Supporting Information:

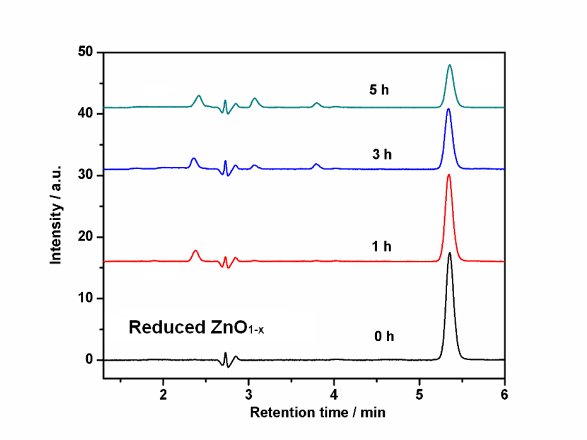


Figure S1 HPLC of intermediates of phenol over reduced ZnO_{1-X} at different irradiation intervals, under visible light (visible light region in the range of 400 ~ 800nm, $\lambda_{main} = 550$ nm)

To demonstrate and reveal some details of the reaction process, the intermediates distribution at different irradiation intervals during the photocatalytic degradation process on phenol over reduced ZnO_{1-x} were monitored by HPLC, under visible light. The results are displayed in **Figure S1**. And the intermediates at different retention time as references were shown in **Table S1**. At 5.45 min the product is phenol, and based on steric effect, those at 2.75 min are 4,4'-dihydroxybiphenyl and 4-phrnoxyphenol.[1,2] The degradation products labeled green were the intermediates, HQ at 2.45min, P-BQ at 3.1 min, catechol at 3.85min, respectively. [3-7]

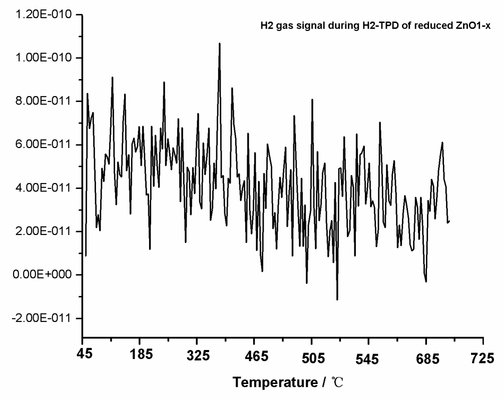


Figure S2 The MS spectrum of H_2 gas during the H_2-TPD of reduced ZnO_{1-x}

From the **Figure S2,** it can be seen that there is no any peak of H_2 in the vent gases after the H_2-TPD of reduced ZnO_{1-x} , which can be obtained that here alomost no H-related defects were produced.

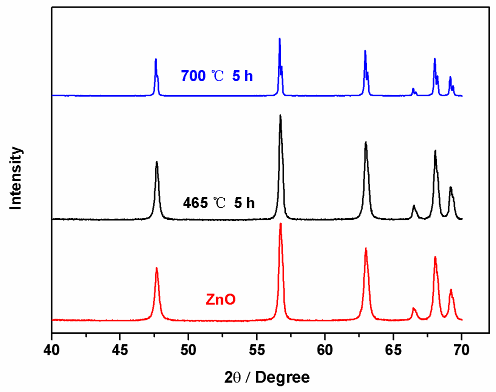


Figure S3 X-ray diffraction pattern of ZnO and ZnO H_2 treated at 465 °C, 700 °C for 5 h, respectively

Figure S3 shows the X-ray diffraction (XRD) of pure ZnO and ZnO_{1-x} samples. No phase transformation or any impurity was observed for reduced ZnO_{1-x} after treated at 465 °C for 5 h. So there only surface oxygen atoms are removed, generating surface oxygen vacancies. While, the XRD of ZnO_{1-x} after treated at 700 °C for 5 h was slightly splitting into two little peaks, maybe owing to produce bulk oxygen vacancy.

