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Ultrathin mesoporous Co_3O_4 nanosheets with excellent photo-/thermo-catalytic activity

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Experimental

Co_3O_4-O preparation

Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, A. R.) and oxalic acid dihydrate ($C_2H_2O_4{\cdot}2H_2O$, A. R.) were purchased from Shanghai Chemical Company. All of the materials were used without further purification.

Co_3O_4-O nanoparticles were synthesized through a template-free strategy of decomposing self-made bimetal oxalate as previously reported.[1] In a typical process, 0.01 mol $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in 40 mL deionized water under magnetic stirring. 0.01 mol $H_2C_2O_4{\cdot}2H_2O$ was dissolved in 15 mL deionized water at 60 ^{o}C. The latter solution was added dropwise to the former under vigorous magnetic stirring, resulting in a precipitation forming. After stirring for another 1 h in an ice bath, the solid residue was separated by filtration, washed copiously with deionized water, and dried in air at 60 ^{o}C followed by calcinations in air at 250 ^{o}C for 2 h (at 1 ^{o}C min^{-1} heating rate). The sample was denoted as Co_3O_4-O.

Electrophoresis of SS-Co_3O_4 (EP)

The electrophoretic deposition was performed on a DC power supply (HY3003) with stainless steel mesh (SS, approximately 2 cm × 3 cm) as both the cathode and anode. 40 mg Co_3O_4-O and 10mg iodine were added to 50 mL acetone, the whole solution were ultrasonic for 3 minutes. The voltage was set to 10 V and the whole electrophoretic deposition process lasted for 4minutes, the as-obtained sample was denoted as SS-Co_3O_4 (EP) and washed with deionized water, then dried in air at 60 ^{o}C.

Electrochemical analysis

The photocurrent spectra were performed in a three-electrode cell (quartz window) with 0.1 M Na_2SO_4 as electrolyte at a potential of 0.5 V. A Pt ring was used as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the catalyst as the working electrode. A CHI 660C electrochemical workstation (Shanghai Chenhua, China) was used for the photocurrent measurements. As for light sources, a 500W Xe lamp (CHF-XM500) was used.

TG/DTA measurement

Thermogravimetric/differential thermal analyzer (TG/DTA) measurements were conducted using a NETZSCH STA 449C apparatus with an air flow of 20 mL min^{-1} and a heating rate of 10 K min^{-1}.

Raman spectra were recorded on a microscopic confocal Raman spectrometer (Renishaw 1000NR) with an excitation of 514 nm laser light.

1 Z. Shu, W. Huang, Z. Hua, L. Zhang, X. Cui, Y. Chen, H. Chen, C. Wei, Y. Wang, X. Fan, H. Yao, D. He, J. Shi, *J. Mater. Chem. A*, 2013, **1**, 10218.

Table S1 The amount of Co_3O_4 grown on each SS substrate

Sample	Co_3O_4 nanosheets scratched down from the SS				
	1	2	3	4	5
Weight (mg)	6.4	6.8	7.0	6.5	6.9

