ and Er³⁺ doped TiO₂ NRs also showed higher photocatalytic efficiencies in degrading MO than the commercial P25 TiO₂. We further demonstrate that lignin can be photodegraded effectively and rapidly at room temperature under simulated sunlight through two reaction routes, which could be important in controlling ways of lignin depolymerization or the formation of reaction products.

Received 29th May 2015,
Accepted 1st September 2015

DOI: 10.1039/c5nr03537f

www.rsc.org/nanoscale

Introduction

Lignin, a complex and recalcitrant phenolic macromolecule, is found in most terrestrial plants at approximately 15 to 40% dry weight.^{1,2} However, this natural macromolecule is resistant to microbial attack and difficult to be degraded biologically due to its complex irregular polymeric structure.² In pulp mills and olive mills, lignin separated from lignocellulose is commonly regarded as pulp black liquor (PBL) and olive mill wastewater (OMW).^{3–5} The chlorination process, which is commonly used to reduce the pollution problems in pulp and paper wastewaters, results in the formation of chlorinated by-products such as polychlorinated biphenyls and chlorophenols.⁶ Photocatalytic degradation is a promising method to directly depolymerize non-biodegradable lignin.⁷ Lignin is one of the most abundant aromatic polymers on earth,⁸ and it is thus of great environmental significance if waste lignin could be converted to renewable chemicals,^{2,9} such as aromatic platform compounds^{10,11} and alternative biofuels^{12–14} through

photocatalytic reactions. To achieve this goal, one of the challenges is to develop highly effective photocatalysts to accelerate depolymerization reactions. Recently, one-dimensional titanium dioxide (1D-TiO₂) nanomaterials,^{15,16} such as nanotubes, nanorods and nanowires, have been widely used as photocatalysts^{17,18} owing to their large specific surface area and small dimension effect. However, the catalytic efficiency of pure TiO₂ is relatively low, particularly under visible light irradiation, due to the fast recombination rate of electron-hole pairs in TiO₂. In order to enhance the interfacial charge-transfer efficiency and utilize a wider spectral range of solar energy, the TiO₂ catalyst has been modified by ion doping^{19,20} and manipulating the nanomaterial composition.^{21,22} Rare earth (RE) ion dopants, such as Ce,²³ La,²⁴ Er²⁵ and Pr,²⁶ have shown unique enhancement effects, resulting from the orbital hybridization of 4f electrons. Positive effects of 4f electron orbital hybridization on the photocatalytic activities of TiO₂ were reported previously.^{27,28}

In this research, we developed a two-step process to incorporate RE ions (rare earth ions La³⁺, Ce³⁺, Pr³⁺, Sm³⁺, Eu³⁺, Tb³⁺, Er³⁺) into 1D TiO₂ nanostructures and obtained novel RE-doped TiO₂ nanorods (RE–TiO₂ NRs) with narrowed band gap energy and enhanced photocatalytic activity. We determined the photocatalytic efficiencies of the synthesized nanocatalysts through photodegradation of methyl orange (MO) and lignin. Commercial P25 TiO₂ nanocatalyst was used as a reference to evaluate the photocatalytic activities of the synthesized 1D TiO₂ nanocatalysts. To achieve a complete degra-

^aKey Laboratory of Biofuel, Chinese Academy of Sciences, Qingdao Institute of Bioenergy and Bioprocess Technology, Qingdao, Shandong 266101, P.R. China. E-mail: songliang@qibebt.ac.cn

^bEnvironmental Sciences and Biosciences Divisions, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

^cInstitute of Materials Science and Engineering, Ocean University of China, Qingdao, Shandong 266100, P.R. China. E-mail: wangw@ouc.edu.cn

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c5nr03537f

dation of lignin, previous studies have used oxidizing agents such as H_2O_2 and O_3 to assist the reactions catalyzed by TiO_2 .^{29,30} In contrast, we report rapid degradation of lignin in aqueous solution using RE- TiO_2 NRs as photocatalysts without adding any oxidizing agents.

Experimental

Chemicals

Praseodymium chloride heptahydrate ($\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$, 99.99%), samarium chloride hexahydrate ($\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, 99.99%), europium chloride hexahydrate ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%), terbium chloride hexahydrate ($\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%) and erbium chloride hexahydrate ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%) were purchased from Aldrich. Lanthanum chloride heptahydrate ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, assay- LaCl_3 64.5–70.0%) was obtained from J. T. Baker, and cerium chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, 99%) was obtained from Alfa-Aesar. TiO_2 powder (surface area of $40 \text{ m}^2 \text{ g}^{-1}$) for synthesis of RE- TiO_2 NRs was obtained from NanoTek. Methyl orange was obtained from Fluka. Alkali lignin (mol wt $\sim 10\,000 \text{ g mol}^{-1}$, 4% sulfur impurity) was obtained from Aldrich. Commercial P25 TiO_2 nanocatalyst (average size of 21 nm, surface area of $50 \text{ m}^2 \text{ g}^{-1}$) was provided by Evonik Degussa. Deionized (DI) water with a resistance of $18.2 \text{ M}\Omega \text{ cm}$ was used in all the experiments.

