## Enhanced Tribocatalytic Degradation using Piezoelectric CdS

### **Nanowires for Efficient Water Remediation**

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#### **Materials Characterization**

X-ray diffraction (XRD) patterns of the as-prepared samples were collected on a SMARTLAB diffractometer with Cu K $\alpha$  radiation. Morphology and microstructure characterization of the material was performed using a Hitachi SU8010 Field-emission scanning electron microscope (FESEM) and JEM-F200 high-resolution transmission electron microscopy (HRTEM). High-resolution trans-mission electron microscopy (HRTEM) and energy-dispersive X-ray (EDX) analysis were carried out using a TEM. X-ray photoelectron spectra (XPS) were obtained by using the ESCALab Xi+ photoelectron spectrometer. UV-vis diffuse reflectance spectroscopy (DRS) were recorded using a UV-visible spectrophotometer with an integrating sphere attachment (PE Lambda950, PerkinElmer) and BaSO<sub>4</sub> as a reference. The photoluminescence (PL) spectra of the samples were measured on a fluorescence spectrometer (FLUOROLOY-3) under a laser excitation of 320 nm. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) method and the nitrogen (N<sub>2</sub>) adsorptiondesorption isotherms at 77 K were recorded by a Micromeritics Quadrasorb si-3 nitrogen adsorption apparatus (USA).

#### **Electrochemical measurements**

The Electrochemical impedance spectrum (EIS) and Mott–Scotty plots were carried out by an electrochemical workstation (CHI660B, CH Instruments) with a typical threeelectrode configuration, that Ag/AgCl (saturated KCl) was used as reference electrode and 0.5 mM CuSO<sub>4</sub> aqueous solution as electrolyte. The work electrode was synthesized CdS nanowires were thoroughly mixed with polyethylene glycol (PEG, Junsei,  $M_w 20,000$ ) as a binder material with 30 wt % of CdS content and then cast on In:SnO<sub>2</sub> (ITO) conducting glass (1 × 1cm<sup>2</sup>). The film was dried at room temperature and calcined under air at 400 °C for 1 h to remove the binder. The ITO substrate was connected to a copper wire by silver paste to make Ohmic contact. Then the portion of silver paste on ITO substrate is again covered with epoxy resin to isolate it from an aqueous electrolyte solution.

#### **Trapping experiments**

To investigate the degradation pathways behind tribocatalytic mechanism, we performed trapping experiments using different scavengers. Ethylene diamine tetraacetic acid (EDTA, 2 mM), tert-butyl alcohol (TBA, 2 mM) and benzoquinone (BQ, 0.5 mM) solutions were prepared in a 5 mg  $L^{-1}$  RhB solution. Next, experiments for tribocatalysis were performed in a similar manner as discussed above, which the solution's intensity was monitored at 554 nm after 7 h.



Fig.S1 EDAX spectra of CdS nanowires prepared at 160 °C for 60 h.



Fig.S2 XPS survey scans of CdS nanowires treated at 160 °C for 60 h.

# Theoretical comparison of piezo-electric performance of different CdS nanowires The theoretical piezo-electric performance of the CdS nanowire in the tribocatalytic degradation was also investigated by the finite element method (FEM) with the aid of the COMSOL Multiphysics<sup>1</sup>. The model consists of a nanowire CdS crystal with the diameter 50 nm, and length of 500 nm and 2 $\mu$ m, respectively. Owing to the piezoelectric materials is more sensitive to the fore, the CdS nanowire could obtain the high voltage output just by capturing the mechanical energy of the fluid flow<sup>2</sup>. The other material parameters used in this simulation, such as density ( $\rho$ = 4826 kg m<sup>-3</sup>), elasticity matrix (*cE*), coupling matrix (*eES*), and relative permittivity ( $\varepsilon_r$ ) are available as predefined material parameters in Comsol Multiphysics. The main parameters are listed as follows:

$$cE = \begin{bmatrix} 9.07 & 5.81 & 5.10 & 0 & 0 & 1.504 \\ 5.81 & 9.07 & 5.10 & 0 & 0 & 0 \\ 5.10 & 0 & 9.38 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1.504 & 0 & 0 \\ 1.504 & 0 & 0 & 0 & 0 & 1.63 \end{bmatrix} \times 10^{10} Pa$$
$$eES = \begin{bmatrix} 0 & 0 & 0 & 0 & -0.21 & 0 \\ 0 & 0 & 0 & -0.21 & 0 & 0 \\ -0.244 & -0.244 & 0.44 & 0 & 0 & 0 \end{bmatrix} Cm^{-2}$$
$$\varepsilon_r = \begin{bmatrix} 9.35 & 0 & 0 \\ 0 & 9.35 & 0 \\ 0 & 0 & 10.33 \end{bmatrix}$$



