Navicula salinicola biosilica-supported TiO_2 prepared with urea and Cu(II): crystallite size, optical properties, and Rhodamine B decolorization

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Abstract

Diatom biosilica is a renewable amorphous silica with a hierarchical pore structure. TiO_2 prepared with urea, Cu(II), or both was deposited on biosilica of the pennate diatom *Navicula salinicola* (DB-NS) by impregnation with titanium oxysulfate and compared with its unsupported counterparts. On the biosilica, anatase formed near-spherical particles of 10.5 to 11.5 nm with smaller crystallites than unsupported TiO_2 (10.1 versus 14.0 nm), and the indirect band gap increased to 3.24 to 3.33 eV. Under visible light, urea-derived TiO_2 on biosilica (DB@N-TiO_2) gave the largest decrease in Rhodamine B absorbance (99.9% within 120 min), although it contains only 28.5 wt% TiO_2, and retained 95% of its mass-normalized activity in a second cycle.

Keywords: Diatom biosilica; TiO_2; Optical properties; Visible-light photocatalysis

Introduction

Anatase TiO_2 is stable and inexpensive, but its band gap of about 3.2 eV restricts light absorption mainly to the ultraviolet region, and its nanoparticles aggregate in water and are difficult to recover. Doping with N or Cu can extend the response to visible light, and a porous support can keep the particles small and dispersed.

Diatom frustules are amorphous silica shells with ordered, hierarchical pores and abundant silanol groups, and they are produced by microalgae under mild conditions. Biosilica from cultured diatoms is therefore an attractive renewable support for TiO_2.

In this work, TiO_2, N-TiO_2, Cu-TiO_2, and Cu/N-TiO_2 were prepared both with and without *N. salinicola* biosilica, so that the effect of the support on the crystallite size, optical properties, and visible-light decolorization of Rhodamine B (RhB) could be compared directly for each composition.

Key findings

10.1 nm
TiO_2 crystallite size on biosilica (14.0 nm unsupported)

99.9%
decrease in RhB absorbance by DB@N-TiO_2 within 120 min

28.5 wt%
TiO_2 content of the supported samples

95%
mass-normalized activity retained in the second cycle

Research Method

Biosilica was obtained from cultured *N. salinicola* and impregnated with TiO_2 prepared from titanium oxysulfate with urea, $CuCl_2$, or both. The unsupported counterparts were prepared by precipitation (Fig. 1).

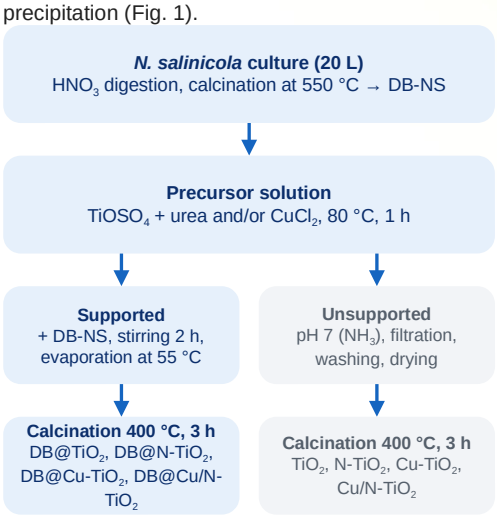


Fig. 1. Preparation of the biosilica-supported and unsupported samples.

The samples were characterized by XRD, FTIR, SEM–EDS, micro-XRF, TEM/SAED, UV–vis DRS, photoluminescence, and CHNS analysis. In the photocatalytic test, 50 mg of catalyst was stirred in 30 mL of RhB (25 mg/L) under a 500 W xenon lamp with a 420 nm cutoff filter (100 mW/cm²) for 150 min, and the absorbance at 555 nm was followed.



Fig. 2. SEM images of (a) DB-NS and (b) DB@N-TiO_2, and (c) TEM image of DB@N-TiO_2.

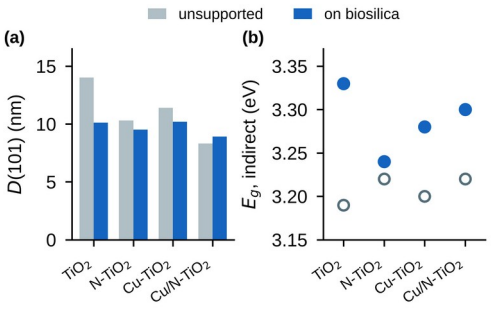


Fig. 3. (a) Crystallite size from the anatase (101) reflection and (b) indirect band gap.

Discussion & Result

All samples showed anatase as the only crystalline phase. On the biosilica, TiO_2 formed near-spherical nanoparticles of 10.5 to 11.5 nm (TEM, Fig. 2c), and the crystallite size of TiO_2 was smaller than without the support (10.1 versus 14.0 nm; Fig. 3a). The indirect band gaps increased from 3.19 to 3.22 eV to 3.24 to 3.33 eV (Fig. 3b). The samples prepared with urea showed an absorption tail between 400 and 500 nm without band-gap narrowing, although CHNS analysis showed only ≤0.03 wt% N; oxygen vacancies or Ti^{3+} may also contribute.

Under visible light, the supported sample gave a larger decrease in RhB absorbance than its unsupported counterpart in each pair that could be compared (Fig. 4). DB@N-TiO_2 decreased the absorbance by 96% within 45 min and by 99.9% within 120 min (k_{app} = 4.96 × 10^{-2} min^{-1}), compared with 49% for N-TiO_2 at 120 min, whereas Cu lowered the activity. The blue shift of the RhB band is consistent with N-deethylation, and dye sensitization may contribute to the decolorization.

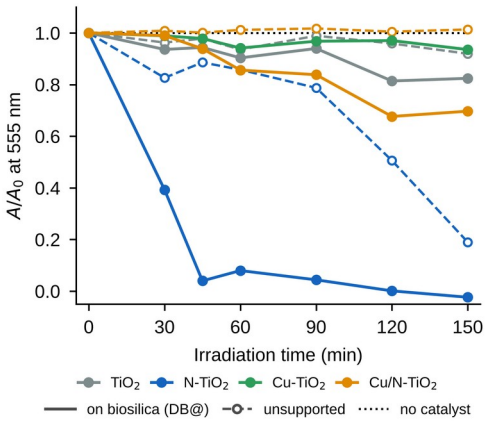


Fig. 4. RhB absorbance at 555 nm relative to the no-catalyst control under visible light (Cu-TiO_2 not evaluated).

Conclusion

N. salinicola biosilica supported near-spherical anatase nanoparticles of about 11 nm, gave smaller TiO_2 crystallites, and increased the band gap of TiO_2. Urea-derived TiO_2 on biosilica gave the largest RhB decolorization although it contained only 28.5 wt% TiO_2, and it retained 95% of its mass-normalized activity in a second cycle. Diatom biosilica is therefore a promising renewable support for TiO_2 photocatalysts. Dark adsorption tests, surface-area measurements, and tests with a colorless probe are needed to clarify the role of the support and the origin of the visible-light activity.

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