Synthesis and characterization of rare earth ion-doped TiO_2 nanorods

Based on the method developed by Kasuga^{31,32} for synthesis of TiO_2 nanotubes and the electrostatic attraction effect of the negative surface of layered nanotubes, we developed a novel two-step method to synthesize RE- TiO_2 NRs. Briefly, 1.5 g TiO_2 powder was dispersed into 85 mL 10 mol L^{-1} NaOH solution followed by magnetic stirring for 3 h. The suspension was then transferred into an autoclave lined with Teflon for hydrothermal treatment at 423 K. Upon reaction completion in 24 h, the synthesized sodium titanate nanotubes were separated and thoroughly washed with DI water and a 0.1 mol L^{-1} HCl solution until the pH value reached ~ 6.0 . The protonated titanate nanotubes were dried at 353 K for use as precursors for the doping procedure. RE ions La^{3+} , Ce^{3+} , Pr^{3+} , Sm^{3+} , Eu^{3+} , Tb^{3+} or Er^{3+} were mixed with protonated titanate nanotubes at a Ti/RE molar ratio of 20 : 1 in aqueous solution. The mixture was stirred vigorously for 12 h at room temperature and the nanotubes were separated and dried at 353 K for 12 h to obtain RE-loaded titanate nanotubes. After calcination at 833 K for 4 h, RE-loaded titanate nanotubes were transformed into RE- TiO_2 NRs.

Chemical and structural properties of the synthesized nanomaterials were characterized by Raman spectroscopy (Renishaw micro-Raman system with a NIR laser at 785 nm excitation). Morphologies of the nanostructures were observed by using transmission electron microscopes (Hitachi H-7000, Hitachi HD 2000, 200 kV) with Energy Dispersive X-ray Spectroscopy (EDS). Optical absorption spectra were recorded by

using a UV-Vis spectrometer (S. I. Photonics 400 with integrating sphere) in reflectance mode, and BaSO_4 was used as the diffuse reflectance material. Optical upconversion properties were analysed with a fluorescence spectrometer (Jobin-Yvon-SPEX Instruments, New Jersey) using a 980 nm laser as the excitation source. Surface charge densities of the as-synthesized 1D nanomaterials were evaluated by zeta (ζ) potential measurements in aqueous suspensions with a dynamic light scattering instrument (Brookhaven 90plus/Bi-MAS). The surface area was measured by the BET method using a surface area analyzer (Micromeritics, Gemini VII 2390).

Determination of photocatalytic activity

The photocatalytic activities of the undoped and RE-doped TiO_2 nanorods, as well as commercial P25 TiO_2 nanocatalysts were estimated by the degradation of MO and lignin in aqueous solution at room temperature. The MO (20 mg L^{-1}) and lignin (100 mg L^{-1}) were irradiated under simulated sunlight (Newport solar simulator, model 66921) at an intensity of $36.8 \pm 0.2 \text{ mW cm}^{-2}$ measured by using a dual channel optical power meter (Thorlabs PM300 with a S310A Thermopile Sensor). Before irradiation with the simulated sunlight, all samples were kept in the dark for 60 min to ensure the adsorption equilibrium of MO and lignin on the surface of the catalysts. The final concentration of the catalysts was 1 g L^{-1} for all photocatalytic reactions. During the photoreactions, the samples were taken out at given time intervals to analyze the supernatant concentrations of MO and lignin by UV-vis absorption spectroscopy. Intermediate products from the reactions were analyzed by FTIR spectroscopy (Nicolet MAGNA-IR 760 Spectrometer equipped with a MCT detector) in the spectral range of $650\text{--}4000 \text{ cm}^{-1}$ with a resolution of 0.964 cm^{-1} .

Results and discussion

Formation and characterization of RE-doped TiO_2 nanorods

A two-step procedure was developed to synthesize the RE- TiO_2 NRs. Step 1 is to prepare 1D titanate nanotubes with layered structures. The layered sodium titanate in the form of hollow nanotubes was obtained by concentrated alkali hydrothermal treatment of titania. In step 2, RE ions were incorporated into the layered nanostructures of titanate nanotubes. For RE incorporation in TiO_2 , the incipient impregnation and solvothermal doping method is known to cause precipitation and aggregation of RE ions. Here, the titanate nanotubes were treated with dilute hydrochloric acid for exchanging sodium ions with protons, and RE ions were thus homogeneously bound to the negatively charged surface of the nanotubes *via* electrostatic interactions.

TEM images of the synthesized 1D nanomaterials are shown in Fig. 1. The protonated titanate nanotubes showed a layered structure and the selected area electron diffraction (SAED) pattern (Fig. 1a and inset) indicated their poor crystallinity, which is consistent with XRD patterns (Fig. S1a†). Protonated titanate nanotubes exhibited vibrational bands at 283,

Fig. 1 HRTEM images of (a) protonated titanate nanotubes, (b) undoped TiO_2 nanorods, (c) Sm-doped titanate nanotubes and (d) Sm-doped TiO_2 nanorods. The insets show their corresponding SAED patterns.

451, and 661 cm^{-1} , as shown in the Raman spectrum (Fig. S1b†), which are assigned to Ti–O–Ti vibration from 2D lepidocrocite-type TiO_6 layers.^{33,34} The band at 824 cm^{-1} is due to a covalent Ti–O–H bond,³⁵ implying that the protonated titanate nanotubes have a monoclinic crystal structure of the trititanate ($\text{H}_2\text{Ti}_3\text{O}_7$) phase.^{35–37} After calcination at 833 K, the protonated titanate nanotubes were dehydrated and converted into TiO_2 . The HRTEM image (Fig. 1b and inset) indicates that the morphology of 1D nanomaterials was transformed to nanorod-like multilayered structures with high crystallinity. The interlamellar spacing of the undoped layered TiO_2 nanorods was 0.72 nm. Doping of RE ions into the layered titanate nanotubes did not affect the rod-like morphology (Fig. 1c). After the same calcination treatment, the RE- TiO_2 NRs showed similar nanostructures to the undoped TiO_2 NRs. The average diameters of the RE ion doped nanorods are about 8–12 nm.

