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Green synthesis of CeO_2 nanoparticles using *Artocarpus heterophyllus* leaf extract for photocatalytic activity

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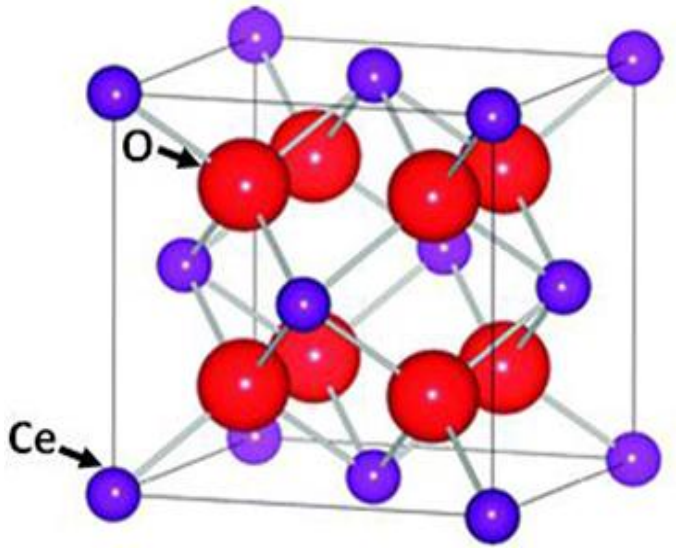
CeO_2- a Promising Material



Structure :
Face-centered cubic

Applications :

- Solid oxide fuel cell [1]
- Gas sensor [2]
- Luminescent materials [3]
- Photocatalyst [4]
- Disease treatment : Oxidative stress, Parkinson's disease [5]

Properties :

- ✓High reactivity
- ✓Unique UV absorption ability
- ✓High temperature stability
- ✓High hardness

Common synthesis methods :

- ✓Sol–gel ,hydrothermal, sonochemical
- ✓Flame spray pyrolysis
- ✓Reverse micelle route
- ✓Combustion
- ✓Complex thermodecomposition method

Why Green Synthesis

Environment friendly

No need of high temperature pressure

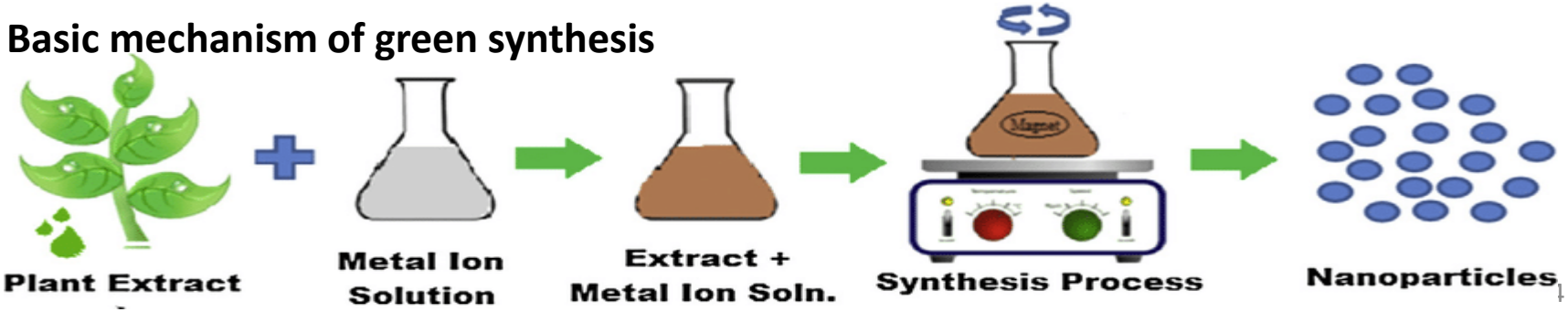
Scaled up for large synthesis of nanoparticles

Energy efficient

Natural coating on nanoparticles

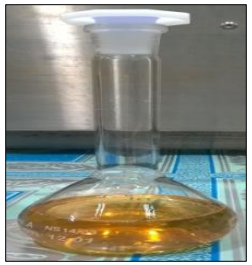
Non-toxic method

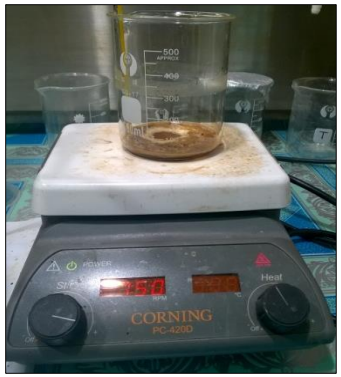
Basic mechanism of green synthesis



Experimental Procedure

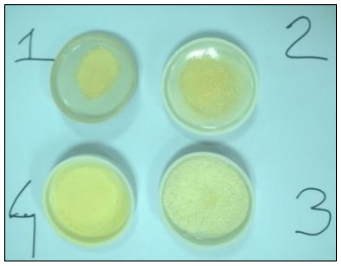
Step-1 Preparation of leaf extract





Step-2 Addition of leaf extract in $Ce(NO_3)_3.6H_2O$ solution and heating it at 80 °C with continuous stirring until it becomes dry and then kept at oven at 120 °C for 12 hours

