

## Supporting Information

### Selective photocatalytic conversion of lignin via metal-doped anodic TiO<sub>2</sub> nanotubes

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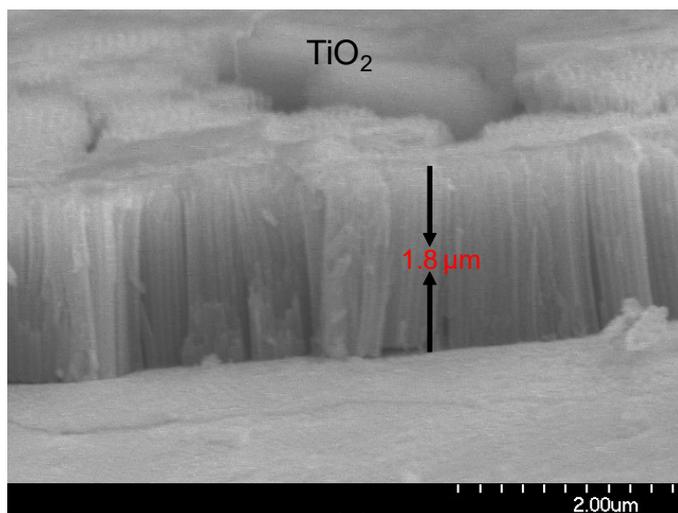
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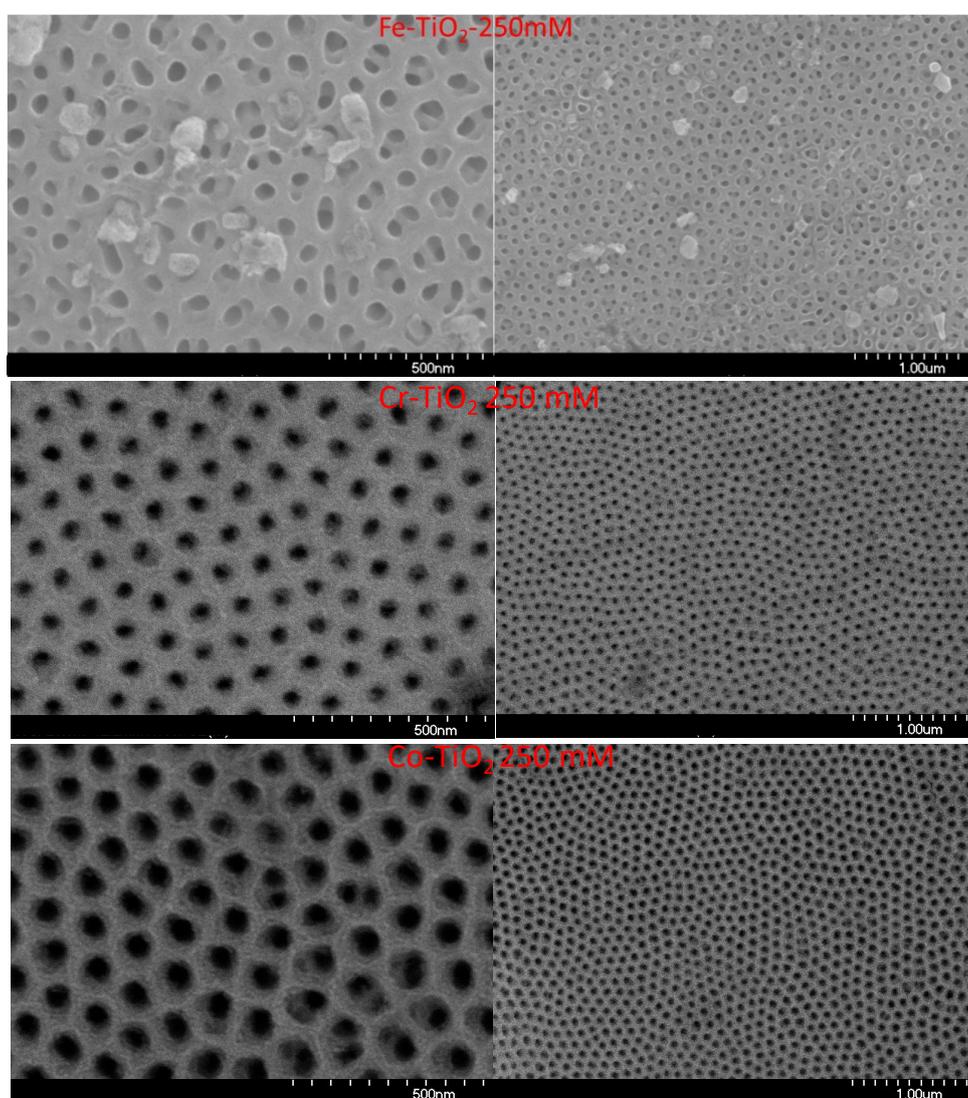
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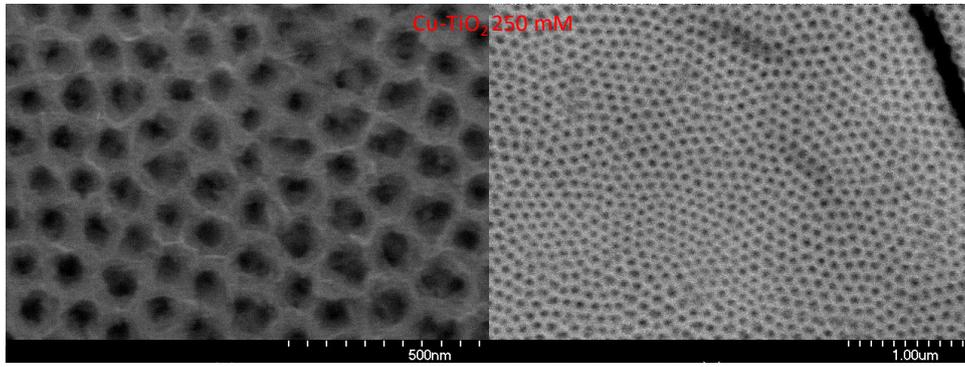
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## 1. Morphology of studied materials