The surface charge density of the synthesized titanium based 1D nanomaterials was evaluated by zeta potential measurements. The results revealed that the layered protonated titanate nanotubes were negatively charged ($\zeta = -31\text{ mV}$) while highly crystalline TiO_2 nanorods became positively charged ($\zeta = +2\text{ mV}$) at the pH value of 6.8. The layered nanotubes with a high BET surface area ($\sim 340\text{ m}^2\text{ g}^{-1}$) provided a large number of adsorption sites for RE cations. Owing to the lamellar spacing of titanate precursors, rare earth metal ions (e.g. ionic diameters, La^{3+} of $1.061\text{ \AA}$, Sm^{3+} of $0.964\text{ \AA}$, Er^{3+} of $0.881\text{ \AA}$) facilely diffused into the adsorption sites between interlayers, and homogeneously grafted onto the negatively charged surface of the titanate nanotubes through electrostatic interactions. The negatively charged and layered surface of titanate nanotubes is crucial to prevent aggregation of RE ions in the calcination treatment.

To evaluate the doping status of RE ions, the synthesized RE- TiO_2 NRs were examined by Raman spectroscopy (Fig. 2). After calcination at 833 K, RE- TiO_2 NRs exhibited charac-

Fig. 2 Raman spectra of undoped and RE-doped TiO_2 nanorods. Vibration modes are labelled. The inset shows the E_g -mode Raman spectra of the undoped and doped samples.

teristics of the anatase phase with typical Raman bands centered at 638, 515, and 395 cm^{-1} for E_g , A_{1g}/B_{1g} and B_{1g} vibrational modes, respectively.³⁸ No rutile phase or rare earth oxide phase was observed in the Raman spectra of RE- TiO_2 NRs. The Raman shift is very sensitive to lattice distortion by dopants. The redshift of the E_g mode (located at 638 cm^{-1}) was observed for the RE ion doped nanorods, indicating lattice disorder and oxygen deficiencies derived from RE ion doping. A similar phenomenon was observed in the doped 3D- TiO_2 nanomaterials.^{39,40} Since Raman peaks usually become weak and broad when the samples have local lattice imperfections,³⁹ full width at half maximum (FWHM) of the vibrational bands was calculated using a Lorentzian peak function. The FWHMs of the E_g peak were $22.8 \pm 0.7\text{ cm}^{-1}$ and $28.4 \pm 0.7\text{ cm}^{-1}$ for the undoped and doped nanorods, respectively (Table 1). The FWHMs of A_{1g} and B_{1g} peaks also increased slightly after doping. The Raman peaks of the doped samples broadened with respect to FWHM, implying lattice distortion induced by the RE dopants.

Trace amounts of RE ions were detected by EDS, as shown in Fig. S2,† though the RE–O bonds were not detected by Raman spectra. However, EDS results could not reveal whether the RE ions were chemically bonded into the TiO_2 lattice. In order to verify this, we measured upconversion fluorescence of Er and Yb co-doped TiO_2 NRs synthesized by using the same procedure, because the upconversion fluorescence derives

Table 1 FWHM of Raman bands of the synthesized TiO₂ nanorods

Sample	Full width at half maximum (FWHM)		
	E _g	A _{1g} & B _{1g}	B _{1g}
TiO ₂	22.8	22.9	21.1
La-TiO ₂	27.7	24.3	22.7
Ce-TiO ₂	29.1	24.9	23.2
Pr-TiO ₂	28.6	24.3	23.2
Sm-TiO ₂	28.1	24.5	23.2
Eu-TiO ₂	28.2	24.4	23.1
Tb-TiO ₂	28.7	24.6	23.4
Er-TiO ₂	28.8	24.3	23.8

Table 2 Absorption edge and bandgap energy of TiO₂ nanorod photocatalysts

Sample	Absorption edge (nm)	Bandgap ^a (eV)
TiO ₂	388	3.20
La-TiO ₂	403	3.08
Ce-TiO ₂	494	2.51
Pr-TiO ₂	407	3.05
Sm-TiO ₂	404	3.07
Eu-TiO ₂	401	3.09
Tb-TiO ₂	419	2.96
Er-TiO ₂	411	3.02

^a Bandgap energies were calculated based on Kubelka-Munk theory. The detailed computational process is described in the ESI.

from the high levels of homogeneously distributed doping in the host lattice and the avoidance of radiationless electronic decay pathways for the excited RE dopant ions.⁴¹ With excitation at 980 nm, emission was clearly observed at 524, 553 and 660 nm for the Er and Yb codoped TiO₂ NRs, which confirmed that the RE ions were chemically incorporated into the lattice of TiO₂ (Fig. S3†).

Reflectance spectra of the RE-TiO₂ NRs were investigated in the spectral range of 350–800 nm, as shown in Fig. 3 and S4.† We observed that the TiO₂ NRs had no absorption in the visible light region because of their relatively high bandgap energy, while the RE-TiO₂ NRs caused a red shift, especially for the Ce- and Tb-doped TiO₂ NRs. The absorption spectra of the Pr, Sm, Eu, or Er doped NRs were observed between spectra of the La-TiO₂ and the Tb-TiO₂.

