Supporting Information

Synergistic Interplay between Oxygen-Vacancy and S-Scheme Charge Transfer Dynamics in LaFeO3/FeOOH Heterojunction Towards Sono Assisted Photo Fenton Antibiotic Degradation and Water Splitting

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Text S1. Experimental section

S1.1. Materials and Methods

La(NO₃)₃.6H₂O (99.99%, AR), Fe(NO₃)₃.9H₂O (\geq 99%), FeSO₄·7H₂O (\geq 99%), C₆H₈O₇.H₂O (\geq 99%), CH₃COONa·3H₂O (\geq 99%), NH₄OH, AgNO₃, FeCl₃, ofloxacin, and Nafion were procured from Sigma-Aldrich. DI water was used to make all the aqueous solutions. All reagents used are of analytical grade and employed without any additional purification.

S1.1.1. Synthesis of LaFeO₃ nanoparticles

The LFO nanoparticles were synthesized by adopting a similar sol-gel method reported earlier in the literature [1], wherein, the raw materials taken were $La(NO_3)_3.6H_2O$, $Fe(NO_3)_3.9H_2O$, NH_4OH , & $C_6H_8O_7.H_2O$. Following a molar ratio of 1:1:2, the calculated mass of $La(NO_3)_3.6H_2O$, $Fe(NO_3)_3.9H_2O$, & $C_6H_8O_7.H_2O$ were suspended in DI water under magnetic stirring. A uniform nitrate-citrate sol was created. The pH was adjusted to 7 by adding NH_4OH to stabilize the sol, followed by stirring the sol overnight at 60°C and gradually increasing the temperature to 130°C, forming a dried gel, which finally underwent calcination at 500°C for 2 h to obtain pure LFO.

S1.1.2. Synthesis of FeOOH

The FeOOH photocatalysts were synthesized at room temperature via the coprecipitation method. 5 mmol of FeSO4·7H2O, 10 mmol of CH3COONa·3H2O, and 50 mL of deionized water were stirred at 40 °C for 6 hours. A reddish-orange precipitate was obtained and washed with ethanol-water solution, followed by centrifugation. The resulting product was then heated at 60 °C for 12 hours in an oven to yield the FeOOH catalyst.

S1.1.3. In-situ synthesis of LFO/FeOOH heterostructure

LFO@FeOOH binary heterostructures were prepared in varying ratios of 1:1, 1:2, 1:3, and 1:4 via the in situ coprecipitation method with varied amounts of prepared LFO. In a standard procedure, the binary 1:1 heterostructure is prepared by adding 5 mmol of FeSO4·7H2O and 10 mmol of CH3COONa·3H2O to 100 mL of DI water under continuous stirring for 15 minutes. This is followed by adding 0.19 g of prepared LFO to the above solution and allowed to stir for another 6 h at 40 °C. A reddish-orange precipitate was formed and washed with an ethanol-water mixture before being centrifuged. The obtained product was then dried in an oven at 60°C for 12 h to produce the catalyst LF11. Similar 1:2 (LF12), 1:3 (LF13), & 1:4

(LF14) heterostructures were prepared following the above procedure by adding 0.095, 0.063, and 0.047 g of LFO, respectively. No unusual hazards were observed during the catalyst preparation process.

Text S1.2. Material Characterization

The structural and crystallographic characteristics of the prepared photocatalysts were examined using a Rigaku Ultima-IV X-ray diffractometer (PXRD) with Cu Ka radiation. Surface morphology, elemental distribution, and color mapping were investigated through scanning electron microscopy (SEM) on a CARL-ZEISS EVO-18 model operated at an EHT of 20 kV. For insights into internal structural features, transmission electron microscopy (TEM) was performed using a Philips Tecnai G2, with high-resolution TEM (HRTEM) imaging at an accelerating voltage of 200 kV. Surface texture characterization has been achieved using a Quantachrome NOVA-2200e instrument. X-ray photoelectron spectroscopy (XPS) was carried out using a VG-Microtech-Multilab ESCA-3000 with Mg Ka radiation to assess the electronic structure and chemical states. Raman spectroscopy measurements, performed with a RENISHAW spectrometer, utilized a 520 nm laser for vibrational analysis. UV-vis DRS (Ultraviolet-visible diffuse reflectance spectroscopy) data were collected on a JASCO 750 spectrophotometer, using BaSO4 as a reference and a scanning speed of 40 nm/min across the 200-800 nm wavelength range. Steady-state photoluminescence (PL) measurements were acquired on a JASCO FP8300 spectrofluorometer with a 350 nm excitation wavelength. Timeresolved photoluminescence (TRPL) profiles were recorded with a HORIBA SCIENTIFIC DeltaPro Fluorescence Lifetime System, utilizing a 360 nm laser source. Additionally, all photoelectrochemical (PEC) tests were conducted in a three-electrode configuration on an IVIUM-n-STAT multichannel electrochemical workstation.