**Figure S1.** Cross-sectional FESEM image of TiO<sub>2</sub> NTs.



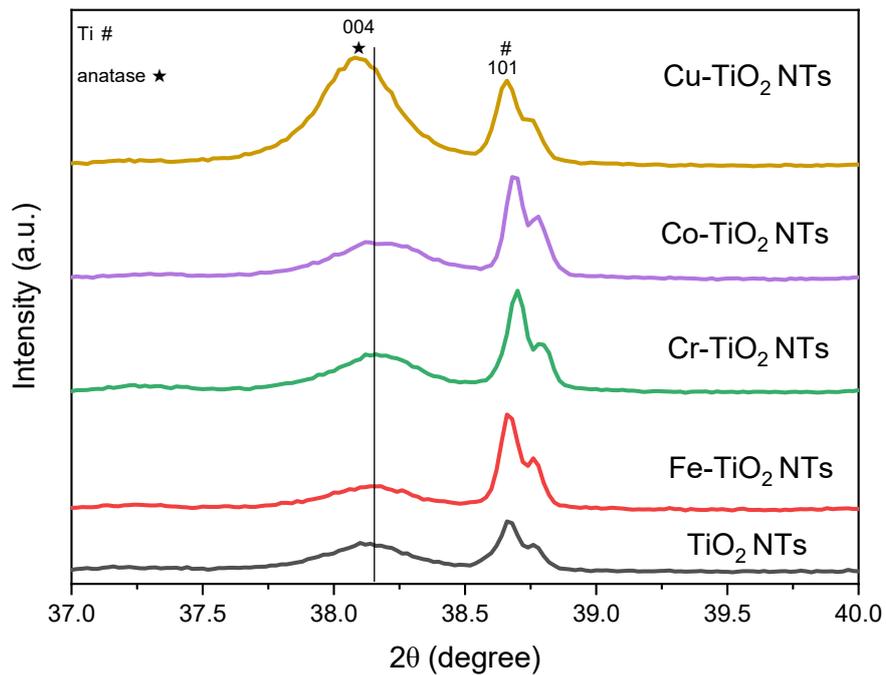


**Figure S2.** FESEM images of Fe-, Cr-, Co-, and Cu-doped TiO<sub>2</sub> NTs synthesized in the electrolyte with a higher concentration of the metal fluoride salt (250 mM).

**Table S1.** Average dopant content estimated from EDS spectra.

Material	Metal content (at.%)
<i>Fe-TiO<sub>2</sub></i>	0.23 ± 0.08
<i>Cu-TiO<sub>2</sub></i>	0.69 ± 0.18
<i>Co-TiO<sub>2</sub></i>	0.71 ± 0.13
<i>Cr-TiO<sub>2</sub></i>	0.52 ± 0.15