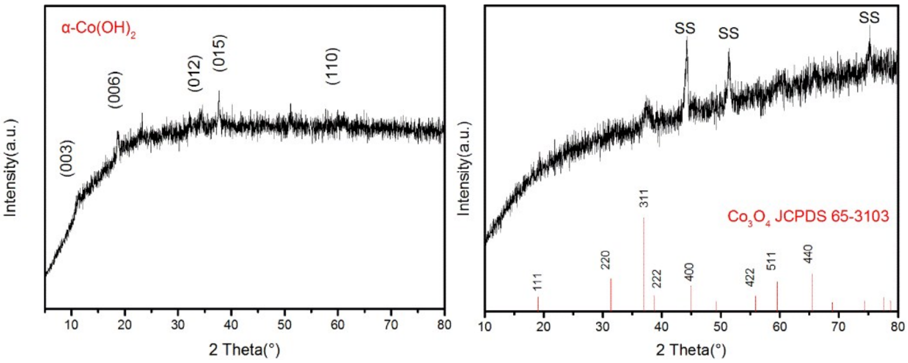

Fig. S1 XRD patterns of $Co(OH)_2$ precursor and SS-Co_3O_4

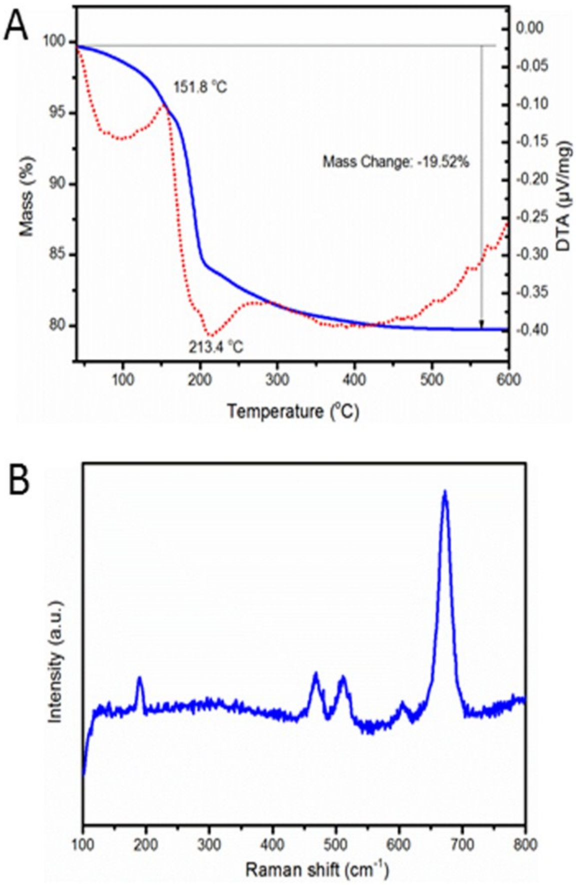

Fig. S2 (A)TG and DTA curves of the α-$Co(OH)_2$ precursor. (B) Raman spectra of Co_3O_4 nanosheets scratched down from the SS

As seen from Fig. S2A, the $Co(OH)_2$ obtained by electrodeposition undergoes a two step weight loss due to dehydration and deposition, rather than a single step weight loss for the β-$Co(OH)_2$.[2] The weight loss below 152 °C is attributed to the removal of the absorbed water and the evaporation of the intercalated water molecules. And the weight loss above 152 °C is associated with the loss of water produced by the decomposition and dehydroxylation of $Co(OH)_2$.[3] After thermally oxidative transformation into Co_3O_4, the net weight loss observed is ca. 19.52%, much larger than that of 13.6% of the β-$Co(OH)_2$. These data further indicates the formed precursor is α-$Co(OH)_2$ phase rather than β-$Co(OH)_2$ and show the crystallization of Co_3O_4.[4]

The sample scratched down from the SS clearly displayed five bands located at approximately 476 (E_g), 191 (F_{2g}), 513 (F_{2g}), 607 (F_{2g}), and 680 (A_{1g}) cm^{-1}, consonant with other references about Co_3O_4.[5,6]

