

Photocatalytic Degradation of Methyl Orange by CeO₂ and Fe-doped CeO₂ Films under Visible Light Irradiation

D. Channei^a, B. Inceesungvorn^a, N. Wetchakun^b, S. Ukritnukun^c, A. Nattestad^d,
J. Chen^d & S. Phanichphant^e

^aDepartment of Chemistry, Faculty of Science, Chiang Mai University, Thailand.

^bDepartment of Physics and Materials Science, Faculty of Science, Chiang Mai University, Thailand.

^cSchool of Materials Science and Engineering, University of New South Wales, Australia.

^dIntelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, Australian Institute of Innovative Materials, University of Wollongong, Australia.

^eMaterials Science Research Center, Faculty of Science Chiang Mai University, Thailand.

*Email: sphanichphant@yahoo.com, anattest@uow.edu.au

Supplementary table

S1

The calculated <i>d</i> -spacing, lattice parameters, unit cell volume and crystalline size					
Iron doping concentration (mol%)	111 plane				
	2θ (degree)	<i>d</i> -spacing (nm)	Lattice parameter (nm)	Unit cell volume (nm ³)	Crystalline size (nm)
0.00	28.3899	0.3140	0.5439	0.1609	5.79
0.50	28.3899	0.3140	0.5439	0.1609	5.79
1.00	28.3899	0.3140	0.5439	0.1609	5.79
1.50	28.6420	0.3113	0.5392	0.1567	5.29
2.00	28.9011	0.3086	0.5344	0.1527	4.56
5.00	29.5159	0.3023	0.5236	0.1435	3.98

The calculated crystallite size by Scherrer formula in equation (1) decreased with increasing the iron doping concentration with the size was about 4–6 nm.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

In this equation¹, *k* is a constant equal to 0.89, λ is the X-ray wavelength equal to 0.154 nm, β is the full width at half maximum, and θ is the half diffraction angle.

[1] Li, B., Wang, X., Yan, M. & Li, L. Preparation and characterization of nano-TiO₂ powder. *Mater. Chem. Phys.* **78**, 184–188 (2002).