Text S2. Procedure of Ofloxacin Degradation

Initially, three batches of 20 ml of 20 ppm solution of OFL were dark-stirred with 10 mg of the photocatalyst. A fixed amount of H2O2 was then added to the mixture solution. The mixture solutions in the 1st batch were subjected to simulated solar light; in the 2nd batch, US waves were applied, and the 3rd batch was put through both simulated solar light and US waves for 1 h each. For the experimental setup, a Vis-LED photoreactor having a 20 W power Lamp and an Ultrasonicator with a frequency of 40kHz and 150 W power were used. The mixture solutions were centrifuged, and the decant was set to record the absorbance spectra. Absorbance spectra of the 20 ppm OFL solution were also recorded. Comparing the above two

spectra for each degradation batch gives the quantity of OFL degraded under simulated solar light, US waves, and both simulated solar light and US waves.

Ultrasound-Assisted O₂ Evolution Experiment.

For a typical OER, 0.02 g of the catalyst is dispersed in 20 mL of AgNO3 (0.05 M) solution and continuously stirred in the dark (30 min) to establish adsorption-desorption equilibrium. To remove dissolved O_2 , the solution is bubbled with N_2 gas for about 20 min before the OER experiment. The resulting suspension is then subjected to ultrasonication and light illumination simultaneously using a 125 W Hg lamp (0.027 W cm⁻²) and an Ultrasonicator with a frequency of 40 kHz and 150 W power. For these experiments, the reactor was placed inside the ultrasonic bath to favor the generation of O_2 . The evolved O_2 is analyzed using an Agilent 7890B-series gas chromatograph equipped with a 5A molecular sieve column and a thermal conductivity detector (TCD). The same procedure is also performed using a FeCl₃ solution.

Text S3. Photoelectrochemical (PEC) measurement

Preparation of FTO (working electrode): The synthesized sample is drop-cast onto the conductive fluorine-doped tin oxide (FTO) glass, which undergoes an initial ultrasonic treatment in a solution of deionized (DI) water and ethanol for 45 minutes before drying at 80°C. A solution is prepared for coating by dispersing 1 mg of the sample in a mixture of 1.6 ml DI water, 40 μ L of Nafion, and 1.4 ml ethanol. This solution is applied to the FTO surface. All photoelectrochemical (PEC) measurements are performed in a three-electrode configuration using the IVIUMn-STAT multi-channel electrochemical workstation, with an electrochemical cell setup that includes the FTO-coated sample (working electrode), a platinum - Pt (counter electrode), and a saturated Ag/AgCl reference electrode. These electrodes are immersed in a 0.1 M Na₂SO₄ electrolyte solution (pH ~ 6.5) for the measurements. The coated area of the FTO working electrode is 1 cm², and the bare FTO shows no photocurrent response under light exposure. The setup is illuminated with a xenon (Xe) lamp to study the photoinduced carrier dynamics and measure photocurrent.

Electrochemical Impedance Spectroscopy (EIS) offers valuable insights into the charge transfer resistance and material conductivity during catalytic reactions. EIS measurements span a frequency range from 106 Hz to 0.01 Hz, i.e., Nyquist plots for LFO, FeOOH, and LF13 were analyzed in Na₂SO₄ solution (0.1 M) at an applied potential of 0.0 V. This technique specifically probes the electrical characteristics at the semiconductor/electrolyte interface within photocatalytic systems, facilitating the analysis of charge transfer dynamics between

two photocatalysts. It also helps differentiate phenomena occurring at various rates, such as electron-hole recombination, transport resistances, and series resistances, as well as electron lifetime in materials like LFO and FeOOH. The photocurrent densities of the as-prepared samples are also evaluated via linear sweep voltammetry (LSV) within a 0.5 to 1.5 V potential bias range.