Bandgap energies of the undoped TiO₂ and the RE doped TiO₂ were estimated according to the reflectance spectra. The bandgaps of RE doped TiO₂ NRs were narrow compared with that of the undoped TiO₂ NRs, as shown in Table 2. These results are in agreement with the literature report on RE ion doped 3D TiO₂.^{27,42,43} The presence of RE ions (4f electrons) in the TiO₂ matrix induced the RE impurity energy level between

the O 2p orbital and Ti 3d orbital, which narrowed the charge transfer band.⁴⁴

Evaluation of photocatalytic efficiency

We used methyl orange (Fig. S6a†), a representative azo dye, as a model pollutant to evaluate the photocatalytic efficiencies of the synthesized RE-TiO₂ NRs. As shown in Fig. 4, the RE-TiO₂ NRs calcined at 833 K showed the highest photocatalytic activity. Because the RE-TiO₂ NRs treated at 833 K have a higher crystallinity than those calcined at lower temperatures, these results indicate that the crystallinity of Ti-based 1D catalysts is one of the key factors affecting the photocatalytic performance.

Control experiments showed that there was no degradation of MO in the absence of photocatalysts (Fig. S5†). Commercial P25 TiO₂ was commonly used as a standard photocatalyst for estimating the photocatalytic activities of aromatic molecules.^{48,49} Here the kinetic processes of degradation of MO were also compared in the presence of the photocatalysts P25 TiO₂ and RE-TiO₂ NRs by presenting $-\ln(C/C_0)$ vs. t plots in

Fig. 3 UV-Vis reflectance spectra of TiO₂ NR and RE-TiO₂ NR photocatalysts. **Fig. 4** Effects of calcination on time-dependent MO photodegradation by Eu³⁺-doped 1D TiO₂ catalysts.

Fig. 5 First order kinetics of photocatalytic degradation of methyl orange (MO): ● photodegradation of MO without catalysts, photodegradation of MO with catalysts of ○ P25 TiO₂, ■ TiO₂ nanorods, □ La doped TiO₂ nanorods, ◆ Ce doped TiO₂ nanorods, ◇ Pr doped TiO₂ nanorods, ▲ Sm doped TiO₂ nanorods, △ Eu doped TiO₂ nanorods, + Tb doped TiO₂ nanorods, and × Er doped TiO₂ nanorods.

Fig. 5. UV decay of organic pollutants usually follows a pseudo first order kinetics, which has been successfully applied to various TiO₂ heterogeneous photocatalytic systems, *e.g.* Fe-TiO₂/MO,⁴⁵ TiO₂/PPCPs⁴⁶ and TiO₂/azo-dye.⁴⁷ The linear relationship at the initial stage of photocatalytic degradation of MO suggested conformity with first order kinetics. Table 3 lists the apparent first order kinetic constants and kinetic equations (the detailed calculation is listed in the ESI†).

The photo-degradation rates of the La³⁺, Sm³⁺, Eu³⁺ and Er³⁺ doped TiO₂ NTs were found to be much more photoactive than those of the undoped TiO₂ nanorods and the commercial P25 TiO₂. The calculated first order rate constant of Eu-TiO₂

nanorods was $42 \times 10^{-4} \text{ s}^{-1}$, about 2 times higher than that of P25 TiO₂. With these efficient catalysts, methyl orange could be degraded nearly 100% within 20 minutes. However, the Ce³⁺, Pr³⁺ and Tb³⁺ doped TiO₂ NR catalysts exhibited lower photocatalytic activities in the degradation of MO with azo groups (-N=N-). The Ce-TiO₂ NTs showed the lowest photocatalytic efficiency, probably due to the detrimental effect of Ce³⁺ ions.⁵⁰

Photocatalytic degradation of lignin

As a recalcitrant phenolic macromolecule, lignin (Fig. S6b and c†) is resistant to be degraded in natural environments, due to its highly irregular polymeric structure.² As shown in Fig. S7,† lignin is hard to be degraded under UV-Vis light irradiation without catalysts. The photochemical reaction of lignin is a slow and complex process.^{51,52}

In our experiments, photocatalytic degradation of lignin was studied at 100 mg L⁻¹ at pH 7.0 in the presence of RE-TiO₂ NRs in solution. UV-Vis absorption spectra and IR spectra are usually employed to evaluate the decay process of water soluble lignin.⁵² The photodegradation process of lignin with Sm-TiO₂ under simulated sunlight irradiation is illustrated in Fig. 6. UV absorption peaks of lignin were observed at 279 nm ($\sim 100 \text{ kcal mol}^{-1}$) and 201 nm ($\sim 140 \text{ kcal mol}^{-1}$). The strong absorption at 201 nm is assigned to the $\pi \rightarrow \pi^*$ electronic transition of aromatics.⁵³ Absorption at 279 nm is attributed to the hydroxyl groups or etherified hydroxyl groups in lignin units, which is assigned to $n \rightarrow \pi^*$ electronic transitions. The symbol "n" is non-bonding electrons, which correspond to the lone electron pairs of the -O- ether bond and the -OH hydroxy bond.