Step-3 Washing and grinding of dried powder



Step-4 Heat treatment for 3 hours at different temperatures

Step-5 Grinding after heat treatment before characterization

Step-6 Repeating step 2 varying precursor and leaf extract concentration

Results and Discussions- DSC Analysis

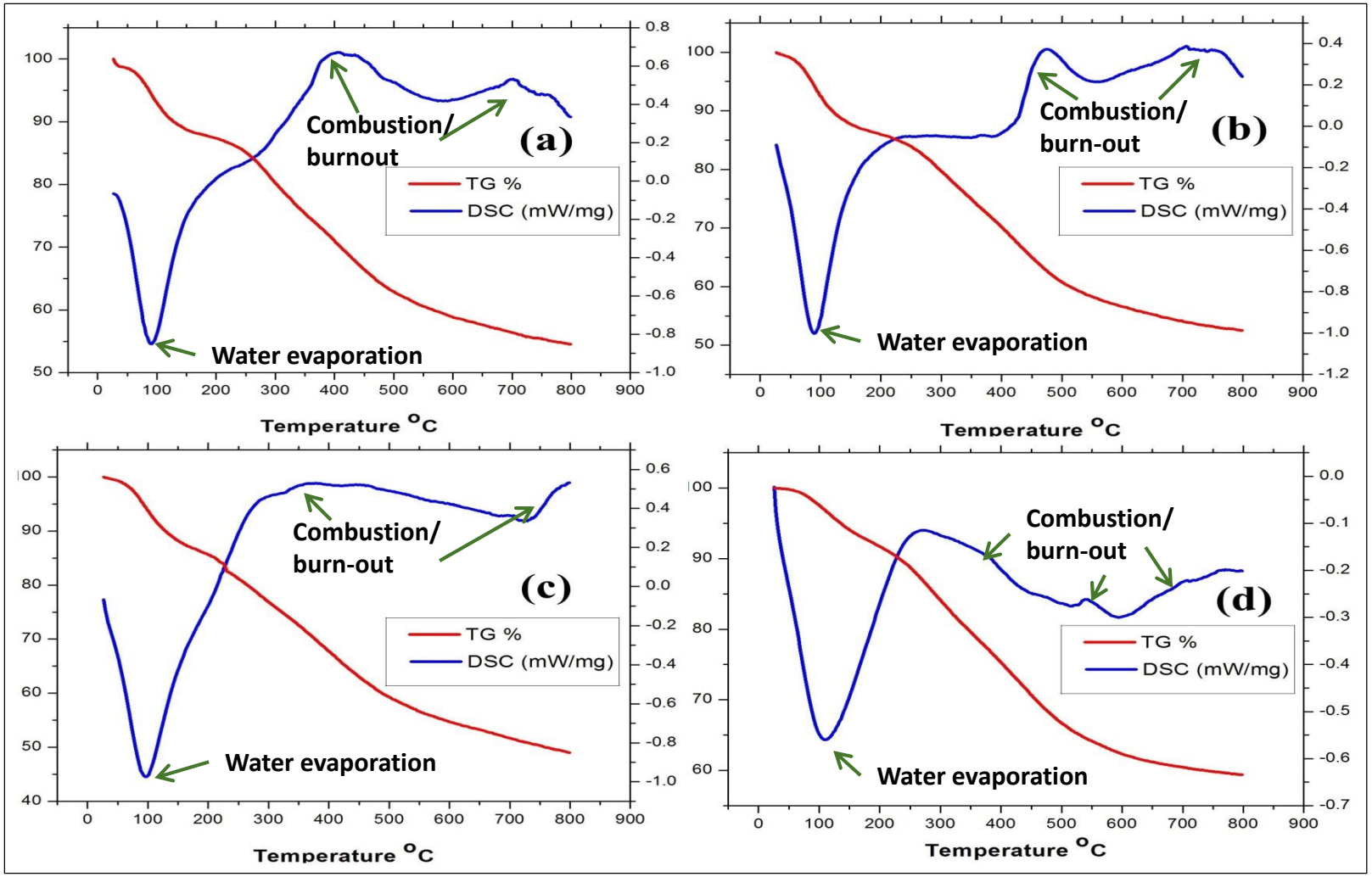
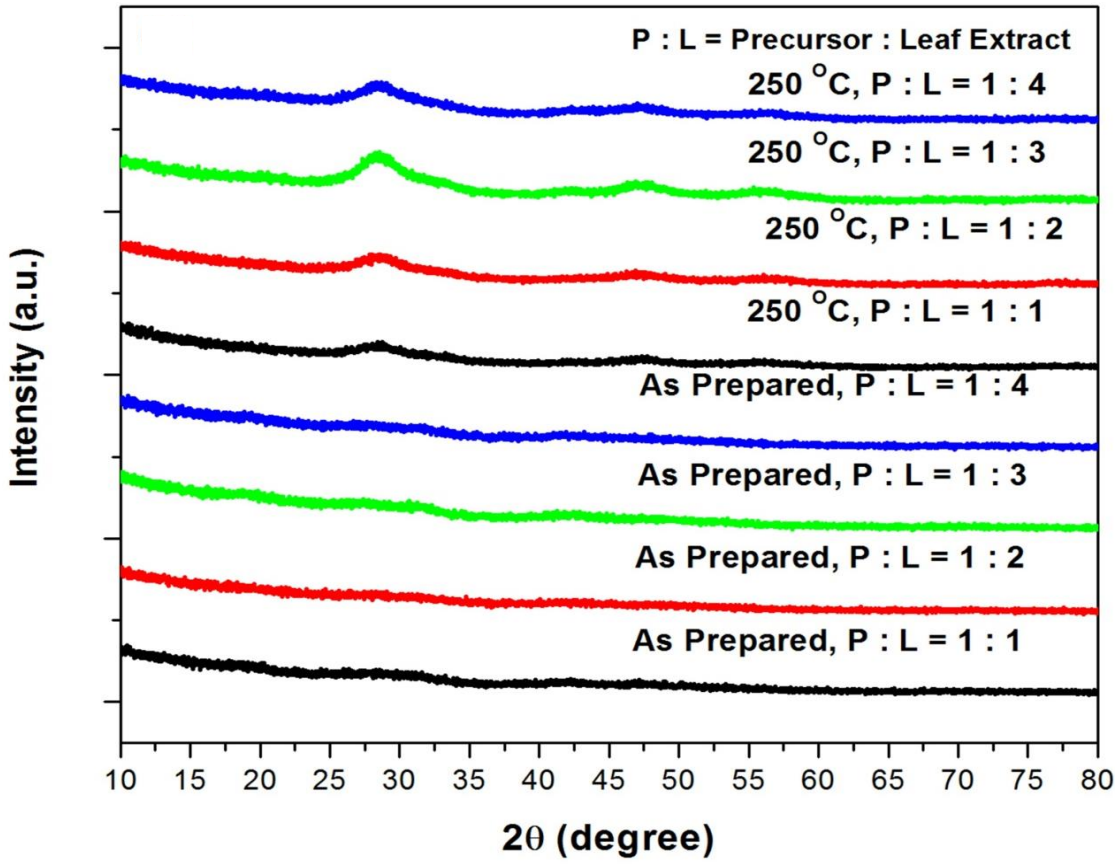


