Supplementary Information

Significant improvement of TiO₂ photocatalytic activity through a controllable ZrO₂ deposition

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Characterization details

1. XRD analysis.

The crystal structure of TiO₂ and ZrO₂/TiO₂ samples was analyzed by X-ray diffraction (XRD) with filtered Cu K α radiation (λ = 1.5406 Å). The scanning range was 2 θ from 20° to 80°, with a scanning rate of 0.025 °/s. The Scherrer equation was applied to calculate the average crystallite

$$D = \frac{K\lambda}{R\cos\theta}$$

sizes of TiO₂ and ZrO₂/TiO₂ samples: $Bcos\theta$, where B is the half-height width of the diffraction peak of anatase, K=0.89 is a coefficient, θ is the diffraction angle, λ is the X-ray wavelength corresponding to the Cu K α irradiation (1.5406 Å) and D is the average crystallite size of the powder sample [1].

2. Raman analysis.

Raman spectra of TiO₂ and ZrO₂/TiO₂ samples were recorded using a Horiba-Jobin Yvon LabRam spectrometer, equipped with a 17 mW He-Ne laser. Spectra were collected using a $10 \times$ objective lens over a wavenumber range of 200-1000 cm⁻¹. The reported spectra were generated from 10-20 scans of the respective wavenumber range, each taking ten seconds.

3. Band gap calculation.

UV–visible absorbance and diffuse reflectance spectra (DRS) of TiO₂ and ZrO₂/TiO₂ samples were obtained with a UV–visible spectrophotometer (Varian Cary 5). BaSO₄ was used as an absorbance standard in the UV–visible reflectance experiments. The UV–DRS was used to evaluate the band gap of TiO₂ and ZrO₂/TiO₂ samples by plotting $[F(R)*hv]^{1/2}$ against *hv*, where *hv* is the energy of the incident photon and F(R) is the reflection in Kubelka-Munk function [2]. The linear part of the curve was extrapolated to zero reflectance and the band gap energy was derived.



Figure S1. EDS spectrum of 80c-Zr/TiO₂ sample for Figure 3c.



Figure S2. UV-visible diffuse reflectance spectra of TiO₂ and ZrO₂/TiO₂ samples.



Figure S3. Band gap determination of pure TiO₂ nanoparticles and TiO₂ nanoparticles deposited with different cycles of ZrO₂ ALD. Blue and red lines represent experimental and extrapolated data, respectively.

Sample	Preparation method	Pollutant	k _{app} (sample):k _{app} (pure TiO ₂) ^a	References
45c-Zr/TiO ₂	ALD	Methylene blue	10.6	This work
40Ce/TiO ₂	ALD	Methylene blue	3.3	[1]
Pt/TiO ₂	ALD	Methylene blue	3.0	[3]
TZ(10:1)-HS	Functionalized polystyrene spheres	Rhodamine B	3.0	[4]
6.9% ZrO ₂ /TiO ₂	Surfactant self- assembly method	Rhodamine B	2.0	[5]
TiO_2/ZrO_2	A two-step method	Methyl orange	1.8	[6]
10% ZrO ₂ /TiO ₂	Sol-gel	Ethanol	1.5	[7]
12% ZrO ₂ /TiO ₂	Sol-gel	4-chlorophenol	1.3	[8]

 Table S1. Comparison of photocatalytic activity of various photocatalysts.

^a k_{app} is the apparent first order constant.

References

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