Mott-Schottky (MS) analysis was conducted at 500 Hz with a 25 mV AC voltage to further investigate the band edge alignment and charge transfer mechanism within these materials. This approach provided insights into the flat band potentials ($E_{ne\beta}$) of the materials. The $E_{ne\beta}$ values, crucial for understanding the band structure and exciton dynamics in semiconductors, were determined by extrapolating the C⁻² = 0 intercept from MS plots. The flat band potentials for LFO (-0.73 V) and FeOOH (-0.51 eV) were established relative to the Ag/AgCl reference electrode and can be converted to the NHE scale using the Nernst equation

$$E_{NHE} = E_{Ag/AgCl} + E_{Ag/AgCl} + 0.059 (7 - pH)$$
(S1)

At 25 °C, $E_{Ag/AgCl} = 0.197$ V, where $E_{Ag/AgCl}$ represents the potential applied of the Ag/AgCl electrode, with an electrolytic pH of 6.5. For n-type semiconductors, E_{fb} typically lies between 0.1 to 0.3 eV below the conduction band minimum (CBM). Assuming a 0.1 eV offset, the conduction band energies for LFO and FeOOH were found as -0.83 eV and -0.61 eV on the NHE scale, respectively. Using their band gaps derived from UV-DRS spectra, the VB (valence band) values were calculated as 1.06 eV for LFO and 1.34 eV for FeOOH on the NHE scale, applying the equation

$$E_{VB} = E_g + E_{CB} \tag{S2}$$

Text S4. Radical Tests

To identify the primary ROS — namely electrons (e⁻), holes (h⁺), superoxide radicals ($\cdot O_2^{-}$), and hydroxyl radicals ($\cdot OH$) — involved in the OFL degradation through an S-P-FP mechanism, quenching experiments were conducted using specific ROS trapping agents. These agents include p-benzoquinone (PBQ) for capturing $\cdot O_2^{-}$, IPA (isopropyl alcohol) for $\cdot OH$, citric acid (CA) for h⁺, and DMSO (dimethyl sulfoxide) for e⁻. The sequence of reactive species contributing to OFL degradation is as follows: $\cdot O_2^{-} > \cdot OH > e^{-} > h^{+}$, indicating the participation of $\cdot O_2^{-}$ and $\cdot OH$ radicals play the most significant roles in the degradation process. To confirm $\cdot O_2^-$ radicals produced by the samples, a nitroblue tetrazolium (NBT) test was performed. The peak absorbance at 260 nm represents the presence of Formazan, formed by the reaction of NBT with $\cdot O_2^-$ in the molar ratio 4:1.

The terephthalic acid (TA) test is commonly utilized as a probe molecule for detecting hydroxyl radicals (•OH) due to its reaction with •OH, which produces a characteristic fluorescence emission peak at 425 nm representing the 2-hydroxyterephthalic acid (HTA). By measuring the fluorescence intensity of the above fluorescence spectrophotometer with a 315 nm excitation source, the concentration of •OH radicals was confirmed.

Text S5. Parameters affecting the degradation process

To assess the impact of inorganic scavengers on pollutant degradation, several anionic scavengers—specifically NaCl, Na₂CO₃, and NaNO₃ (each at a concentration of 0.05 M)—are employed to examine the influence of anions. This can be explained as follows: (i) Radicals produced by reactions between ROS and anions like Cl⁻, CO₃²⁻, and NO₃⁻ generally exhibit lower oxidation potentials than hydroxyl radicals, affecting pollutant degradation rates. (ii) Anions in solution may also block the active sites on the LF13 catalyst and scavenge the ROS responsible for the degradation performance. The anions follow the $CO_{3^{2-}} > NO_{3^{-}} > Cl^{-}$ trend, where Cl⁻ known to exhibit the lowest scavenging effect. The Cl⁻ functions as a scavenger for HO•. However, the resulting intermediate (ClOH•⁻) may either regenerate the HO• radical or interact with hydrated electrons (e_{aq}) and H₃O⁺ ions, ultimately producing Cl• radicals. which in turn, helps to eliminate H• and $\bar{e_{aq}}$ species from the reaction medium. Also, a substantially high concentration of Cl⁻ ions is required to react with HO• [2]. Additionally, the role of various cationic scavengers—such as CaCl₂, KCl, and Mg(NO₃)₂—is analyzed through the use of corresponding salts. Cations like Ca2+ and Mg2+ reduce photocatalytic efficiency, likely by altering ionic strength. Some inhibition may result from the complexation of these cations with pollutant molecules on the catalyst surface, with their impact ranked as follows: $Mg^{2+} > Ca^{2+} >$ K^{+} [2]. This could also be attributed to the decreasing hydrated ionic radius from K^{+} to Mg^{2+} , resulting in a slower ion exchange rate than K⁺ [3]. Lastly, oxidizing agents, including H₂O₂ and K₂S₂O₈, are tested to assess their influence on degradation efficiency, where not much difference is observed as the HO• responsible for the ofloxacin degradation is produced by the addition of both the oxidizers. Moreover, upon adding persulfate, HO• generation predominates at higher alkaline levels, introducing the inhibition phenomenon with lower rate constants [4, 5].

