Electronic Supplementary Information

Synthesis of Rare Earth Doped TiO₂ Nanorods as Photocatalysts for Lignin Degradation

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I. Calculation of bandgap energy of Ti-based oxide photocatalysts

In order to quantify the effect of RE\(^{3+}\) ions modification on the bandgap of nanorods, the bandgap energy was calculated by Kubelka–Munk theory. According to the hypothesis of plural scattering, diffuse reflection spectrum can be transformed into a plot of the square root of F(R)\(\sigma\nu\) versus the energy of irradiation light. The Kubelka–Munk function\(^1\) is shown as in Eq. (1).

\[
F(R) = \frac{(1 - R)^2}{2R} \tag{1}
\]

Here, \(R\) is the measured reflectance (\(R = R_{\text{sample}}/R_{\text{reference}}\)). The use of \(F(R)\) as the equivalent of absorbance relies on the assumption that the scattering coefficients are consistent throughout the reference samples\(^2\). From Yeong Kim’s results, the optical absorption behavior of lamellar titanate is consistent with an indirect gap semiconductor\(^3\). So, bandgap can be estimated from the plot of the square root of \(F(R)\nu\) versus photon energy (as shown in Eq. (2)). Here, \(\nu\) is photon energy, and \(E_g\) is bandgap energy of semiconductor.

\[
\sqrt{F(R)\nu} = c(\nu - E_g) \tag{2}
\]
II. Calculation of apparent reaction rate constants

Decrement of MO concentration \((C)\) during the treatment time \((t)\) was described by the first order kinetics, as shown in Eq. (3).

\[
\frac{d(C)}{dt} = -kC^n \quad \text{Eq. (3)}
\]

where \(r\), \(k\) and \(n\) represent the rate of photocatalytic degradation of dye, the apparent reaction rate constant, and reaction order, respectively. To simplify the heterogeneous catalytic process, the initial concentration of the methyl orange substrate \(C_0\) was kept constant. The apparent first order reaction rate constant \(k\) (s\(^{-1}\)) was obtained by fitting the experimental data from Eq. (4).

\[
-ln\left(\frac{C}{C_0}\right) = kt \quad \text{Eq. (4)}
\]

The \(k\) values were determined by the slope of the linear curve (plotting \(-ln(C/C_0)\) versus time). Consequently, reaction half-times \(t_{1/2}\) were calculated using Eq. (5).

\[
t_{1/2} = \frac{ln2}{k} \quad \text{Eq. (5)}
\]
III. Supplementary figures

Fig. S1 XRD patterns (a) and Raman scattering (b) of as-prepared protonated titanate nanotubes.
Fig. S2 EDS of Ce-TiO$_2$ nanorods.
**Fig. S3.** Up-conversion fluorescence emission of Er$^{3+}$ and Yb$^{3+}$ co-doped TiO$_2$ nanorods under excitation of 980 nm.
Fig. S4 UV-Vis reflectance spectra of TiO$_2$ nanorods and RE ions doped TiO$_2$ photocatalysts. (a) undoped TiO$_2$ nanorods, (b) La-TiO$_2$ nanorods, (c) Ce-TiO$_2$ nanorods, (d) Pr-TiO$_2$ nanorods, (e) Sm-TiO$_2$ nanorods, (f) Eu-TiO$_2$ nanorods, (g) Tb-TiO$_2$ nanorods, and (h) Er-TiO$_2$ nanorods.
Fig. S5 Photodegradation of MO in aqueous solution. Initial concentration of dye was 20 mg L\(^{-1}\) and concentration of catalysts was 1 g L\(^{-1}\). Data symbols stand for:

- Photodegradation of MO without catalysts, photocatalytic degradation of MO with catalyst P25 TiO\(_2\), TiO\(_2\) nanorods, La doped TiO\(_2\) nanorods, Ce doped TiO\(_2\) nanorods, Pr doped TiO\(_2\) nanorods, Sm doped TiO\(_2\) nanorods, Eu doped TiO\(_2\) nanorods, Tb doped TiO\(_2\) nanorods, and Er doped TiO\(_2\) nanorods.
**Fig. S6** Molecular structure of (a) micromolecular –N=N– dye methyl orange, (b) macromolecular lignin with phenol group and ether bond, (c) three types of lignin monomers.
Fig. S7 UV-Vis absorption spectra of lignin solution before irradiation and after 3h UV irradiation. Reaction condition: 100mL lignin aqueous solution with a concentration of 250 mg L\(^{-1}\) was illuminated under 100 W near-ultraviolet light (UVA) without catalyst.
### IV. Supplementary table

**Table S1** Assigned IR peaks of lignin

| Wavenumber (cm\(^{-1}\)) | Assigned chemical structure                                      |
|--------------------------|------------------------------------------------------------------|
| 1596                     | C=C stretching in aromatic lignin\(^4\)                         |
| 1504                     | C=C vibrations of the aromatic lignin\(^4,7-9\)                 |
|                           | C-H deformations in methyl, methylene and methoxyl groups in lignin\(^4,5\) |
| 1464                     | C-H deformations in methyl, methylene and methoxyl groups in lignin\(^4,5\) |
| 1425                     | C-H deformations in methyl, methylene and methoxyl groups in lignin\(^4,5\) |
| 1335                     | C-O vibration in syringyl derivatives\(^4\)                     |
|                           | Aromatic ring vibrations of syringyl and guaiacyl\(^10\)         |
| 1328                     | C-O stretching in lignin\(^4\)                                 |
| 1262                     | C-O stretching\(^9\)                                          |
V. References

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