Supplementary table

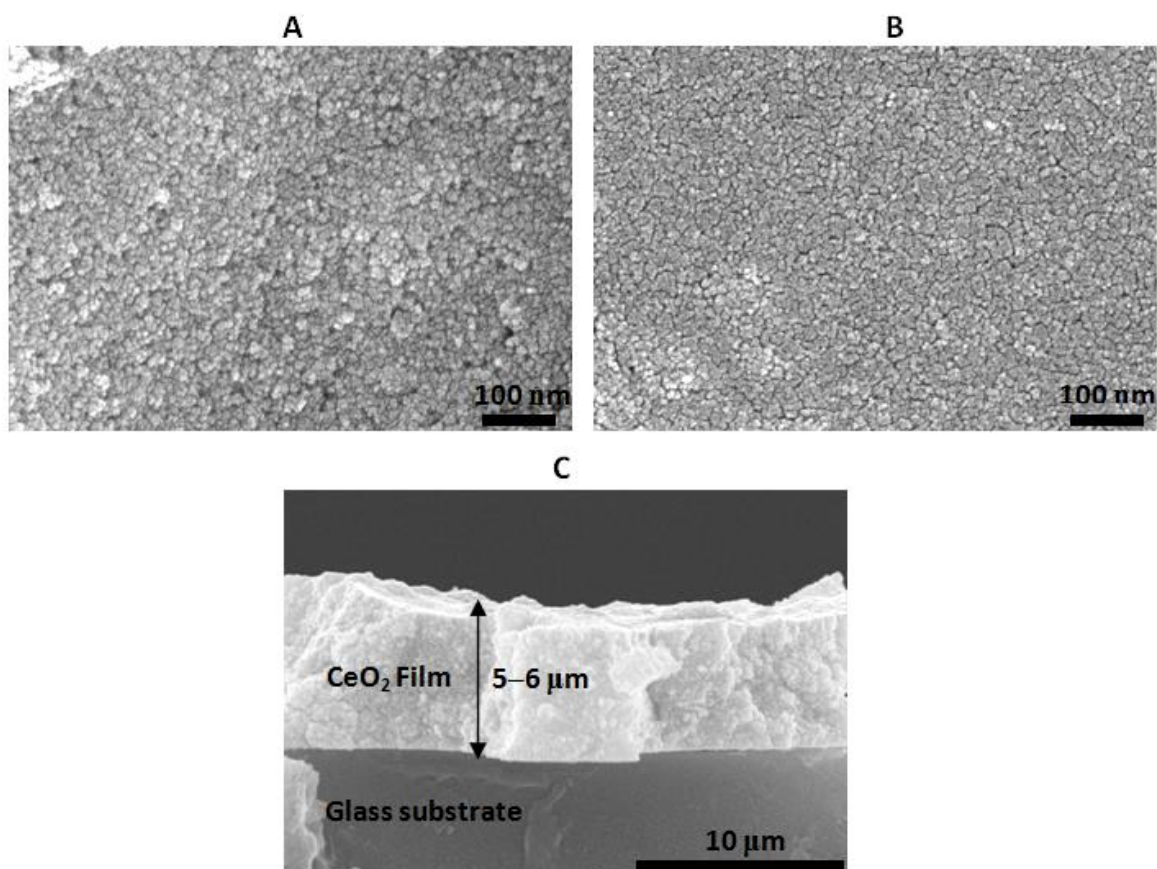
S2

The surface properties of the CeO ₂ catalysts with different iron doping			
Iron doping concentration (mol%)	Specific surface area (m ² /g)	Pore volume (cc/g)	Average pore diameter (nm)
0	124.10	0.1131	2.435
0.50	136.22	0.1741	2.554
1.00	136.77	0.1740	2.545
1.50	171.74	0.2276	2.651
2.00	130.68	0.1713	2.622
5.00	88.59	0.1016	2.293

The BET specific surface area (SSA), pore volume, and average pore diameter results were found to increase as increasing amount of iron doping in CeO₂ and possibly increase in photocatalytic activity. Even the calculated crystallite size by Scherrer formula decreased upon increasing the iron doping content, the higher amount of 2.00 and 5.00 mol% of iron doping were causing the lower specific surface area due to the aggregation of the particles. Hence, the decrease in specific surface area possibly decreased the photoactivity due to the smaller surface area of catalyst to adsorb the MO dye on the catalyst surface.

Supplementary figures

S3

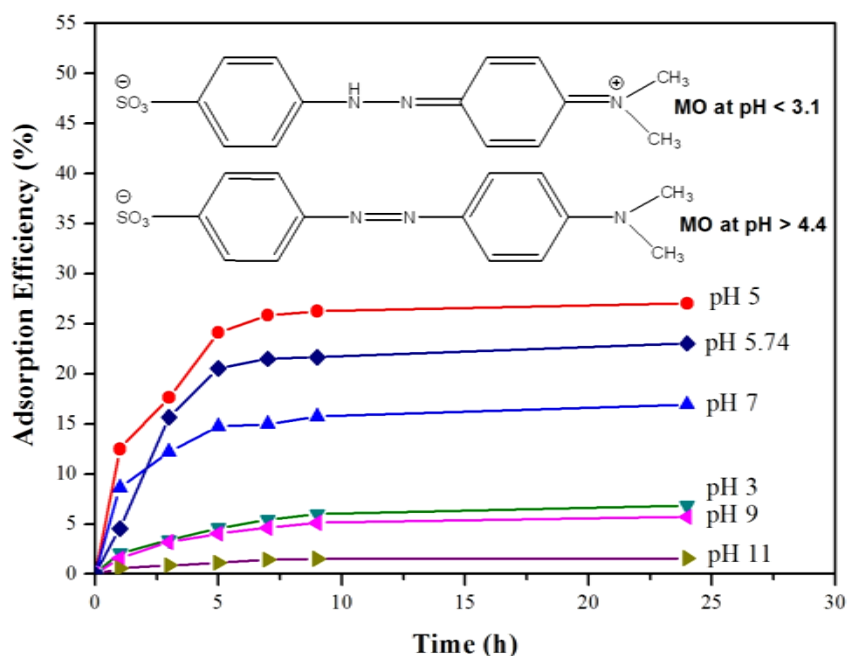


FESEM images of films (A) surface of undoped CeO₂ film, (B) surface of 5.00% Fe-doped CeO₂, and (C) cross section of undoped CeO₂, respectively.