## 2. Crystalline structure



**Figure S3.** Zoomed-in views of the (004) diffraction peak of pristine and metal-doped TiO<sub>2</sub> NTs.

### 3. Optical properties

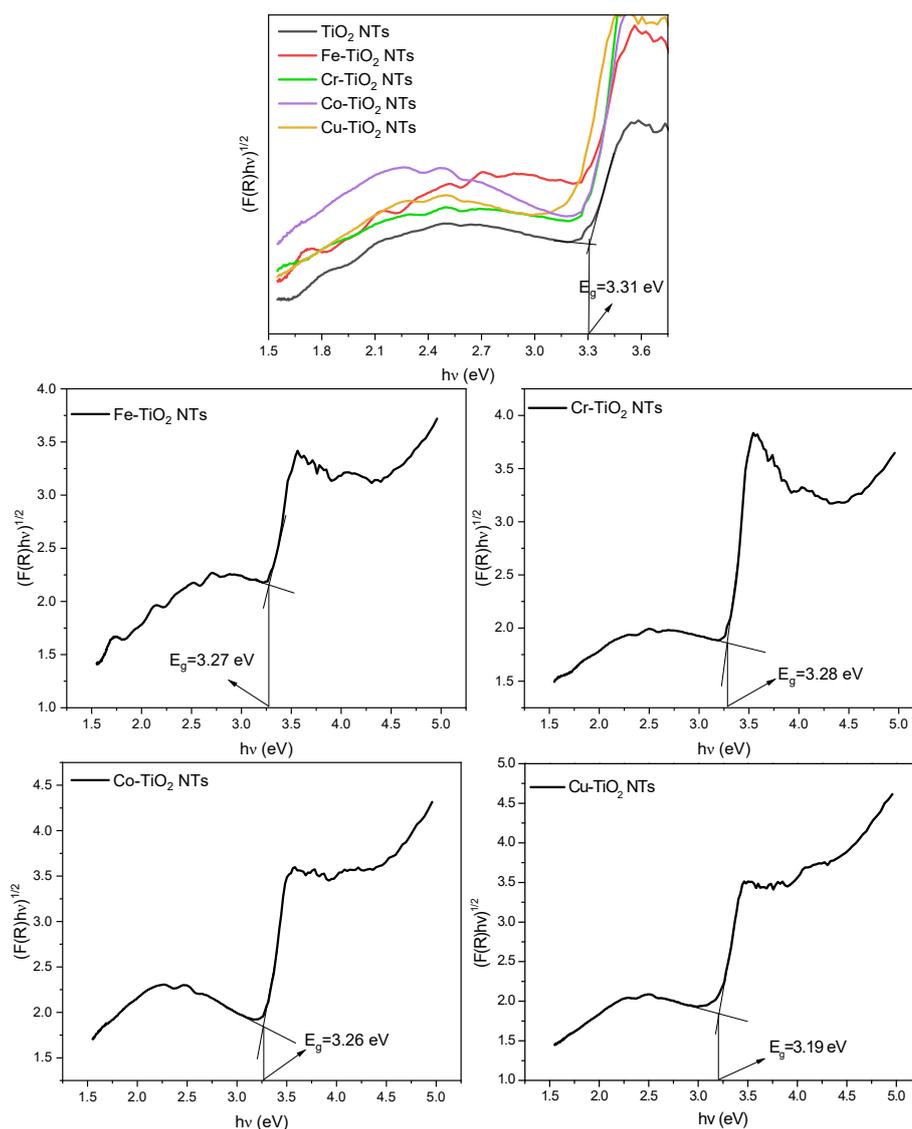