Fig.1: DSC and TGA graphs for (a) 0.01M, (b) 0.025M, (c) 0.055M and (d) 0.1M precursor concentration obtain at 10 °C/min heating rate

Structural Analysis- XRD



- ✓No peak appeared before heat treatment – amorphus
- ✓Crystallization starts at 250°C
- ✓Better crystallinity for 1:3 ratio

Fig.2: PXRD patterns of all samples in as prepared and at 250 °C annealed condition with precursor to leaf extract ratio of 1:1, 1:2, 1:3 and 1:4 respectively

Structural Analysis- XRD

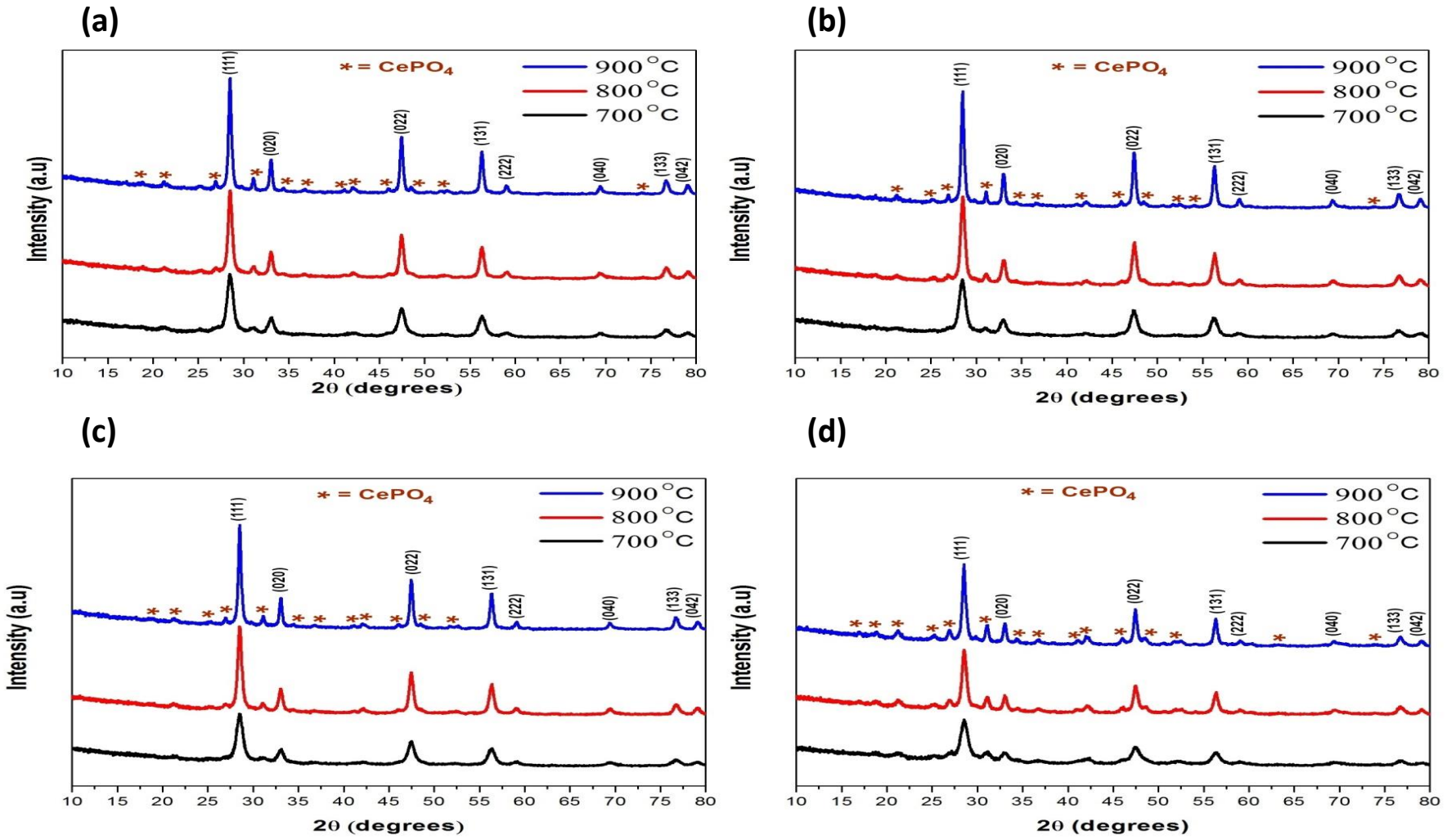


Fig.3: PXRD patterns for (a) 0.01M, (b) 0.025M, (c) 0.055M and (d) 0.1M precursor concentration samples after heat treatment at 700, 800 and 800 °C