In the absence of the catalyst, there is little degradation of aromatics, as indicated by the UV absorption peak at 201 nm (Fig. 7). The absorption peak at 279 nm, representing oxygenated groups of lignin, did not show any noticeable changes

Table 3 Kinetic constants (*k*), half-life of reaction (*t*_{1/2}) and kinetic equation during photocatalytic treatment for methyl orange employing both the as-synthesized nanorods and commercial Degussa P25 catalysts^a

Catalyst	Reaction rate constant <i>k</i> (10 ⁻⁴ s ⁻¹)	Kinetic equation	Reliability	Half-life of reaction <i>t</i> _{1/2} (s)
Eu-TiO ₂	42	$C_t = C_0 e^{-0.0042t}$	97.7	165
La-TiO ₂	34	$C_t = C_0 e^{-0.0034t}$	97.9	204
Er-TiO ₂	34	$C_t = C_0 e^{-0.0034t}$	97.8	204
Sm-TiO ₂	32	$C_t = C_0 e^{-0.0032t}$	98.7	217
TiO ₂	25	$C_t = C_0 e^{-0.0025t}$	99.0	277
P25 TiO ₂	24	$C_t = C_0 e^{-0.0024t}$	98.8	289
Pr-TiO ₂	11	$C_t = C_0 e^{-0.0011t}$	99.3	630
Tb-TiO ₂	9	$C_t = C_0 e^{-0.0009t}$	99.9	770
Ce-TiO ₂	8	$C_t = C_0 e^{-0.0008t}$	99.2	866

^a The initial concentrations of MO and catalysts were 20 mg L⁻¹ and 1 g L⁻¹, respectively.

Fig. 6 UV absorption spectra of lignin following its photodegradation in the presence of Sm-TiO₂ catalysts.

Fig. 7 Time-dependent photodegradation of lignin as indicated by decreased UV-absorption at 201 nm under simulated sunlight with RE-TiO₂ NRs: ● photodegradation of lignin without catalysts, photocatalytic degradation of lignin with the catalyst ○ P25 TiO₂, ■ TiO₂ nanorods, □ La doped TiO₂ nanorods, ◆ Ce doped TiO₂ nanorods, ◇ Pr doped TiO₂ nanorods, ▲ Sm doped TiO₂ nanorods, △ Eu doped TiO₂ nanorods, + Tb doped TiO₂ nanorods, and × Er doped TiO₂ nanorods.

Fig. 8 Time-dependent photodegradation of lignin as indicated by UV-absorption at 279 nm under simulated sunlight with RE-TiO₂ NRs: ● photodegradation of lignin without catalysts, photocatalytic degradation of lignin with the catalyst ○ P25 TiO₂, ■ TiO₂ nanorods, □ La doped TiO₂ nanorods, ◆ Ce doped TiO₂ nanorods, ◇ Pr doped TiO₂ nanorods, ▲ Sm doped TiO₂ nanorods, △ Eu doped TiO₂ nanorods, + Tb doped TiO₂ nanorods, and × Er doped TiO₂ nanorods.

either (Fig. 8). This is attributed to the stability of the conjugated aryl groups and oxygenated structures, such as the hydroxyl group and the methoxy group in lignin monomers,⁵⁴ which are hard to break down.

The absorption peak at 201 nm decreased consistently over time using the synthesized RE-TiO₂ NRs as the photocatalyst. However, with the Pr³⁺, Ce³⁺, and Eu³⁺ ion doped TiO₂ NRs as

photocatalysts, we found that the peak value at 279 nm first increased and then decreased over time (Fig. 8). This observation is similar to that found in the degradation of lignin dimer model compounds.⁵⁵ The Sm³⁺, La³⁺, Er³⁺, Tb³⁺, and Pr³⁺ ion doped TiO₂ NRs were more effective than the standard catalyst P25 TiO₂. Unlike the degradation of the dye with the azo group (–N=N–), the Ce³⁺, Tb³⁺ and Pr³⁺ ion-doped TiO₂ NRs showed enhanced reactivities for photocatalytic degradation of aromatics.

Reaction routes of photocatalytic depolymerization of lignin

When using Sm³⁺, Er³⁺, La³⁺ and Tb³⁺ ion-doped TiO₂ NRs as photocatalysts, the UV absorbance at both 201 nm and 279 nm decreased, suggesting photodegradation of the lignin aromatic structures. However, the peak intensity at 279 nm increased at the initial stage, when the Eu³⁺, Ce³⁺, and Pr³⁺ ion doped TiO₂ NRs were used. The initial increase in UV absorbance at 279 nm was generated from the decay of oxygen bonds (e.g. phenolic hydroxyl groups, phenolic methoxyl groups and alkyl-aryl ether bonds). These results pointed out that there were two photocatalytic degradation routes of lignin over different RE doped TiO₂ nanocatalysts.

FTIR spectroscopy was used to investigate the functional groups or chemical bonds of lignin.^{56,57} The most representative vibrational bands and their assignment in the spectral range of 1600–1200 cm^{−1} (Fig. 9 and 10) are summarized in Table S1.† The bands at 1596 and 1504 cm^{−1} are due to C=C stretching of the aromatic skeletal vibrations.^{58–60} The bands at 1464 and 1425 cm^{−1} are assigned to C–H deformations in methyl, methylene and methoxyl groups in lignin.^{58,61} The bands between 1270 and 1200 cm^{−1} are due to C–O and C–O–C stretching in lignin.⁶² Significant spectral changes can be observed in the fingerprint region during photocatalytic reactions for all samples. The degradation of lignin was reflected

Fig. 9 FTIR spectra of lignin following photocatalytic degradation with Sm-TiO₂ NRs as the photocatalyst. The characteristic IR bands of lignin are located at (w1) 1596 cm^{−1}, (w2) 1504 cm^{−1}, (w3) 1464 cm^{−1}, (w4) 1425 cm^{−1}, (w5) 1262 cm^{−1}, and (w6) 1225 cm^{−1}.