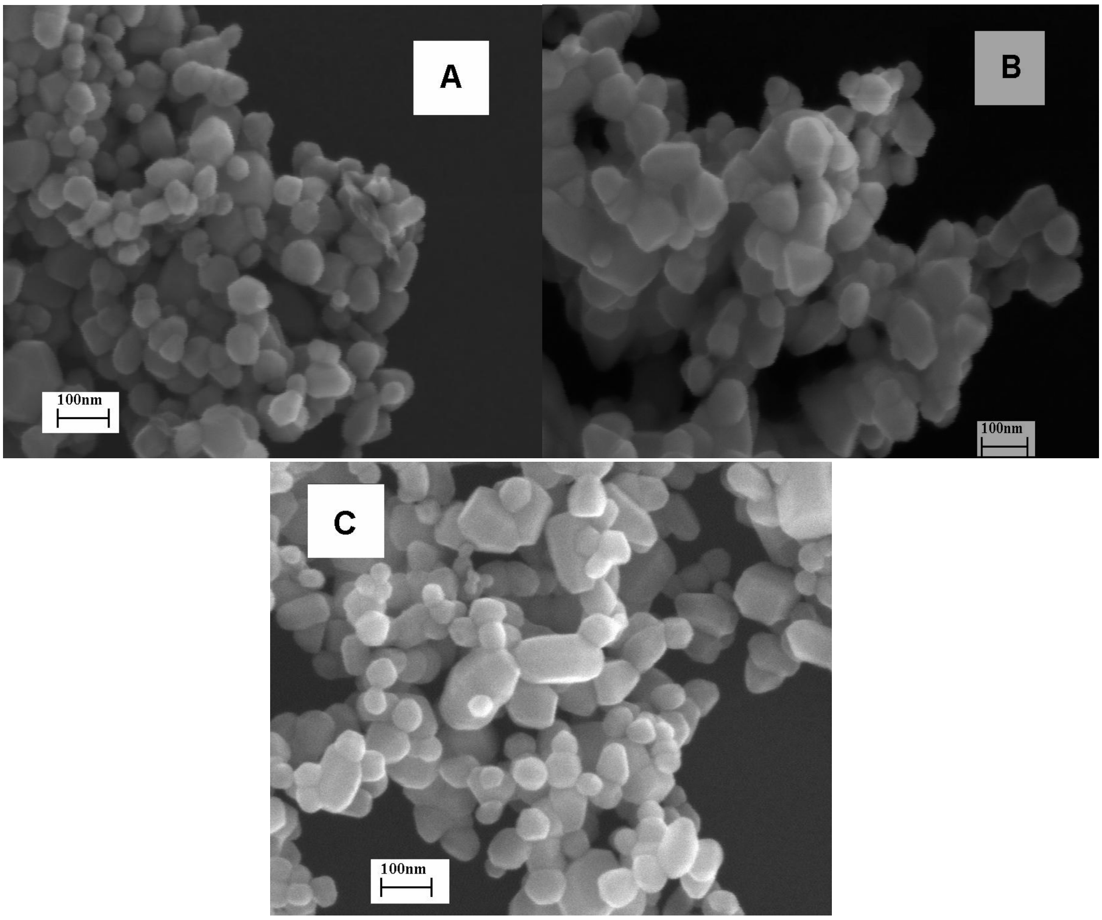


Figure S4 SEM images of **(A)** ZnO, **(B)** ZnO after H_2 treated at 465 $^{\circ}$C 5 h and **(C)** ZnO after treated in air at 465 $^{\circ}$C 5 h, respectively.

Figure S4 shows the SEM micrograph for the samples, respectively. It can be seen that the edge of untreated ZnO particles is clearly seen, as shown in **Figure S4 A**. The boundary between the particles are also clearly visible and the mean grain size about 30~50 nm. However, the ZnO particles after H_2 treated occurs a little aggregation, the edge of the particles are becoming dim and the size is becoming a little bigger than that of untreated ZnO, average size about 35~55 nm, as shown in **Figure S4 B**. This might be in the process of H_2 treatment for ZnO, the original inerratic structure of ZnO particles is badly destroyed, attributing to the generation of oxygen vacancies on the surface of ZnO. In addition, in order to prove the surface change is not caused by high temperature, the SEM of ZnO treated in air (other conditions are same with in H_2 treatment) was given in **Figure S4 C**. The SEM of ZnO treated in air is alike as that of untreated ZnO and no reunion phenomenon was occurred. Therefore, the morphology change of reduced ZnO_{1-x} is caused by H_2 reduction rather than high temperature.

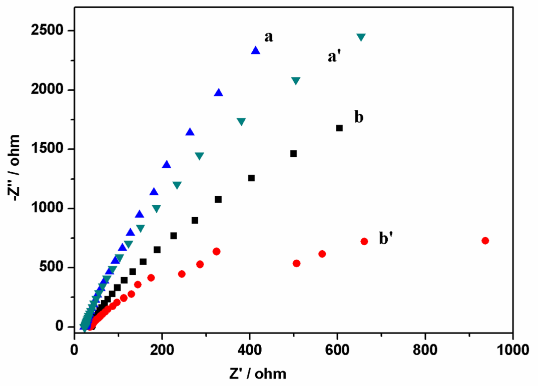


Figure S5 Electrochemical impedance spectroscopy Nynquist plots of ZnO and reduced ZnO$_{1-x}$ electrodes before and after visible light irradiation (λ > 420 nm) (**a.** ZnO-dark; **a′.** ZnO-light; **b.** Reduced ZnO$_{1-X}$-dark; **b′.** Reduced ZnO$_{1-X}$-light).