Figure S4. Tauc's plots for pristine and metal-doped TiO<sub>2</sub> NTs.

### 4. XPS measurements

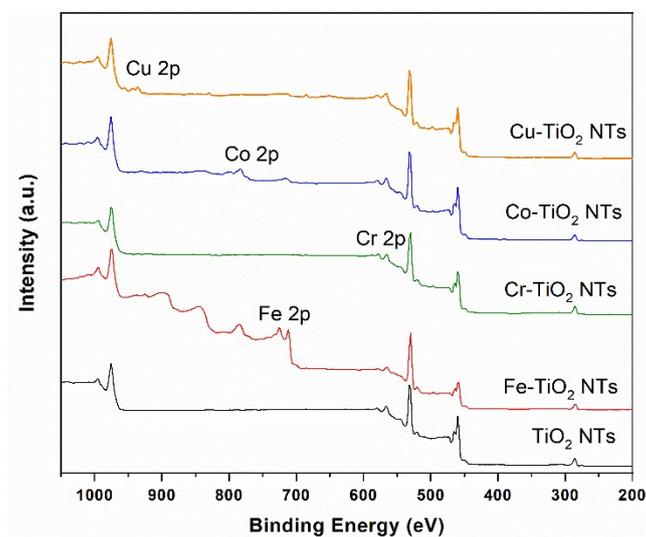
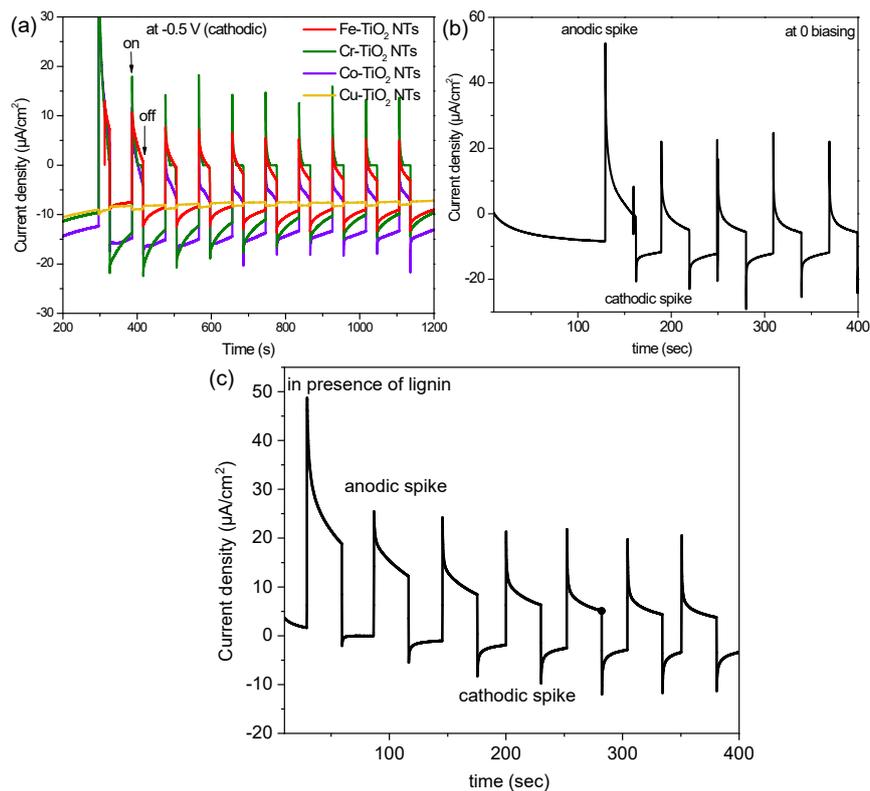