Fig. 10 FTIR spectra of lignin following photocatalytic degradation with Eu-TiO₂ NRs as the photocatalyst. The characteristic IR bands of lignin are located at (w1) 1596 cm⁻¹, (w2) 1504 cm⁻¹, (w3) 1464 cm⁻¹, (w4) 1425 cm⁻¹, (w5) 1262 cm⁻¹, and (w6) 1225 cm⁻¹.

by the decrease in intensities of these bands. After the photocatalytic reaction for ≥ 100 min, these characteristic bands of lignin disappeared by using Eu-TiO₂ NRs or Sm-TiO₂ NRs as catalysts. These results demonstrated that lignin could be completely photodegraded with the RE-TiO₂ NR catalysts. The disappearance of the band at 1504 cm⁻¹ is indicative of lignin photodegradation since the band arises from aromatic skeletal vibration of the benzene ring in lignin. However, using Eu-TiO₂ NRs as the catalyst, the lignin degradation was accompanied by an increase in the intensity of the band at 1425 cm⁻¹, relative to the band at 1504 cm⁻¹ at an early stage of the photocatalytic reaction. The result suggests the formation of new non-conjugated intermediate compounds during the photodegradation.

The degradation of lignin was also shown by the decreased intensity at 1262 and 1225 cm⁻¹ over time. Importantly we note that these two bands decreased much faster on using the Sm-TiO₂ NRs than the Eu-TiO₂ NT catalysts. This indicates that the lignin units with C-O linkages depolymerized more efficiently with the Sm-TiO₂ NRs than the Eu-TiO₂ NT photocatalyst. These results also indicate that there are two possible photocatalytic depolymerization routes when using Sm-TiO₂ NTs and Eu-TiO₂ NTs. This observation is important in controlling the depolymerization of lignin with the possibility to convert it into value-added chemicals, although additional studies will be needed to better understand the mechanism of lignin depolymerization.

RE ions modified 1D nanorods showed better photocatalytic activities, likely due to the effects of decreased surface defects and increased electron-hole recombination. We thus propose the following reaction schemes (eqn (1)–(6)): under photo-irradiation, the excited electrons and holes diffuse to the surface (eqn (1)) and react with surface species. With RE ions doped TiO₂ NRs, the surface charge became more posi-

tive, resulting in more OH⁻ ions adsorbed on the surface for charge balance.²⁷ The adsorbed OH⁻ ions accept holes to form hydroxyl radicals ([•]OH)^{63–66} (eqn (3)). The hole sites attack the adsorbed lignin molecules directly (eqn (2)), while [•]OH radicals attack the conjugated oxygenated structure (eqn (4)) to form lignin fragments. Subsequently the lignin fragments react with the active sites, such as holes and [•]OH radicals (eqn (5) and (6)). For this reason, more absorption sites of $n \rightarrow \pi^*$ are formed at the initial stage due to [•]OH attack, as shown with the commercial P25 TiO₂ catalyst (Fig. 8). The Eu-TiO₂ NRs, Ce-TiO₂ NRs, Pr-TiO₂ NRs and Tb-TiO₂ NRs showed the same photocatalytic oxidation route as P25 TiO₂ nanoparticles.

Conclusions

A facile two-step process, utilizing electrostatic incorporation between positively charged rare earth ions and negatively charged titanate nanotubes, is presented as an alternative route to synthesize RE-doped TiO₂ NRs. The structure and morphology of the synthesized nanomaterials were characterized by TEM, Raman scattering and up-conversion fluorescence spectroscopy. The as synthesized La³⁺, Sm³⁺, Eu³⁺ and Er³⁺ doped TiO₂ catalysts showed enhanced photocatalytic efficiency in degrading azo dye compounds such as MO. The Eu-TiO₂ NRs showed the highest reaction rate ($42 \times 10^{-4} \text{ s}^{-1}$) with MO. Lignin could be photodegraded completely using the as-synthesized RE-TiO₂ NR catalysts under simulated sunlight. We also found that photodegradation of lignin can proceed through two different routes by forming different intermediate products, suggesting the possibility of controllable ways of lignin depolymerization.

Acknowledgements

This work was supported in part by the National Natural Science Foundation of China (NSFC Grant No. 21306214) and by the Laboratory Directed Research and Development (LDRD) program at Oak Ridge National Laboratory (ORNL), U.S. Department of Energy (DOE). ORNL is managed by UT-Battelle LLC for US DOE under contract DE-AC05-00OR22725. We thank Drs Wang Zheng, Yuan Li, Tommy J. Phelps, and Zhenyu Zhang for valuable discussion of the research.