Under visible light (λ > 420 nm), the EIS Nynquist plots of ZnO and reduced ZnO$_{1-x}$ electrodes were investigated,which show that the efficiency of charge separation of reduced-ZnO$_{1-x}$ is also much higher than that of pure ZnO **(Figure S5),** thus the high visible photocatalytic activity of reduced-ZnO$_{1-x}$ is produced.

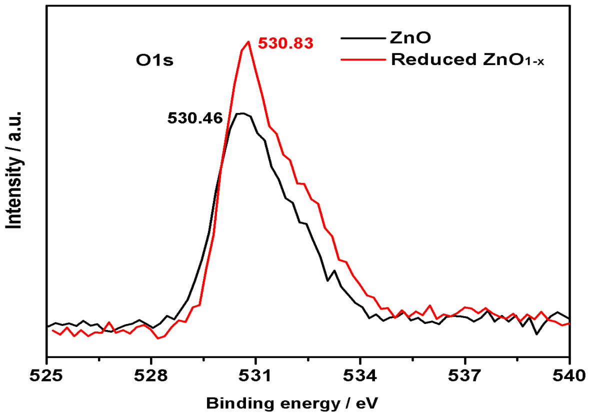


Figure S6 The XPS spectra of O 1 s for ZnO and reduced ZnO_{1-x}

In order to test for oxygen vacancies, O 1s XPS spectra of ZnO and reduced ZnO_{1-x} were measured, as shown in **Figure S6**. The peaks at 530.46 for ZnO is ascribed to Zn–O and small part of oxygen defect, and the binding energy at 530.8 eV for reduced ZnO_{1-x} is related to oxygen vacancies [8,9].

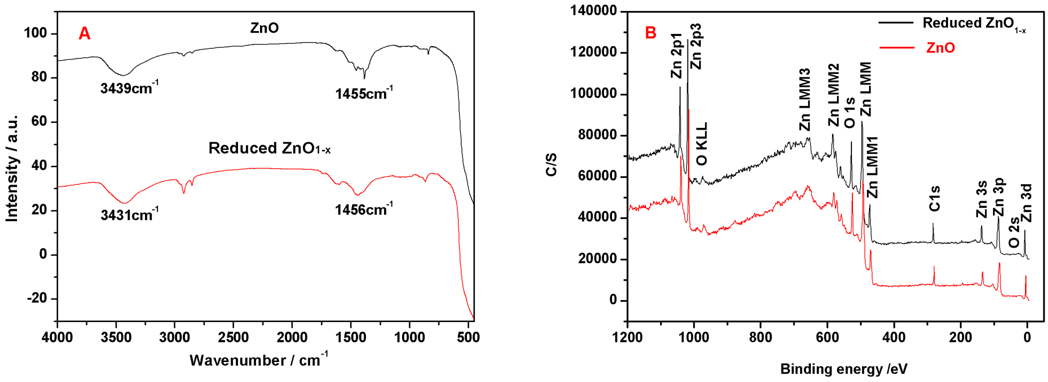
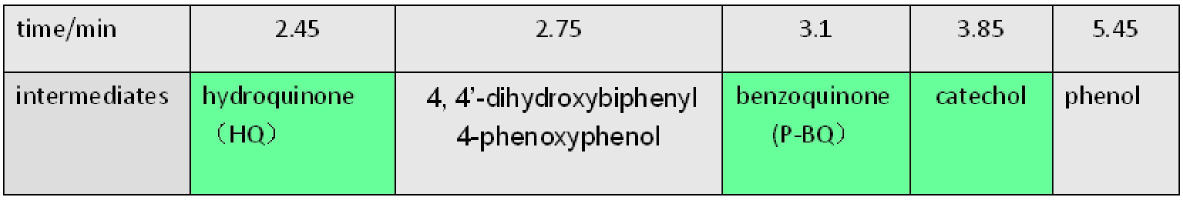


Figure S7 (A) IR spectra of ZnO and reduced ZnO$_{1-x}$; **(B)** XPS spectra of of ZnO and reduced ZnO$_{1-x}$。

Table S1 the intermediates distribution at different irradiation intervals during the photocatalytic degradation process on phenol



time/min	2.45	2.75	3.1	3.85	5.45
intermediates	hydroquinone （HQ）	4, 4'-dihydroxybiphenyl 4-phenoxyphenol	benzoquinone （P-BQ）	catechol	phenol

Table S2. Surface Atomic Concentration Table from XPS

	O1s	Zn2p3	Zn : O
ZnO	40.07	25.81□	0.644
Reduced ZnO_{1-x}	38.47	33.23□	0.863

From **Table S2,** it can be found that the surface atomic concentration ratio of Zn:O increases from 0.644 for untreated ZnO to 0.863 for reduced ZnO_{1-x}.

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