Structural Analysis- Lattice

Table 1: Lattice Parameter Calculation for Cubic CeO2 (ICDD 01 – 078 – 5328) from Nelson-Riley plot

Temp (°C)	Conc. (M)	a_{NR} Nelson – Riley (A°)	a_D Database (A°)	$\Delta a = a_{NR} - a_D$ (A°)
900	0.01	5.4	5.41	– 0.01
	0.025	5.4		– 0.01
	0.055	5.4		– 0.01
	0.1	5.4		– 0.004

Negligible difference between standard & our observed value

Required equations: $$f(\theta) = \frac{1}{2}\left[\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right] \ldots\ldots\ldots\ldots (1)$$ **and** $$a = \frac{\lambda\sqrt{(h^2 + k^2 + l^2)}}{2\sin\theta} \ldots\ldots\ldots\ldots (2)$$

Structural Analysis- Crystal Size

Crystal size of the nanoparticles is determined by using Scherrer formula-

$$D = \frac{k\lambda}{\beta cos\theta}$$

Where,

D = Crystallite size (in nm) = FWHM of hkl peak (in radians)

K = 0.9 (For spherical shape)

θ = Bragg angles (in degrees)

λ= 0.15405980 nm

Williamson-Hall method

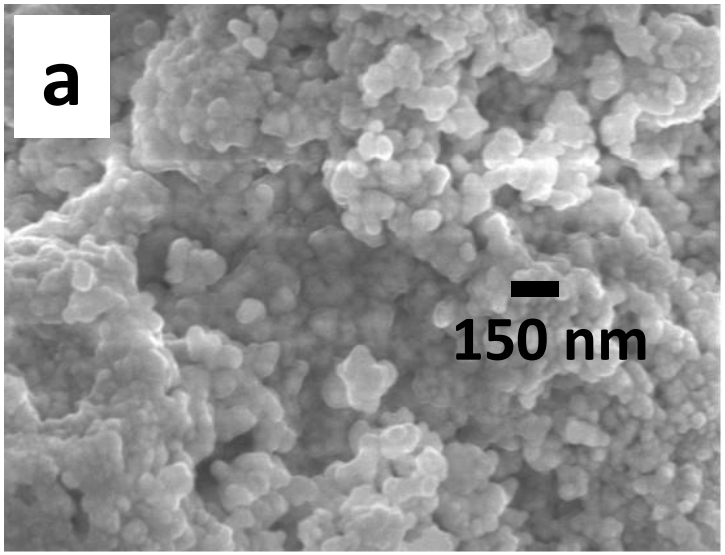
$$\beta \cos\theta = K\lambda / D + 4\varepsilon \sin\theta$$

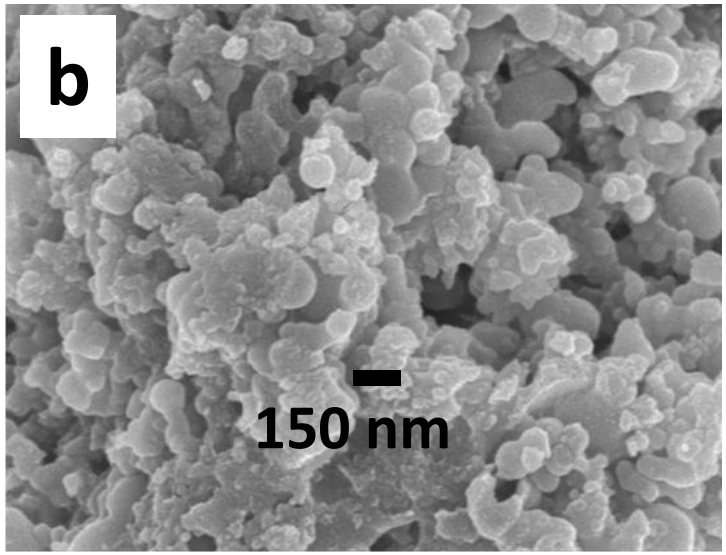
Structural Analysis- Crystal Size

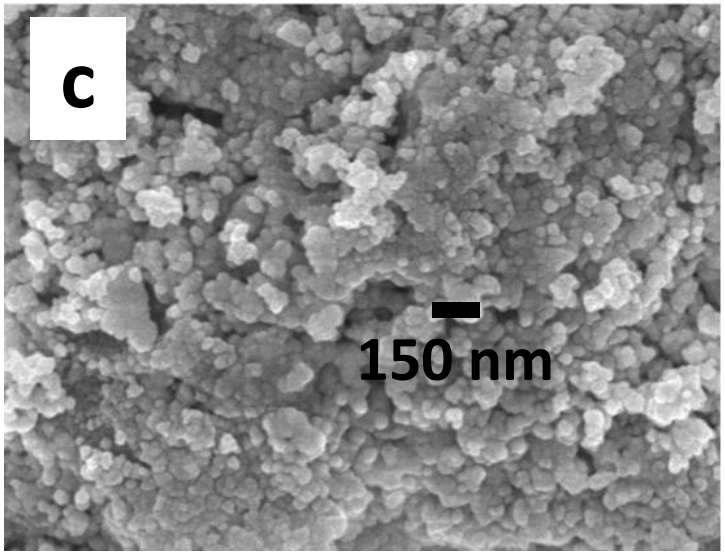
Table 3: Crystallite Size of the samples annealed 900 °C calculated from Scherer equation, modified Scherer equation and Williamson-Hall method