The morphology of undoped CeO₂ and Fe-doped CeO₂ were nearly spherical particles with diameters less than 10 nm corresponding well with calculated crystalline size from Sherrer equation and XRD data. The size of undoped CeO₂ particles decreased upon doping CeO₂ with iron. The determined thickness film was 5–6 μm by the cross-section FESEM image.

Supplementary figure

S4



The adsorption efficiency of MO in dark at different pH value (inset shows dye structures)

A film of undoped CeO₂ was employed to study the effect of pH on MO adsorption efficiency in the absence of light, based on the decrease in absorption of the solution in which the film was placed. No significant dye degradation takes place during this process but rather equilibrium is formed for dye adsorption-desorption from the semiconductor surface. This is to avoid testing effect caused by dye adsorption during photocatalytic testing (which may be mistakenly attributed to degradation).

The results of the dark experiments revealed that MO adsorption decreased in the following order: pH 5 > pH 5.74 (dye in DI water) > pH 7 > pH 3 > pH 9 > pH 11.

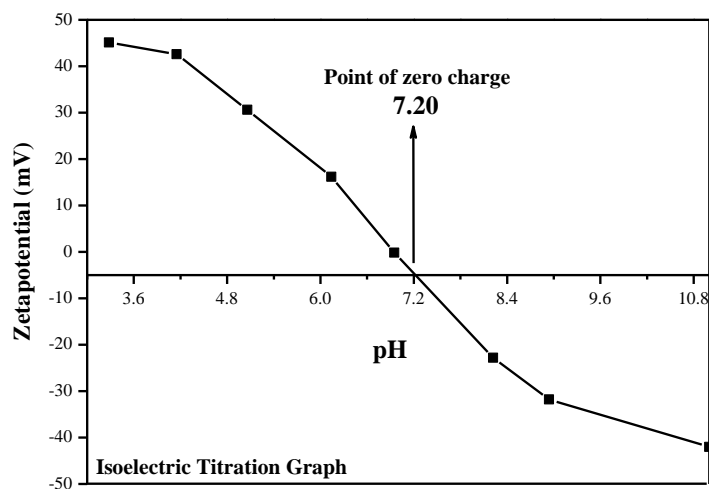
This observation could be explained largely by the different catalyst surface, as characterised by zeta potential measurements (Supplementary Information 5) and the variation of the MO charged structure at different pH values^{1,2}. In acidic solution, the catalyst showed very poor adsorption efficiency (ca. 5–6%) as MO is in its zwitterionic form, and hence the coulombic attraction between the positively charged CeO₂ surface and neutral MO

molecule is low. At pH values higher than the point of zero charge of CeO₂ (pH 7.2), there is a repulsive interaction between the negatively charged CeO₂ surface and negative MO molecule. The results in Supplementary Information 4 above clearly showed that pH 5 results in the greatest level of MO adsorption and this was employed as a basis for further experiments. It is reasonable to expect that this modest adjustment to the pH value could be made at large scale in order to facilitate speedy dye degradation without adverse environmental impact resulting from the release of treated water.

- [1] Andeonic, A. & Duta, A. The influence of TiO₂ powder and film on the photodegradation of methyl orange. *Mater.Chem. Phys.* **112**, 1078–1082 (2008).
- [2] Mehra, M. & Sharma, T. R. Photocatalytic degradation of two commercial dyes in aqueous phase using photo catalyst TiO₂. *Adv. Appl. Sci. Res.* **2**, 849–853 (2012).

Supplementary figure

S5



The point of zero charge (pzc) of CeO₂.