A gas sparging study has also been conducted to study the impact of dissolved gases in the Ofloxacin degradation system. Three key properties of gases can significantly affect Sono-Photo-Fenton activity: (1) higher values of 'polytropic ratio' increase the intensity of bubble collapse, raising local temperature and pressure; (2) lower 'thermal conductivity' limits heat loss during collapse, enhancing temperature and catalytic efficiency; and (3) more excellent 'solubility in water' boosts free radical generation by increasing nucleation sites, facilitating cavitation and enhancing the generation of ROS. Hence, catalytic degradation of 20-ppm Of loxacin solution with 20 mg of catalyst individually purged with Argon (Ar), Oxygen (O_2) , and Nitrogen (N₂) into the solution, and the reaction proceeded for one hour. Notably, the Arpurged system achieved the highest - 92% degradation, following the trend – $Ar > O_2 > N_2$, likely due to Ar's relatively high solubility in water (0.056 mL⁻¹), a polytropic ratio of 1.67, and small thermal conductivity of 0.018 W m⁻¹ K⁻¹. In comparison, degradation efficiencies dropped to 86% with O₂ and 80% with N₂, attributed to their lower solubilities (0.049 & 0.015 mL⁻¹, respectively), the polytropic ratio of 1.40, and miniature thermal conductivities of 0.0263 & 0.0258 W m⁻¹ K⁻¹. The introduction of Ar gas enhances the cavitational effects by creating new nucleation points, thereby promoting free radical formation [6].

The impact of pH on the reaction was investigated by adjusting the solution's pH by adding 1M HCl or 1M NaOH to the mixture containing 20 mg of the catalyst and a 20 ppm Ofloxacin solution. To understand the underlying mechanisms, PZC (Point of Zero Charge) determination employing the drift method [7] was conducted on the binary hybrid (Figure S8). The model pollutant, Ofloxacin, has two pKa values of 6.05 and 8.22 [8]; thus, at pH levels below 6.05, it predominantly exists in a cationic state (OFL⁺), while at pH values above 8.22, it transitions to an anionic form (OFL⁻). Between these pKa values, Ofloxacin exists as a zwitterion (OFL⁰). At lower pH levels (pH < pH_{PZC} ~ 4.52), the surface of the catalyst is positively charged, and at pH > pH_{PZC}, the surface is negatively charged. Hence, a sturdy electrostatic attraction exists among the negatively charged catalyst surface and the positively charged and Zwitter ionic OFL (pH = 4.52 - 8.22). Therefore, the S-P-FR degradation performance of the model pollutant OFL follows the trend pH 5 >pH 7 >pH 3 >pH 9, following the above science. Conversely, at elevated pH (3 & 9), the catalyst and OFL acquire positive and negative charges, respectively, resulting in electrostatic repulsion and reduced catalytic activity.

To investigate the degradation products, Liquid Chromatography (LC) and Mass Spectrometry (MS) analyses were performed using an Agilent 6890 and Agilent 5973, respectively, with the fragmentation results illustrated in Fig. 8. For the kinetic analysis during the degradation experiments, aliquots (2 mL) of the reaction mixture were regularly withdrawn, filtered. The absorbance of the supernatant was measured using a UV-Vis spectrophotometer. Control experiments were conducted under ultrasonic and light conditions without adding LF13 and another with LF13 present but without US and light exposure (Figure S9).