2 H. Zhou, A.L. Wang, G.R. Li, J.W. Wang, Y.N. Ou and Y.X. Tong, *J. Mater. Chem.*, 2012, **22**, 5656.

3 Z. Liu, R. Ma, M. Osada, K.Takada, and T. Sasaki, *J. Am. Chem. Soc.* 2005, **127**, 13869-13874

4 C. Yuan, L. Yang, L. Hou, L. Shen, X. Zhang and X. W. Lou, *Energ. Environ. Sci.*, 2012, **5**, 7883.

5 V.G. Hadjiev, M.N. Iliev and I. V. Vergilov, *J. Phys. C. Solid State Phys.*, 1988, L199–L201.

6 F. Rubio-Marcos, V. Calvino-Casilda, M. A. Bañares and J. F. Fernandez, *ChemCatChem*, 2013, **5**, 1431-1440.

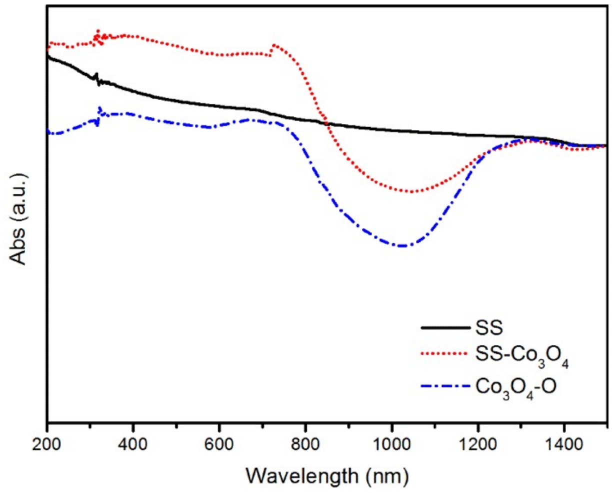

Fig. S3 UV-Vis-IR spectra of SS, SS-Co_3O_4 and Co_3O_4-O

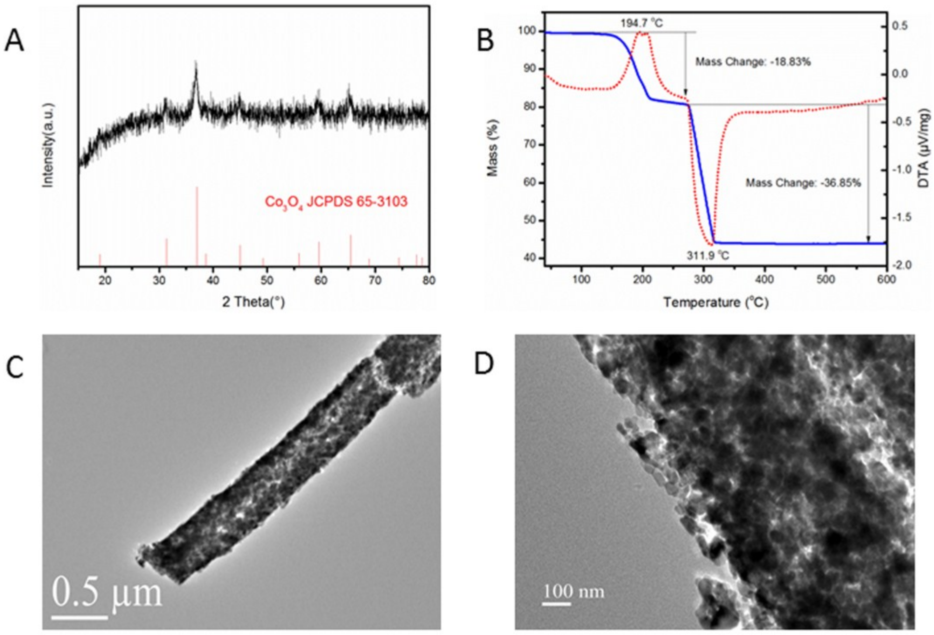

Fig. S4 (A) XRD patterns of Co_3O_4-O. (B) TG and DTA curves of the Co-oxalate precursor. (C)(D)Transmission electron microscopy (TEM) images of Co_3O_4-O

Mainly, one endothermic peak and one exothermic peak can be found for the Co-oxalate precursor. The endothermic and exothermic peaks represent the loss of structural water (weight loss of 18.83%) and decomposition of the $C_2O_4^{2-}$ groups (weight loss of 36.85%), respectively. [1]

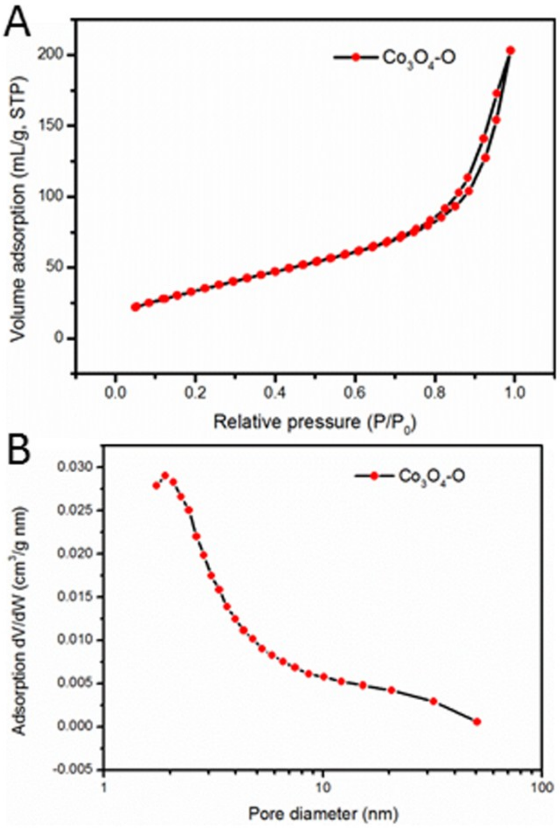

Fig. S5 N_2 adsorption-desorption isotherm and pore size distributions of the Co_3O_4-O

The Brunauer–Emmett–Teller (BET) specific surface area was measured to be 128.3 m^2g^{-1}.