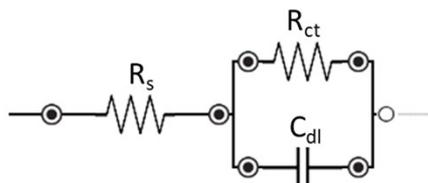
Figure S5. XPS survey spectra for pristine and doped TiO<sub>2</sub> NTs.

## 5. PEC characterization



**Figure S6.** Light on-off I-t curve of different metal-doped TiO<sub>2</sub> NTs at applied negative bias (a), Cu-TiO<sub>2</sub> NTs at zero bias in the absence (b) and in the presence (c) of lignin in KNO<sub>3</sub>.

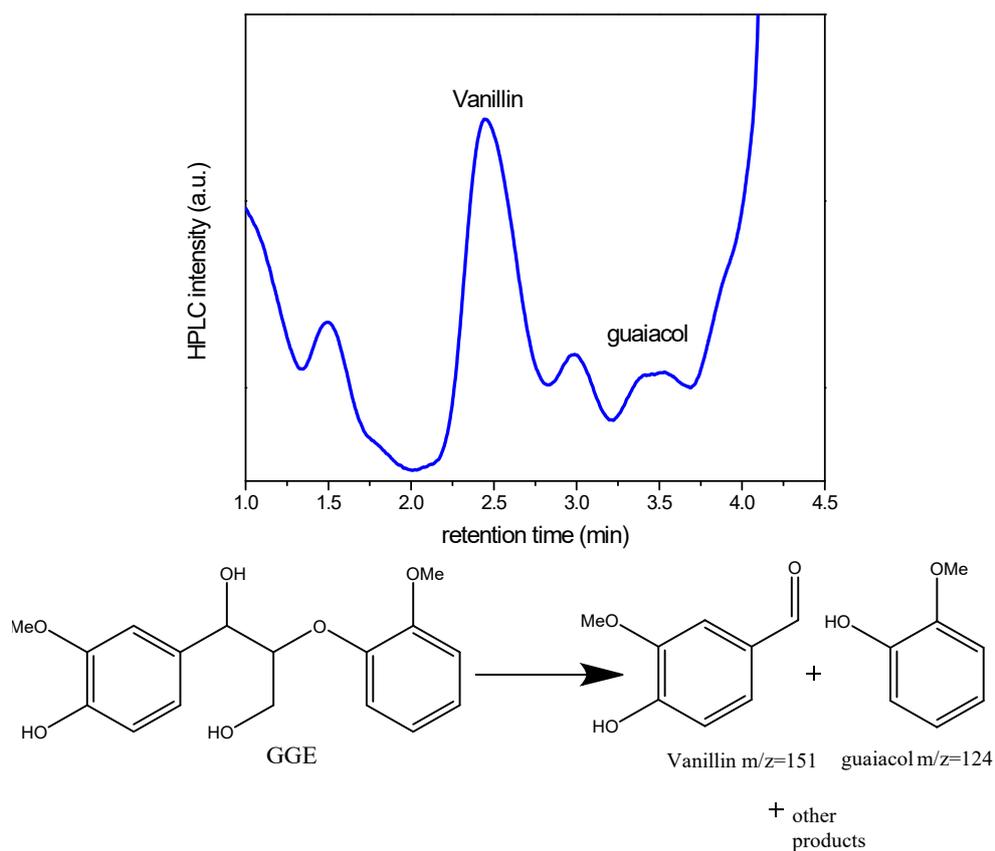