Text S6. Optoelectronic features analysis

The UV-Vis DRS are obtained using a JASCO 750 UV-visible spectrophotometer, with Barium sulfate (BaSO₄) as the reference material. Measurements are conducted across the 200–800 nm wavelength range at a 40 nm per minute scanning rate. The optical band gap (Eg) is calculated according to the Kubelka-Munk function, as described by Equation S3.

$$\alpha hv = A \left(hv - E_g\right)^{n/2} \tag{S3}$$

Where h = Planck's constant, v = frequency of incident light, $\alpha =$ proportionality-constant, Eg = optical band-gap of material, and A = absorption-coefficient. 'n' denotes various electronic transitions like n = 1: direct transition (allowed), and n = 3: direct transition.

Text S7. Kinetic Studies using the Langmuir-Hinshelwood model

The kinetic studies of the observed catalytic activity toward OFL degradation are investigated using the Langmuir-Hinshelwood (L-H) model. According to the model, the reaction rate (r) is evaluated with the Equation S4.

$$r = -\frac{dC}{dt} = \frac{kKC}{1+KC}$$
(S4)

When KC << 1,

$$\Rightarrow r = -\frac{dC}{dt} = kKC$$

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 $\therefore r = -\frac{dC}{dt} = K_{app}C$

But $kK = K_{app}$.

Rearranging the above, $\Rightarrow r = \frac{dC}{C} = -K_{app} dt$

Integrating both sides from time 0 to t,

$$\Rightarrow \int_{C_0}^{C_t} \frac{1}{C} dC = -K_{app} \int_0^t dt$$

$$\Rightarrow \ln \frac{C_t}{C_0} = -K_{app} t$$

$$\therefore r = \ln \frac{C_0}{C_t} = K_{app} t$$
 (S5)

Hence, the L-H model reduces to the pseudo-first-order kinetics expression (Equation S5) at

very low concentrations of OFL (20 ppm), where the plot of $\ln \frac{C_0}{C_t}$ against time 't', whose slope gives the value of K_{app} . Following the above method, the calculated k_{app} , R^2 , and $t_{1/2}$ values for the nanomaterials are summarized in Table S1.

Table S1. OFL degradation Efficiencies, R^2 , K_{app} , and $t_{1/2}$ values of all synthesized samples via different processes.

Process	Photocatalyst	DE (%)	R ²	K _{app} (10 ⁻³ min ⁻¹)	t _{1/2} (min)
Sono-Photo-	Blank	-	0	0	-
Fenton	LFO	55	0.913	8.04	86
	FeOOH	65	0.912	10.52	65
	LF11	70	0.912	12.29	56
	LF12	82	0.914	15.05	46
	LF13	92.3	0.913	21.95	32
	LF14	80	0.911	13.91	50
Photo	Blank	-	0	0	0
Fenton	LFO	42	0.910	6.32	109
	FeOOH	45	0.912	6.37	108
	LF11	54	0.909	8.54	81
	LF12	58	0.912	9.83	70
	LF13	50	0.913	8.06	85
	LF14	42	0.913	6.3	110
Sono Fenton	Blank	-	0	0	0
	LFO	50	0.911	7.36	94

FeOOH	45	0.913	6.55	105
LF11	54	0.911	8.17	84
LF12	50	0.910	7.28	95
LF13	47	0.913	6.8	101
LF14	40	0.911	5.52	125

Table S2. Comparison of the Degradation performances reported of Ofloxacin.

Catalyst	Method	Source	Reaction	Experimental	% DE	Ref.
			time (min)	Conditions		
LaFeO ₃	PMS			Catalyst dose =	15	[9]
	activation			20 mg		
				OFL = 10 ppm		
BaTiO ₃ /CuO	Piezocatalytic		120	Catalyst dose =	83	[10]
				10 mg		
				OFL = 30 ppm		
EBFO-3	Fenton-like +		19	Catalyst dose =	22.35	[11]
	PMS			25 mg		
				OFL = 10 ppm		
MIP-PDI/g-	Photocatalysis	300 W	100	Catalyst dose =	92	[12]
C_3N_4				50 mg		
				OFL = 10ppm		
RPGM	Fe activated			OFL = 20 ppm	96.91	[13]
	persulfate					
CuFe-LDHs	Persulfate		120	Catalyst dose =	80	[14]
	activation			0.5 g L-1		
				OFL = 10 ppm		
CoOOH/LaFe _{0.}	PMS		15	OFL = 20 ppm	91.84	[15]
5Ni0.5O3	activation					
Hem/Fe ₂ TiO ₅	Photocatalysis		60	Catalyst dose =	50	[16]
				0.5 g L-1		
				OFL = 50 ppm		