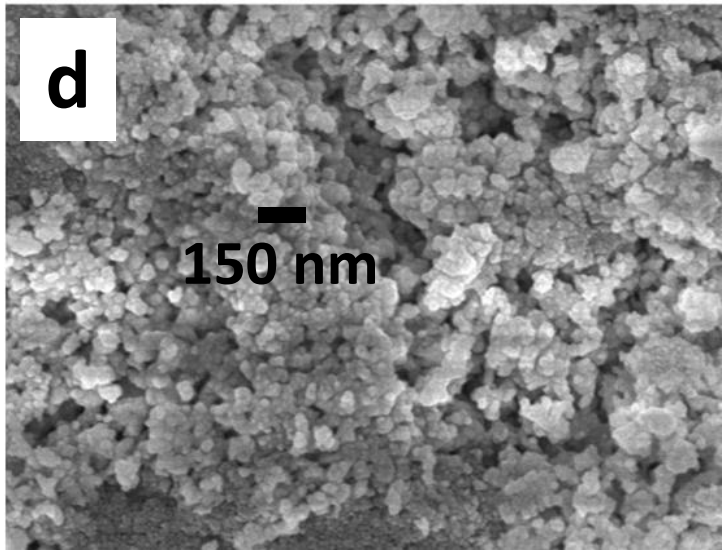
Temp (°C)	Precursor Concentration (M)	Crystallite Size Scherrer for (111) only (nm)	Crystallite Size Williamson – Hall (nm)
900	0.01	27	20
	0.025	25	21
	0.055	29	14
	0.1	29	21

Microstructure Analysis









Magnification X 50000

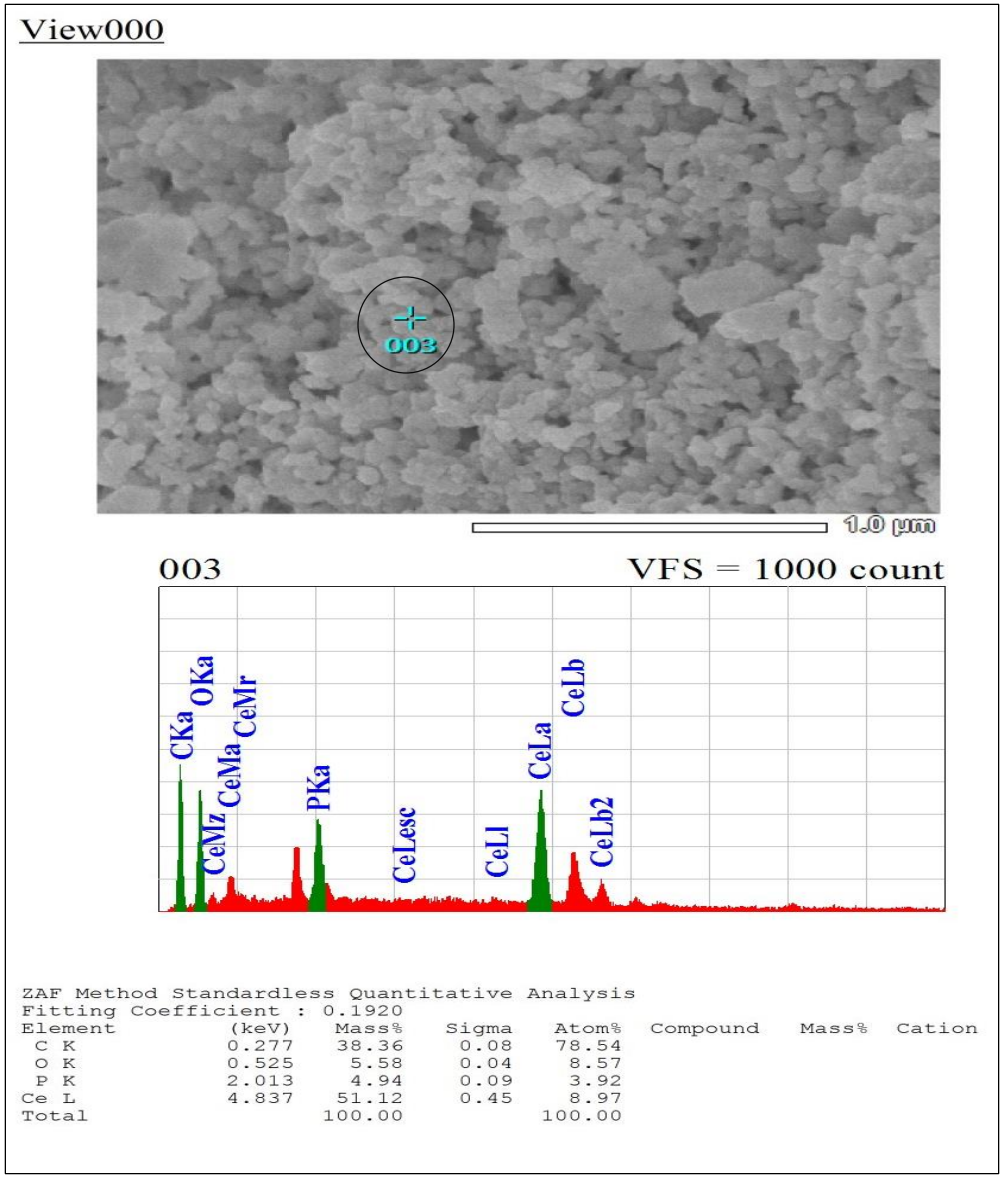
a = 0.01 M

b = 0.025 M

c = 0.055 M

d = 0.1 M

Microstructure Analysis



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1920

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation
C K	0.277	38.36	0.08	78.54			
O K	0.525	5.58	0.04	8.57			
P K	2.013	4.94	0.09	3.92			
Ce L	4.837	51.12	0.45	8.97			
Total		100.00		100.00			

Presence of Phosphorus (P) is confirmed by EDX results.