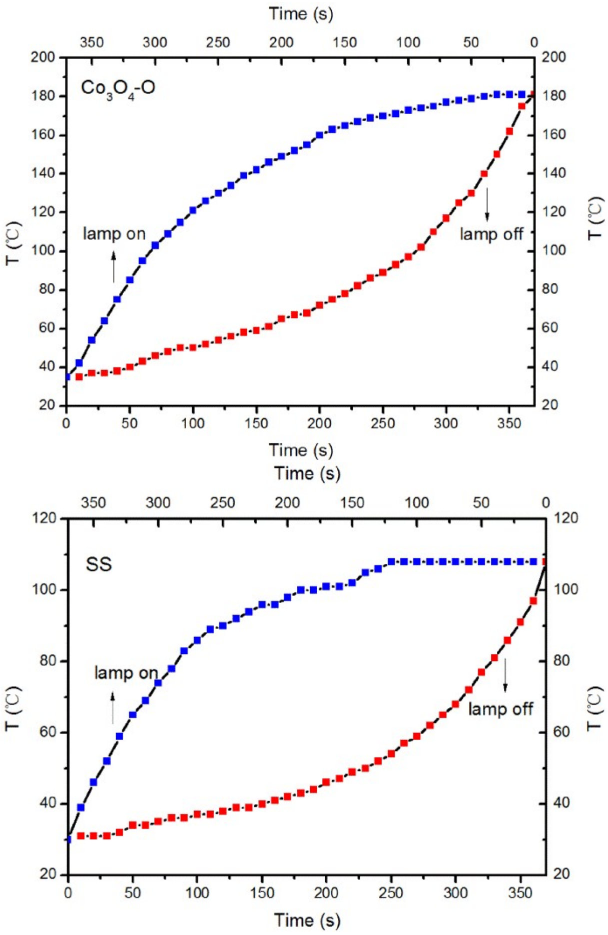

Fig. S6 Temporal change of the temperature on the Co_3O_4-O and SS under the irradiation of the Xe lamp.

