

Electronic Supplementary Information (ESI)

**Ce³⁺ and oxygen defects affecting the photocatalytic performance of
CeO₂ nanoparticles**

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Experimental details

I. Synthesis of CeO₂ nanoparticles

The chemicals used in the present study were of analytical grade. Cerium nitrate hexahydrate (Sigma Aldrich, purity 99.99 %), ethanol (Merck), aqueous NH₃ (Sigma Aldrich, 28-30 %), methyl orange (Merck) were purchased from the chemical suppliers without further purification. For synthesis and for photocatalytic study the chemicals were used as received without further purification.

CeO₂ nanoparticles were synthesized by basic hydrolysis of cerium nitrate hexahydrate. In a typical synthesis, 0.1 M cerium nitrate hexahydrate solution was prepared in 46 mL water. The cerium nitrate hexahydrate solids were completely dissolved in water after stirring for 15 min, with temperature of the solution maintained at ~40 °C. This was followed by dropwise addition of aqueous NH₃ solution to the mixture. The addition of NH₃ solution was continued till the pH of the solution becomes 8-10. During the addition of NH₃, the solution first acquired light brownish colour which gradually turned into purple. The solution was stirred for 2 h and at the end of the reaction the precipitated product became light yellow. The product was centrifuged and washed for 3 times in water and 2 times in ethanol. The final product was dried in a vacuum oven at 80 °C for 3 h. After vacuum drying the product was calcined in vacuum at 200 °C for 3 h. The sample was labeled as CV200. This sample was divided into three parts. One part remained as CV200 while the other two parts were annealed in air for 3 h at 200 °C and 500 °C respectively. The samples were labeled as CA200 and CA500 respectively.

II. Characterization details

X-ray diffraction pattern of the nanoparticles was monitored in a Bruker AXS D8 focus X-ray diffractometer (XRD) equipped with intense $Cu K\alpha$ radiation ($\lambda=0.154$ nm). The scanning speed was 0.5 sec/step with an increment of 0.0057 degree. High resolution transmission electron microscope (HRTEM) images of the prepared nanoparticles were obtained with JEOL JEM 3010 transmission electron microscope operating at a voltage of 300 kV. Nitrogen adsorption – desorption isotherms were measured at 77 K in a Quantachrome iQ autosorb analyzer. Surface area was determined using multipoint Brunauer-Emmett-Teller (BET) method. The pore size distributions of the prepared samples were determined based on Barrett-Joyner-Halenda (BJH) model. X-ray photoelectron spectra (XPS) was recorded on a Kratos Axis 165 XPS spectrometer equipped with dual aluminium–magnesium anodes using $Mg K\alpha$ radiation ($h\nu = 1253.6$ eV) operated at 5 kV and 15 mA with pass energy 80 eV and an increment of 0.1 eV. Raman spectra of the samples were obtained with Renishaw in Via Raman spectrometer with 514.5 nm Ar ion laser at a spectral resolution of 0.3 cm^{-1} . UV-vis absorption spectra of entire CeO_2 nanoparticles were taken in diffuse reflectance mode (DRS) in Shimadzu 2450 UV-vis spectrophotometer. Photoluminescence (PL) spectra were monitored in a Perkin Elmer LS 55 fluorescence spectrometer.

III. Photocatalytic activity

Photocatalytic activity of vacuum annealed (CV200) and air-annealed (CA200 and CA500) samples were carried out to degrade 10-ppm (10 mgL^{-1}) methyl orange (MO) followed by measurement of wavelength of maximum absorbance at 464 nm at the time intervals of 15 min, 30 min, 45 min and 60 min respectively. To prepare this MO solution, 50 mg of each of the

prepared CeO₂ nanoparticles was added to 50 mL of methyl orange (MO) with an initial MO concentration of 10 mgL⁻¹. Now the catalyst added MO solution was stirred in dark for 45 min for adsorption-desorption equilibrium and for the pre-concentration of the dye solution on the semiconductor surface. The dye solution was placed in a UV-vis chamber at a distance of 6 cm from UV/vis light. The wavelength of the UV light is 365 nm. For visible irradiation a 23 watt white lamp was used having wavelength range from 400-700 nm. The intensity of the visible lamp was measured with a Field Max II Top energy power meter by placing the MO solution at a distance of 6 cm from the lamp. The measured intensity of the light was 2.3 mW/cm². The time intervals for UV/visible irradiation was 15, 30, 45 and 60 min respectively. When irradiation was completed, the irradiated solution was centrifuged at 10,000 rpm to get the catalyst free MO solution. 5 mL of each of the MO solution was taken for absorption measurement. The percent degradation of MO was calculated using the equation

$$\%D = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

Where C_0 is the initial concentration of MO (10 ppm) and C_t is the concentration of MO after irradiation for time (t) period of 15 min, 30 min, 45 min and 60 min. In order to investigate the self degradation of MO, the blank MO solution was irradiated under UV and visible light for the aforementioned time periods and then the absorption is measured. We also studied the photocatalytic activity of CV200 under dark condition. In this process neither UV nor visible light is turned on. For carrying out the degradation under dark, 50 mg of CV200 was added to 50 mL of methyl orange (MO) with an initial MO concentration of 10 mgL⁻¹. The reaction was carried out under dark by stirring the solution for the time intervals of 15, 30, 45 and 60 min.

Then 5 mL of the MO solution is extracted and taken absorbance to observe any changes occurring at the measuring wavelength of 464 nm.

Fig. S1 Photocatalytic degradation of MO by CV200 after stirring for 15, 30, 45 and 60 min under dark condition.