Fig.S3 COMOSOL multiphysics simulations for the piezoelectric potential distribution in different CdS nanowires: (a) the finite element method (FEM) simulation for a CdS nanowire strained by a lateral force with the bottom fixed and grounded; CdS nanowire showing different deformation under vertical force(b,d) and lateral force (c,e). (b, c) the length of nanowire is 500nm; (d, e) the length is  $2 \mu m$ .

Fig.S3 illustrates the FEM simulation of CdS nanowire (50 nm x 500 nm and 50 nm x 2  $\mu$ m) in accordance with the investigated samples. As the material is not isotropic, the preferred growth directions of [001] for the CdS nanowire had to be taken into account in all simulations. On the basis of the results obtained, the polarization potential is distributed mainly on the bottom when undergoes a fixed lateral force 100 nN (Fig.S3a), which similar to that of the BTO nanowire<sup>3</sup>. When the CdS nanowire undergoes the compressive by applied on the top surface along the vertical direction, the piezoelectric potential distributes continuously along the polar axis as shown in

Fig.S3b. An obvious deform could be observed in Fig.S3c when a small additional force applied to the lateral surface. As is evident by comparing Fig. S3d and e, the piezoelectric potential is dependence on the morphologies and a larger potential presents in the CdS nanowire with aspect ratio increased, which is also supported by the results obtained from the degradation experiments.



Fig.S4 The absorption spectra of RhB solution mediated by different CdS nanowires in the container of the glass under magnetic stirring with four PTFE stirring rods in dark at room temperature.



Fig. S5 (a) Nitrogen adsorption/desorption isotherm of the CdS nanowires prepared at different solvothermal time. (b) Total organic carbon (TOC) analyses of RhB solution at different time after tribo-catalytic degradation. Catalytic conditions: RhB solution (5 ppm) 30 ml, CdS nanowires (S-60) 30 mg, reaction temperature = 293K, stirring rate = 300 rpm, PP container, four stirring rods.

Nanoparticles usually have a strong adsorption capacity. It is necessary to know whether adsorption affects the degradation result. For this purpose, the nitrogen adsorption/desorption isotherms (Fig. S5a) reveal that the higher adsorption ability was obtained in S-15. With the increase of solvothermal reactive time, CdS nanowires possess lower adsorption activity compared with S-15, which however present the

higher catalytic activity (Fig.4c). Additionally, physical adsorption will generally reach saturation after cycling test, resulting in the decrease of RhB removal rate. While the cycling test for the RhB degradation in Fig. 6c shows a similar degradation ratio, which indirectly verify the piezoelectricity induced RhB degradation rather than adsorption. The total organic carbon content (TOC) analysis of the solution shows the mineralization of RhB (Fig.S5b). The TOC content of the solution gradually decreased with the decomposition of RhB dyes. On the basis of these results, we believe that the adsorption of dye molecules is not the main reason for degradation.



Fig.S6 The absorption spectra of RhB solution mediated by S-60 in the container of the polypropylene (PP) under magnetic stirring with different PTFE stirring rods in dark at room temperature.



Fig.S7 Reaction kinetics (a) and reaction rate constant (b) mediated by S-60 nanowires under different catalytic conditions.

A quantitative analysis on CdS tribo-catalysis induced RhB degradation was performed by

comparing the reaction rate constant k, which can be defined by

$$k = (\ln \frac{c_0}{c})/t \tag{1}$$

where  $c_0$  is the initial RhB concentration and c is the RhB concentration at time t.



Fig.S8 The absorption spectra of 5 ppm MO (a), 10 ppm MB (b) and 10 ppm MG (c) solution mediated by S-60 in the container of the polypropylene (PP) under magnetic stirring with four PTFE stirring rods in dark at room temperature, respectively; The decomposition efficiency (d-e) and reaction kinetics (f) mediated by S-60 nanowires for different organic dye solution in the PP container with four PTFE stirring rods.



Fig.S9 XRD pattern of CdS nanowires before and after tribo-catalytic degradation.



Fig.S10 SEM of CdS nanowires before and after tribo-catalytic degradation.