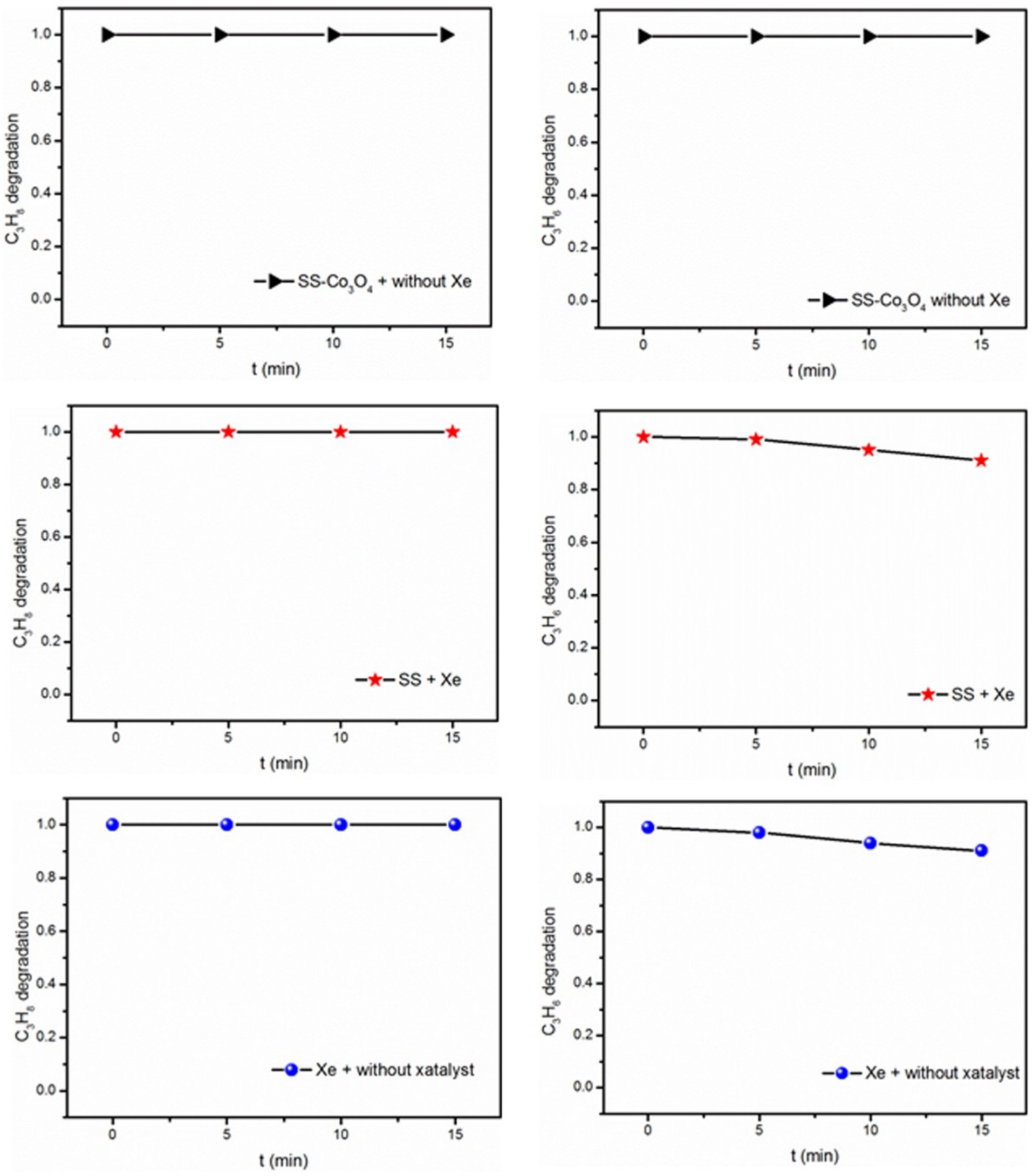

Fig. S7 Blank experiments for C_3H_8 and C_3H_6 oxidation

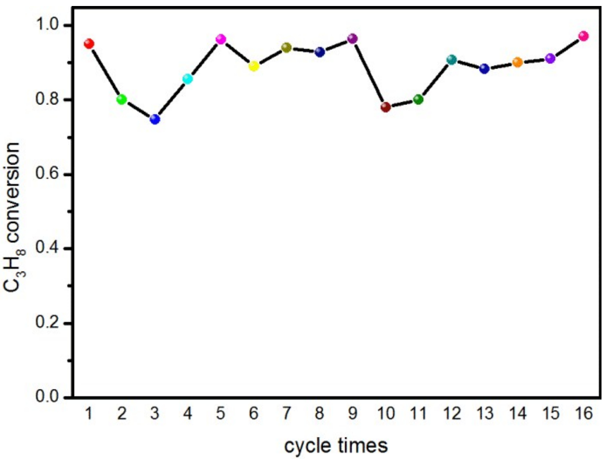

Fig. S8 Consecutive cyclic tests for C_3H_8 oxidation over SS-Co_3O_4 under PTC conditions