Fig.5: EDX analysis of 0.1M sample annealed at 900 °C

Magnetic Property Analysis

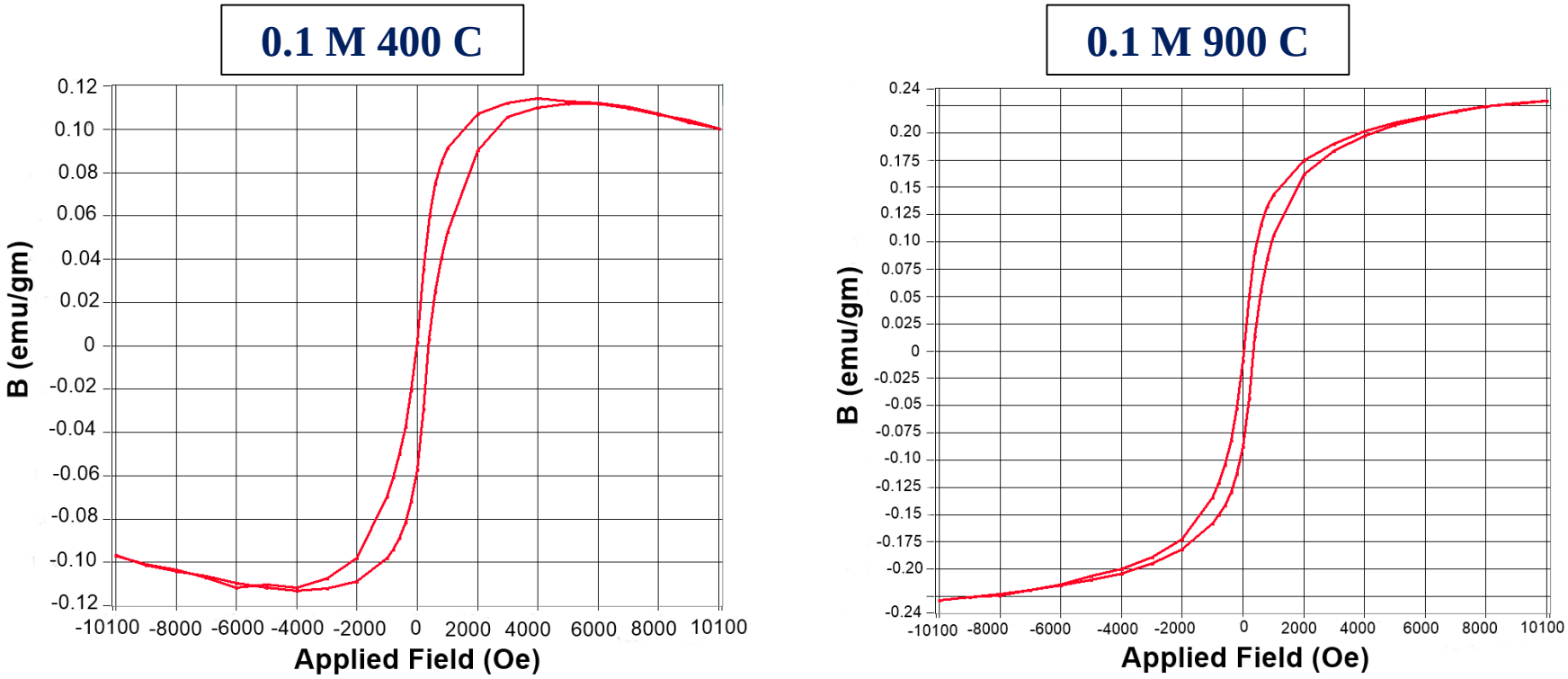


Fig.6: Magnetic property of 0.1M sample annealed at 400 ° C and 900 °C