Fig. S11 (a) The •OH-trapping fluorescence spectra of suspensions containing CdS nanowires and TA under excitation wavelength of 315 nm; (b) DMPO spin-trapping ESR spectra of S-60 nanowires in a methanol dispersion for DMPO–• $O_2^-$ .

Particle size (nm)	<b>S-15</b>	S-45	S-60	S-72
(100) peak	11.1276	22.8296	24.1986	26.5229
(002) peak	339.0418	384.1859	515.0792	850.3758
(101) peak	10.10612	11.86776	23.3179	25.6497

Table S1 Average crystallite sizes determined by Scherrer's equation for different CdS samples.

Normally, the high-angle diffraction peaks in the XRD patterns were used to calculate the grain size based on the Scherrer's equation:

$$D_{hkl} = \frac{0.89\lambda}{\beta_{hkl}\cos\theta} \tag{2}$$

In which  $D_{hkl}$  represents the size in the vertical direction of the (hkl) plane,  $\beta_{hkl}$  is the full width at half maximum (FWHM) of the diffraction peak,  $\lambda$  is the wavelength of the Cu K $\alpha$  radiation (0.15405 nm), and  $\theta$  is the glancing angle. The average crystallite sizes determined by Scherrer's equation by fitting the line broadening of the (100), (002) and (101) peaks. The particle size for S-15 sample was estimated to be 10.11 nm according to the (100) and (101) peaks, while the particle size is 339 nm based on the (002) peak. This result indicates that the CdS present nanowire shape with the preferential growth along the *c*-axis direction. To increase the solvothermal reactive time, one can see that the length of CdS nanowires increases from 339 nm up to 850 nm, and the average diameter almost preserves 25 nm. This regularity coincides well with the morphology observed from the SEM. While these values smaller than these obtained from SEM observation due to mostly nanowires mixed and disorderly stack during XRD measurement and it shows the average data of the whole sample. The Scherrer's

equation can estimate the grain size of spherical particles, which may cause the computational errors of CdS nanowire grain size.

Catalyst	Catalytic conditions ( dye concentration)	Catalytic activity	ref
Pb(Zr,Ti)O <sub>3</sub> /TiO <sub>2</sub>	LED(15 mW·cm <sup>-2</sup> )+stirring (RhB 10 ppm)	$k = 0.058 \text{ min}^{-1}$	[4]
KNbO3 nanosheets	xenon lamp (300 W) + ultrasound (40 kHz, 110 W) (RhB 10 ppm)	$k = 0.022 \text{ min}^{-1}$	[5]
BaTiO <sub>3</sub> nanowires	ultrasound (40 kHz, 80 W) (MO 6 mg $\cdot L^{-1}$ )	$k = 0.015 \text{ min}^{-1}$	[3]
Ag <sub>2</sub> O/BaTiO <sub>3</sub>	mercury lamp/xenon lamp + ultrasound (40 kHz, 50 W) degradation of RhB (15 mg $\cdot$ L <sup>-1</sup> )	$k = 0.051 \text{ min}^{-1}$	[6]
NaNbO3 nanorods	UV light + ultrasound (40 kHz, 100 W) degradation of MB (0.01 mM)	$k = 0.024 \text{ min}^{-1}$	[7]
ZnO nanorods	UV irradiation (24 W) + ultrasound (40 kHz, 150 W) (degradation of AO7 10 mg $\cdot$ L <sup>-1</sup> )	$k = 0.044 \text{ min}^{-1}$	[8-9]
BiFeO3 nanoparticles	thermal cycling between 27 and 38°C degradation100% within 85of RhB (5 ppm )cycles (about 28 h)		[10]
Ba <sub>0.7</sub> Sr <sub>0.3</sub> TiO <sub>3</sub> /Ag nanoparticles	thermal cycling between 25 and 50 $^{\circ}\mathrm{C}$ degradation of RhB (5 ppm )	100% within 50 cycles (16 h)	[11]
Pb(Zr <sub>0.52</sub> Ti <sub>0.48</sub> )O <sub>3</sub>	thermal cycling between 27 and 60 °C degradation	100% within 140	140 [12]
polarized ceramic	of RhB (5 ppm)	cycles (about 23 h)	
CdS nanowire	Only stirring in PP container (RhB 5ppm), without	$k = 0.32 \text{ h}^{-1}$	This
	light	98% within 7 h	work

Table S2 Comparison of the catalytic performance of representative piezoelectric materials.

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