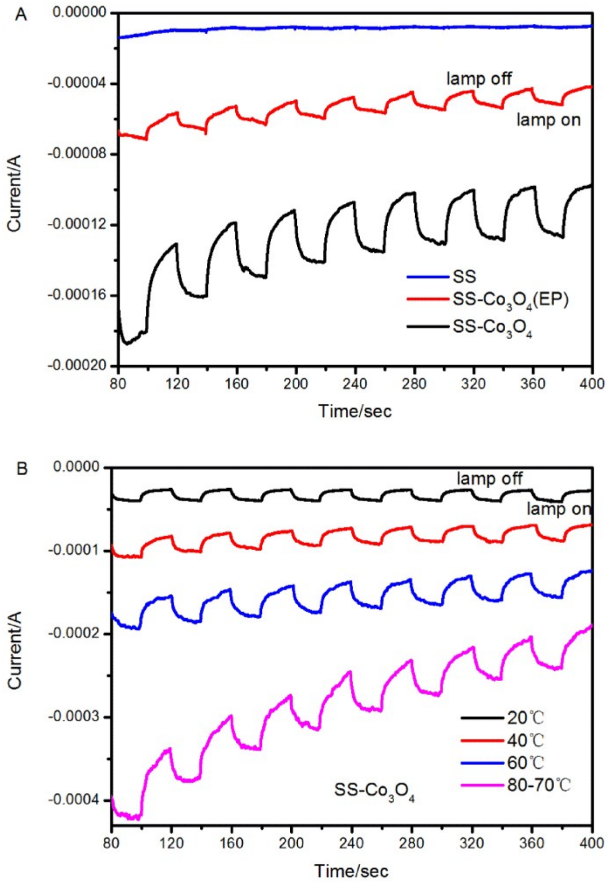

Fig. S9 (A) Current–time (i–t) curves of SS, SS-Co_3O_4(EP), and SS-Co_3O_4 electrodes recorded at 0.5V vs. SCE. (B) Current–time (i–t) curves of SS-Co_3O_4 under different temperature.

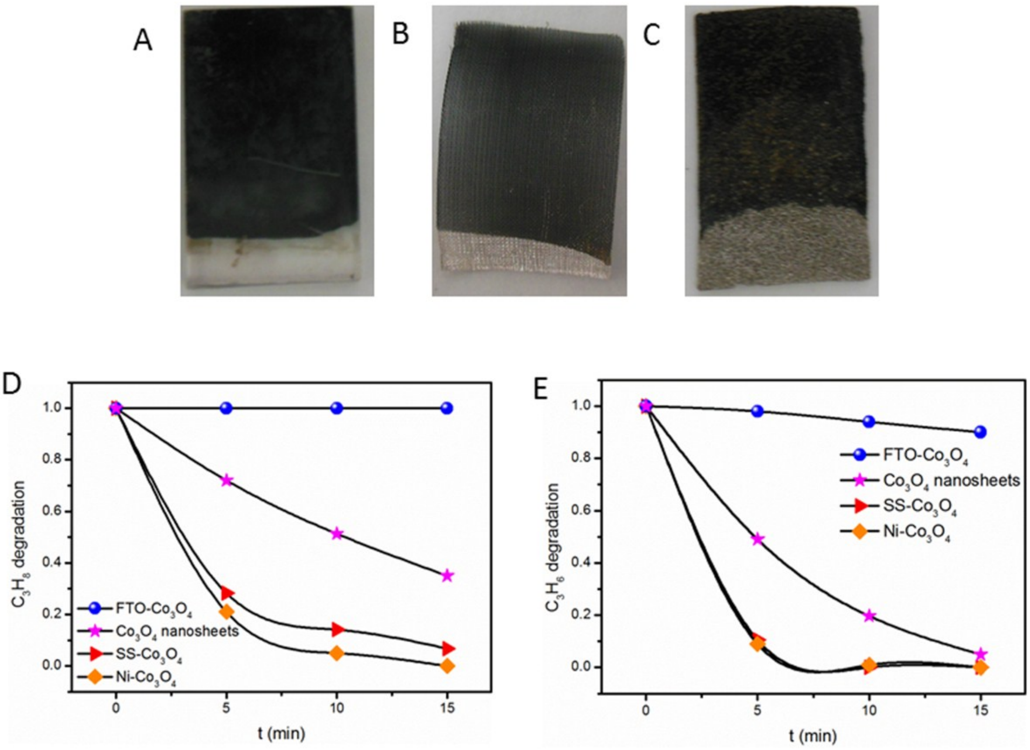

Fig. S10 (A) FTO-Co_3O_4 (6.1 mg) (B) SS-Co_3O_4 (7.0 mg) (C) Ni-Co_3O_4 (6.8 mg) (D) (E)C_3H_8 and C_3H_6 oxidation over SS-Co_3O_4, Ni-Co_3O_4, FTO-Co_3O_4, and Co_3O_4 nanosheets scratched down from the SS substrate (50 mg) under simulated sunlight (Xe lamp).