Higher magnetization obtained at higher temperature

Optical Property Analysis

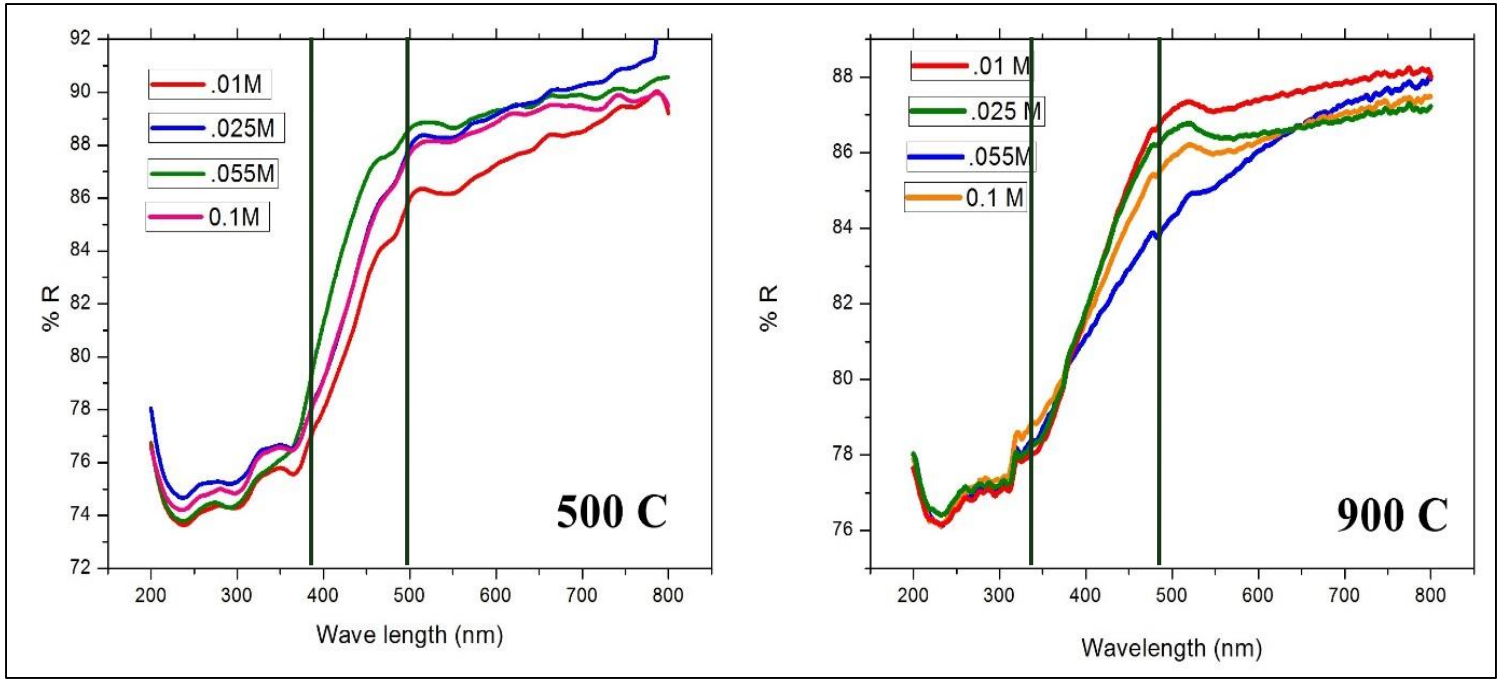
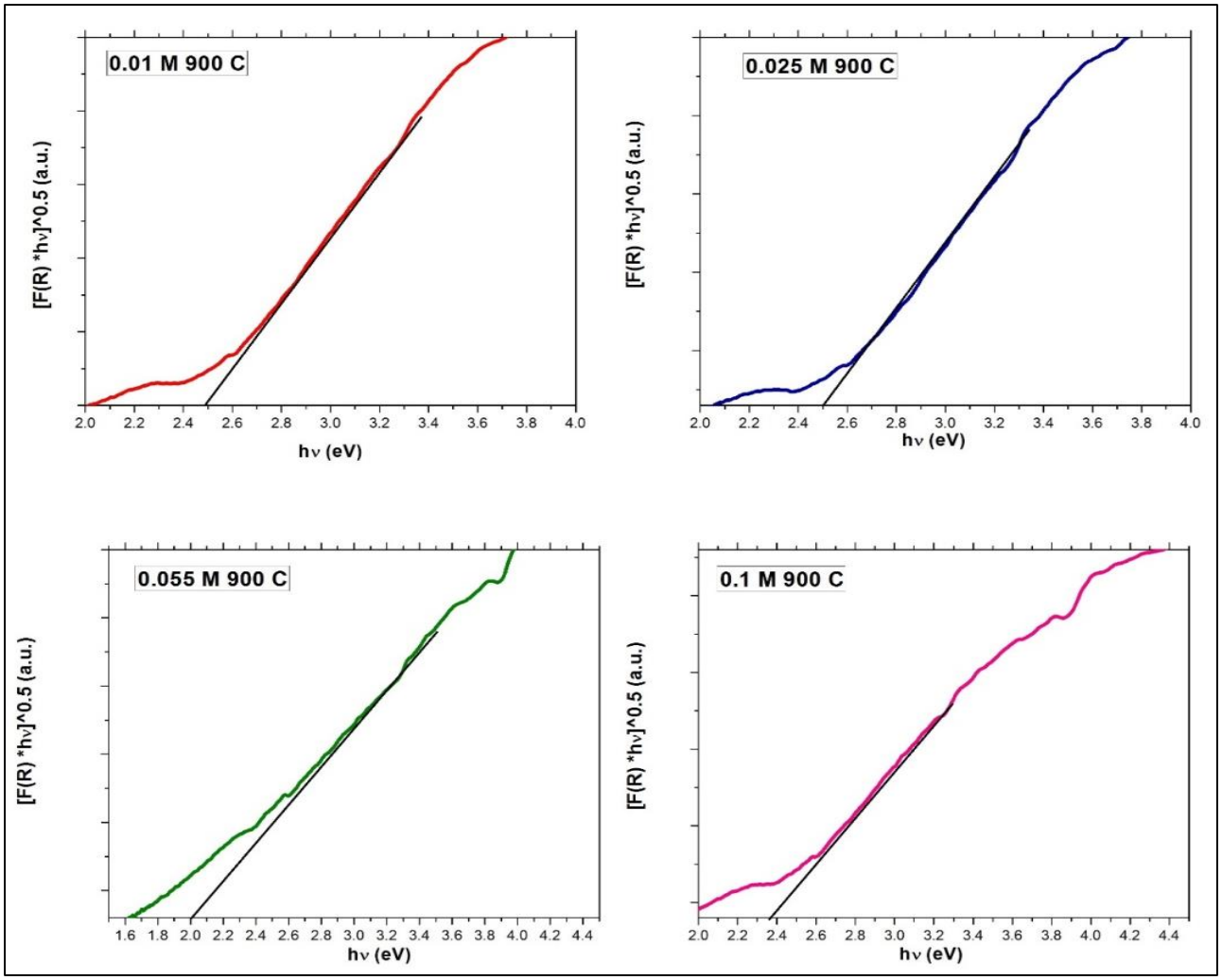