## 6. EIS studies



	TiO <sub>2</sub> NT	Fe-TiO <sub>2</sub> NT	Cr-TiO <sub>2</sub> NT	Co-TiO <sub>2</sub> NT	Cu-TiO <sub>2</sub> NT
<b><i>R<sub>s</sub></i> (Ω)</b>	33.1	30.9	29.9	31.1	35.1
<b><i>R<sub>ct</sub></i> (Ω)</b>	1993	1739	1643	1980	2328
<b><i>C</i> (nF)</b>	3119	3202	3218	3193	2631

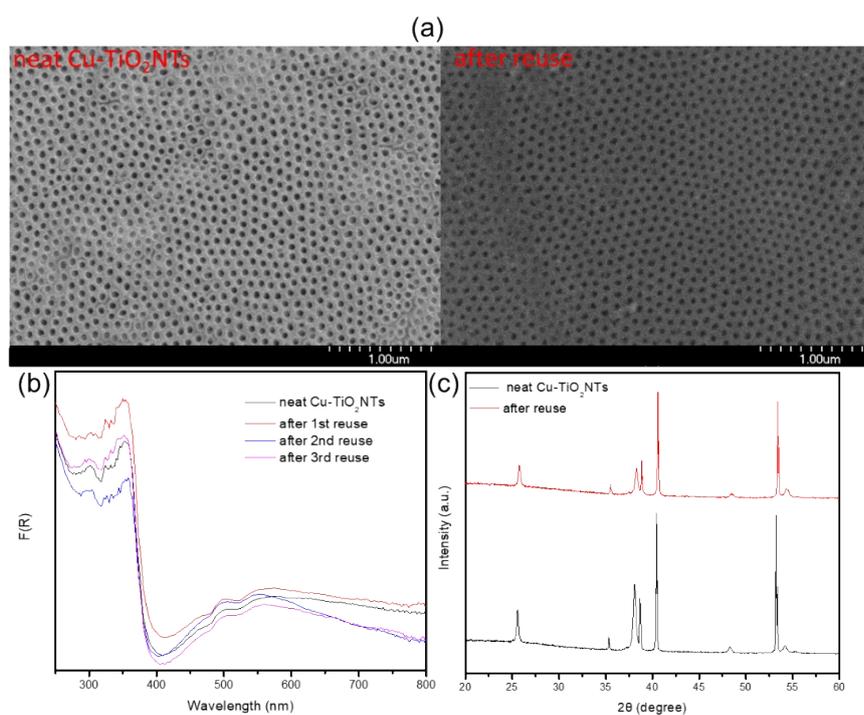
**Figure S7.** EIS fitted equivalent circuit and corresponding fitting data.