$Fe_3O_4/g-C_3N_4$	Photocatalysis	2 A	300	1g L-1/3 mg	87.4	[17]
	+ Rotating	RMF		L-1/		
	Magnetic field					
LFO/FeOOH	Sono-Photo-	Solar	60	10 mg/ 20	92.3	This
	Fenton	Light +		ррт		work
		40 kHz				

Table S3. Comparison of the OER performances reported for different catalysts.

Catalyst	Method	Source	Catalyst Dose	Time	Yield	Ref.
			/ Sacrificial	(h)		
			Agent			
LFO	Photocatalysis	125 W Hg	50 mg / 50 ml	1	640 µmol	[18]
		Vis lamp	10 vol%		g-1	
			AgNO ₃			
LFO/RGO	Photocatalysis	125 W Hg	50 mg / 50 mL	1	316.24	[19]
		Vis lamp	of 10 vol.% of		mmol g ⁻¹	
			AgNO ₃			
LFO/RGO/NiO	Photocatalysis	125 W Hg	50 mg / 50 ml	1	465 µmol	[20]
		Vis lamp	10 vol %		g-1	
			methanol			
α-FeOOH	Photocatalysis	300W Xe	100 mg / 100	12	4.7 μmol	[21]
		lamp	ml water			
FeOOH/BiVO ₄	Photocatalysis	300W Xe	100 mg / 100	6	723 µmol	[22]
		lamp	mL 0.02 M			
			NaIO ₄			
FeOOH/CdS	Photocatalysis	300W Xe	20 mg / 50 mL	1	676.50	[23]
		lamp	0.1 M NaOH		μmol	
α-	Photocatalysis	150W Xe	20 mg / 20	2	485 µmol	[24]
FeOOH/CeO ₂ NS		lamp	mL 0.05M			
			AgNO ₃ /FeCl ₃			

FeOOH/BiOBr	Photocatalytic		100 mg / 100	1	284.34	[25]
			ml DI water		μmol	
			with 1.0 g			
			AgNO ₃			
NaNbO ₃ /FeOOH	Piezophotocata	125W	15 mg / 15 ml	1	1155 μmol	[6]
	lysis	Hg lamp	0.05 M FeCl ₃		g-1	
		40 kHz				
		100 W				
LFO/FeOOH	Sono-Photo-	125 W Xe	20 mg / 20 ml	1	1270	This
	Catalysis	lamp, 40	0.05 M FeCl ₃		μmol	work
		kHz				



Scheme S1. Formation of Ovs in LFO and FeOOH



Scheme S2. Band offset at LFO/FeOOH heterointerface.



Figure S1. Average particle size determination of (a) LFO, (b) FeOOH, and (c) LF13 from their respective Histograms.



Figure S2. (a) Color mapping and (b) EDAX spectra of nanocomposite LF13.



Figure S3. The XPS survey spectra for (a) LFO, (b) FeOOH, and (c) LF13.



Figure S4. (a-c) BET surface area and pore size (inside) for LFO, FeOOH, and LF-13, respectively.



Figure S5. (a-b) Work function determination of the pristine materials from the VB-XPS spectra.



Figure S6. The (a-c) absorbance spectra for Sono Fenton, Photo Fenton, and Sono-Photo-Fenton degradation of OFL, and its corresponding (d) comparative plot.



Figure S7. The before and after reaction images of (a) PXRD, (b) HR-TEM, and (c) Absorbance spectra for the best nanocomposite LF13.



Figure S8 The (a) Point of Zero Charge (PZC) and the (b) pKa representation of Ofloxacin.



Figure S9. Control experiments of OFL degradation efficiency (a) under ultrasonication and light but without catalyst, and (b) with catalyst but without light and ultrasonication.

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