Fig.7 : UV-Vis reflectance spectra of all samples annealed at 500 °C and 900 °C

Reflectance/absorption range increases with the increasing annealing temperature

Optical Property Analysis



Kubelka-Munk function:

$$F(R) = \frac{(1-R)^2}{2R}$$

Fig.8 : Band gap of all samples at 900 °C

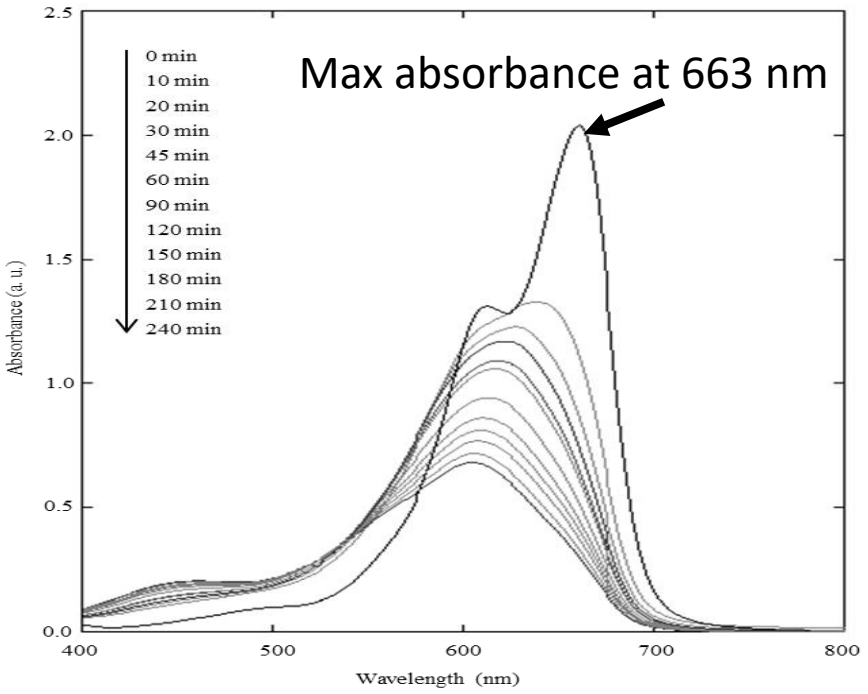
Optical Property Analysis

Table 4: Band gap of all samples annealed at 900 °C determined by Kubelka-Munk Plot

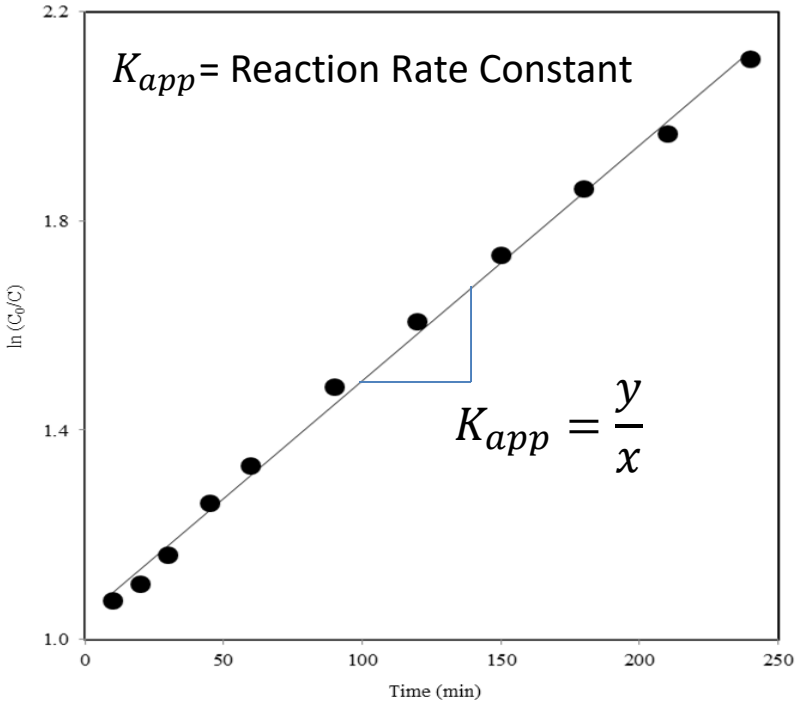
Precursor concentration	Band gap (eV)
0.01M	2.3
0.025 M	2.4
0.055 M	1.9
0.1 M	2.2

- ✓Band gap of bulk CeO_2 3.3 eV
- ✓Band gap obtained by green synthesis is lower
- ✓Enhanced photocatalytic property

Photocatalytic Activity



UV-vis spectra of 30µM MB solution before and after charging CeO_2 nanoparticles



Pseudo first order kinetic model for the degradation of MB dye using CeO2 nanoparticles

Slow Degradation Rate due to Absence of O_2 Vacancies in CeO_2 which were grabbed by $CePO_4$

Conclusions

- ✓Use of abundant leaf as reducing agent to avoid toxic chemicals
- ✓Structural analysis of the synthesized samples
- ✓Particle size 20 nm after annealing at 900 °C
- ✓Better optical property obtained
- ✓Magnetic property observed
- ✓Better photocatalytic property attained

References

[1] Yahiro et al. “High Temperature Fuel Cell with Ceria-Yttria Solid Electrolyte” J. Electrochem. Soc. 135, 2077 (1988)

[2] Noriya et al. “Performance of a carbon monoxide sensor based on zirconia-doped ceria” Sens. Actuators B 87, 95 (2002).

[3] Yu et al. Size-dependent optical properties of nanocrystalline CeO 2: Er obtained by combustion synthesis Phys. Chem. Chem. Phys. 3, 5266 (2001)

[4] Bekyarova et al. CO oxidation on Pd/CeO2–ZrO2 catalysts Catal. Today 45, 179 (1998)

[5] Cehn et al. Rare earth nanoparticles prevent retinal degeneration induced by intracellular peroxides. Nat. Nanotechnol. 1, 142 (2006).