Notes and references

- 1 A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan and C. E. Wyman, *Science*, 2014, **344**, 1246843.
- 2 C. P. Xu, R. A. D. Arancon, J. Labidi and R. Luque, *Chem. Soc. Rev.*, 2014, **43**, 7485–7500.
- 3 Y. Qian, Y. Deng, X. Qiu, H. Li and D. Yang, *Green Chem.*, 2014, **16**, 2156–2163.
- 4 B. Ruggeri, F. Battista, M. Bernardi, D. Fino and G. Mancini, *Chem. Eng. J.*, 2015, **259**, 630–639.
- 5 M. Ugurlu and M. H. Karaoglu, *Chem. Eng. J.*, 2011, **166**, 859–867.
- 6 C. N. Chang, Y. S. Ma, G. C. Fang, A. C. Chao, M. C. Tsai and H. F. Sung, *Chemosphere*, 2004, **56**, 1011–1017.
- 7 J. D. Nguyen, B. S. Matsuura and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2013, **136**, 1218–1221.
- 8 S. Y. Lin and C. W. Dence, *Methods in lignin chemistry*, Springer-Verlag, New York, 1992.
- 9 J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552–3599.
- 10 M. S. Talmadge, R. M. Baldwin, M. J. Biddy, R. L. McCormick, G. T. Beckham, G. A. Ferguson, S. Czernik, K. A. Magrini-Bair, T. D. Foust, P. D. Metelski, C. Hetrick and M. R. Nimlos, *Green Chem.*, 2014, **16**, 407–453.
- 11 A. Rahimi, A. Ulbrich, J. J. Coon and S. S. Stahl, *Nature*, 2014, **515**, 249–252.
- 12 D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493–1513.
- 13 L. Hu, Y. Luo, B. Cai, J. Li, D. Tong and C. Hu, *Green Chem.*, 2014, **16**, 3107–3116.
- 14 Z. Jiang, T. He, J. Li and C. Hu, *Green Chem.*, 2014, **16**, 4257–4265.
- 15 X. D. Wang, Z. D. Li, J. Shi and Y. H. Yu, *Chem. Rev.*, 2014, **114**, 9346–9384.
- 16 K. Lee, A. Mazare and P. Schmuki, *Chem. Rev.*, 2014, **114**, 9385–9454.
- 17 X. Zhang, V. Thavasi, S. G. Mhaisalkar and S. Ramakrishna, *Nanoscale*, 2012, **4**, 1707–1716.
- 18 I. Paramasivam, H. Jha, N. Liu and P. Schmuki, *Small*, 2012, **8**, 3073–3103.
- 19 W. Zhu, X. Qiu, V. Lancu, X. Chen, H. Pan, W. Wang, N. Dimitrijevic, T. Rajh, H. Meyer, M. Paranthaman, G. Stocks, H. Weitering, B. Gu, G. Eres and Z. Zhang, *Phys. Rev. Lett.*, 2009, **103**, 226401.
- 20 Y. Li, W. Wang, X. Qiu, L. Song, H. Meyer, M. Paranthaman, G. Eres, Z. Zhang and B. Gu, *Appl. Catal., B*, 2011, **110**, 148–153.
- 21 F.-X. Xiao, S.-F. Hung, H. B. Tao, J. Miao, H. B. Yang and B. Liu, *Nanoscale*, 2014, **6**, 14950–14961.
- 22 Z. Zhang, C. Shao, X. Li, Y. Sun, M. Zhang, J. Mu, P. Zhang, Z. Guo and Y. Liu, *Nanoscale*, 2013, **5**, 606–618.
- 23 P. Sun, L. Liu, S. C. Cui and J. G. Liu, *Catal. Lett.*, 2014, **144**, 2107–2113.
- 24 R. B. Comes, P. V. Sushko, S. M. Heald, R. J. Colby, M. E. Bowden and S. A. Chambers, *Chem. Mater.*, 2014, **26**, 7073–7082.
- 25 D. Hou, R. Goei, X. Wang, P. Wang and T. T. Lim, *Appl. Catal., B*, 2012, **126**, 121–133.
- 26 P. M. Martins, V. Gomez, A. C. Lopes, C. J. Tavares, G. Botelho, S. Irusta and S. Lanceros-Mendez, *J. Phys. Chem. C*, 2014, **118**, 27944–27953.
- 27 Z. M. El-Bahy, A. A. Ismail and R. M. Mohamed, *J. Hazard. Mater.*, 2009, **166**, 138–143.
- 28 H. X. Shi, T. Y. Zhang, T. C. An, B. Li and X. Wang, *J. Colloid Interface Sci.*, 2012, **380**, 121–127.
- 29 K. Kamwilaisak and P. C. Wright, *Energy Fuels*, 2012, **26**, 2400–2406.
- 30 Y. Lu, X.-Y. Wei, Z. Wen, H.-B. Chen, Y.-C. Lu, Z.-M. Zong, J.-P. Cao, S.-C. Qi, S.-Z. Wang, L.-C. Yu, W. Zhao, X. Fan and Y.-P. Zhao, *Fuel Process. Technol.*, 2014, **117**, 8–16.
- 31 T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino and K. Niihara, *Langmuir*, 1998, **14**, 3160–3163.
- 32 T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino and K. Niihara, *Adv. Mater.*, 1999, **11**, 1307–1311.
- 33 B. C. Viana, O. P. Ferreira, A. G. Souza, C. M. Rodrigues, S. G. Moraes, J. Mendes and O. L. Alves, *J. Phys. Chem. C*, 2009, **113**, 20234–20239.
- 34 M. A. Cortes-Jacome, G. Ferrat-Torres, L. F. F. Ortiz, C. Angeles-Chavez, E. Lopez-Salinas, J. Escobar, M. L. Mosqueira and J. A. Toledo-Antonio, *Catal. Today*, 2007, **126**, 248–255.
- 35 A. Gajovic, I. Friscic, M. Plodinec and D. Ivekovic, *J. Mol. Struct.*, 2009, **924–26**, 183–191.
- 36 S. Chatterjee, S. Bhattacharyya, D. Khushalani and P. Ayyub, *Cryst. Growth Des.*, 2010, **10**, 1215–1220.
- 37 M. Qamar, C. R. Yoon, H. J. Oh, N. H. Lee, K. Park, D. H. Kim, K. S. Lee, W. J. Lee and S. J. Kim, *Catal. Today*, 2008, **131**, 3–14.
- 38 T. Ohsaka, F. Izumi and Y. Fujiki, *J. Raman Spectrosc.*, 1978, **7**, 321–324.
- 39 W. F. Zhang, Y. L. He, M. S. Zhang, Z. Yin and Q. Chen, *J. Phys. D: Appl. Phys.*, 2000, **33**, 912–916.
- 40 B. Karunakaran, K. Kim, D. Mangalaraj, J. S. Yi and S. Velumani, *Sol. Energy Mater. Sol. Cells*, 2005, **88**, 199–208.
- 41 M. Haase and H. Schafer, *Angew. Chem., Int. Ed.*, 2011, **50**, 5808–5829.
- 42 C. H. Liang, F. B. Li, C. S. Liu, H. L. Lu and X. G. Wang, *Dyes Pigm.*, 2008, **76**, 477–484.
- 43 L. Bian, M. X. Song, T. L. Zhou, X. Y. Zhao and Q. Q. Dai, *J. Rare Earths*, 2009, **27**, 461–468.
- 44 A. W. Xu, Y. Gao and H. Q. Liu, *J. Catal.*, 2002, **207**, 151–157.
- 45 X. H. Wang, J. G. Li, H. Kamiyama, Y. Moriyoshi and T. Ishigaki, *J. Phys. Chem. B*, 2006, **110**, 6804–6809.