## 7. HPLC-MS analysis

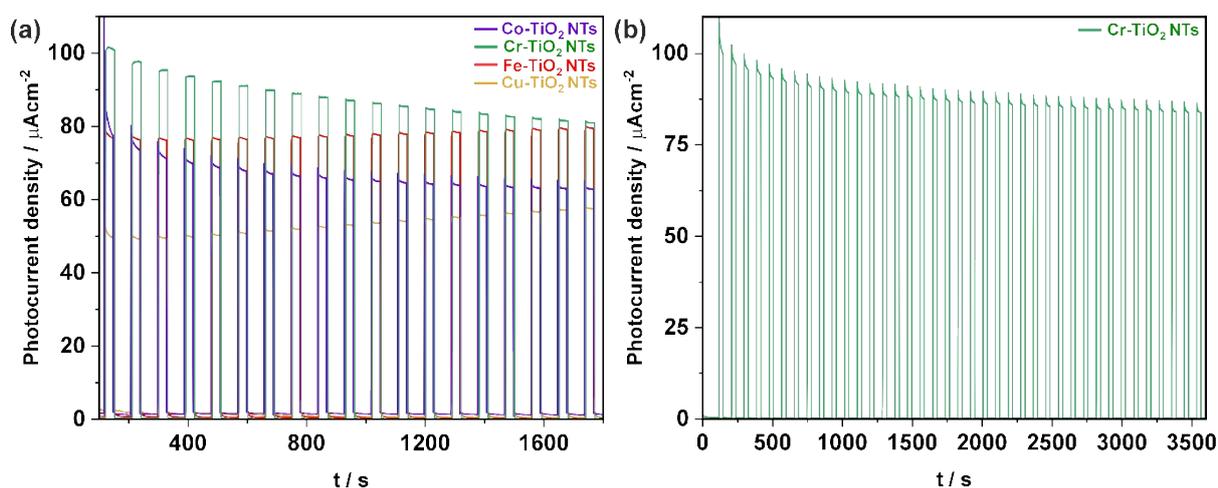


**Figure S8.** LC chromatogram of GGE conversion for Fe-TiO<sub>2</sub> NTs and estimated conversion products.

## 8. Repeatability, stability



**Figure S9.** SEM images (a), UV-Vis spectra (b), and XRD patterns (c) of neat Cu-TiO<sub>2</sub> and after reuse.



**Figure S10.** PEC performance of doped materials after one year of storage (a) and stability test of Cr-TiO<sub>2</sub> NTs material (b).

**Table S2.** Literature review on photocatalytic lignin decomposition - state of the art.

Photocatalyst	Lignin type	Solvent	Light	Lignin conversion %	Products	Ref
TiO <sub>2</sub> derived from MIL-25 Mesoporous structure regular pancake-like morphology	Sodium lignosulfonate	Aq.	300 W Xenon lamp $\lambda=350-780$ nm	2.1 mg g <sup>-1</sup> <sub>lignin</sub> /6h	Vanillin	1
Bi-Pt/TiO <sub>2</sub>	Sodium lignosulfonate	Aq.	UV-Vis 125 mW/cm <sup>2</sup> Batch reactor	84.5/ 1.5 h 5 mg g <sup>-1</sup> <sub>lignin</sub> /1h	Lignin conversion Vanillin Guaiacol (22.7%/1 h), vanillic acid, 4-phenyl-1-buten-4-ol	2
Pancake-like 3D-flower morphology of BiOI-TiO <sub>2</sub> nanoparticles	Sodium lignosulfonate	Aq.	300 W Xenon ( $\lambda > 400$ nm)	5.8 mg g <sup>-1</sup> <sub>lignin</sub> /6h	Vanillin	3
Cd <sub>x</sub> Zn <sub>1-x</sub> S Stacked layered structure	Alkali lignin	Acetonitrile+water	Simulated sunlight 300 W Xe-lamp,	89.5%/3 h 46.5 mg g <sup>-1</sup> <sub>lignin</sub> /7 h	Vanillin Phenol (66.2%) and acetophenone (33.5%)	4
TiO <sub>2</sub> -NiO core-shell	Kraft lignin	Alkaline solution	UV-vis light (320-780 nm)	89.2%/ 12 h	Palmitic acid (35%), stearic acid (25%) and butanedioic acid	5

					(7%)	
TiO <sub>2</sub> /lignin	Kraft lignin	acetonitrile	400 W Hg lamp ( $\lambda_{\max} = 365$ nm)	40.28%/5 h	Aromatic aldehydes, ketones, alcohols and phenolic derivatives	6
(Fe, Cr, Co and Cu)M-doped TiO <sub>2</sub> NTs	Alkali lignin (Kraft)	Acetonitrile+water	UV-Vis 110 mW/cm <sup>2</sup>	100%/12 h 9.2 $\mu\text{g} \cdot \text{g}_{\text{lignin}}^{-1}$	Lignin conversion Vanillin concentration	This work

## References

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