- 46 S. Murgolo, F. Petronella, R. Ciannarella, R. Comparelli, A. Agostiano, M. L. Curri and G. Mascolo, *Catal. Today*, 2015, **240**(Part A), 114–124.
- 47 A. O. Ibhaddon, G. M. Greenway, Y. Yue, P. Falaras and D. Tsoukleris, *Appl. Catal., B*, 2008, **84**, 351–355.
- 48 V. Augugliaro, G. Camera-Roda, V. Loddo, G. Palmisano, L. Palmisano, F. Parrino and M. A. Puma, *Appl. Catal., B*, 2012, **111–112**, 555–561.
- 49 E. Portjanskaja, K. Stepanova, D. Klauson and S. Preis, *Catal. Today*, 2009, **144**, 26–30.
- 50 S. Chang and W. Liu, *Appl. Catal., B*, 2014, **156**, 466–475.
- 51 H. T. Chang, Y. C. Su and S. T. Chang, *Polym. Degrad. Stab.*, 2006, **91**, 816–822.
- 52 U. Muller, M. Ratzsch, M. Schwanninger, M. Steiner and H. Zobl, *J. Photochem. Photobiol., B*, 2003, **69**, 97–105.
- 53 Y. Chen, R. Chen, X. Cheng, X. Yang, G. Wu and Y. Chen, *Spectrosc. Spect. Anal.*, 2006, **26**, 1880–1883.
- 54 J. D. Young, M. Staniforth, J. C. Dean, G. M. Roberts, F. Mazzoni, T. N. V. Karsili, M. N. R. Ashfold, T. S. Zwieter and V. G. Stavros, *J. Phys. Chem. Lett.*, 2014, **5**, 2138–2143.
- 55 C. Gardrat, R. Ruggiero, W. Hoareau, A. Nourmamode, S. Grelier, B. Siegmund and A. Castellan, *J. Photochem. Photobiol., A*, 2004, **167**, 111–120.
- 56 J. C. Dean, P. S. Walsh, B. Biswas, P. V. Ramachandran and T. S. Zwieter, *Chem. Sci.*, 2014, **5**, 1940–1955.
- 57 R. J. Sammons, D. P. Harper, N. Labbe, J. J. Bozell, T. Elder and T. G. Rials, *Bioresources*, 2013, **8**, 2752–2767.
- 58 M. Tian, J. Wen, D. MacDonald, R. M. Asmussen and A. Chen, *Electrochem. Commun.*, 2010, **12**, 527–530.
- 59 K. Tanaka, R. C. R. Calanag and T. Hisanaga, *J. Mol. Catal. A: Chem.*, 1999, **138**, 287–294.
- 60 F. Kačik and I. Kubovský, *J. Photochem. Photobiol., A*, 2011, **222**, 105–110.
- 61 C. M. Popescu, M. C. Popescu and C. Vasile, *Int. J. Biol. Macromol.*, 2011, **48**, 667–675.
- 62 Q. Luo, H. Peng, M. Y. Zhou, D. Lin, R. Ruan, Y. Q. Wan, J. S. Zhang and Y. H. Liu, *Bioresources*, 2012, **7**, 5817–5828.
- 63 K. M. Parida and N. Sahu, *J. Mol. Catal. A: Chem.*, 2008, **287**, 151–158.
- 64 J. H. Li, X. Yang, X. D. Yu, L. L. Xu, W. L. Kang, W. H. Yan, H. F. Gao, Z. H. Liu and Y. H. Guo, *Appl. Surf. Sci.*, 2009, **255**, 3731–3738.
- 65 P. Du, A. Bueno-Lopez, M. Verbaas, A. R. Almeida, M. Makkee, J. A. Moulijn and G. Mul, *J. Catal.*, 2008, **260**, 75–80.
- 66 K. Ishibashi, A. Fujishima, T. Watanabe and K. Hashimoto, *J. Photochem. Photobiol., A*, 2000, **134**, 139–142.