

# Synthesis and Characterization of Metal-Doped Titania Systems Obtained through Sol-Gel Chemistry

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# Abstract

Metal-doped iron, manganese, nickel, and cobalt titania systems were synthesized through solution-gel (sol-gel) chemistry. After a drying and annealing process, the resulting powders were characterized by x-ray diffraction. Magnetic properties were then briefly analyzed using electron paramagnetic resonance. Manganese, nickel, cobalt, and two series of iron titanium dioxide were evaluated.

# Introduction

- Oxide diluted magnetic semiconductors with room temperature ferromagnetism, such as transition metal-doped  $\text{TiO}_2$  have been investigated for potential applications as spin injectors in spintronic devices. Titania exists in two forms, rutile and anatase, both having a tetragonal crystal system. Although ferromagnetism at room temperature has been observed in doped  $\text{TiO}_2$ , in some cases secondary phases have been observed or precipitated magnetic clusters as the origin of ferromagnetism, whereas other results indicated the existence of intrinsic ferromagnetism of transition metal substitution in the titanium sublattice.
- The end goal of this research is to synthesize single-phase transition metal-doped  $\text{TiO}_2$  nanostructures and characterize different metal-doped titania systems. A detailed examination of the magnetic would provide key information about the origin of ferromagnetism in these nanoscale materials.

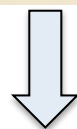
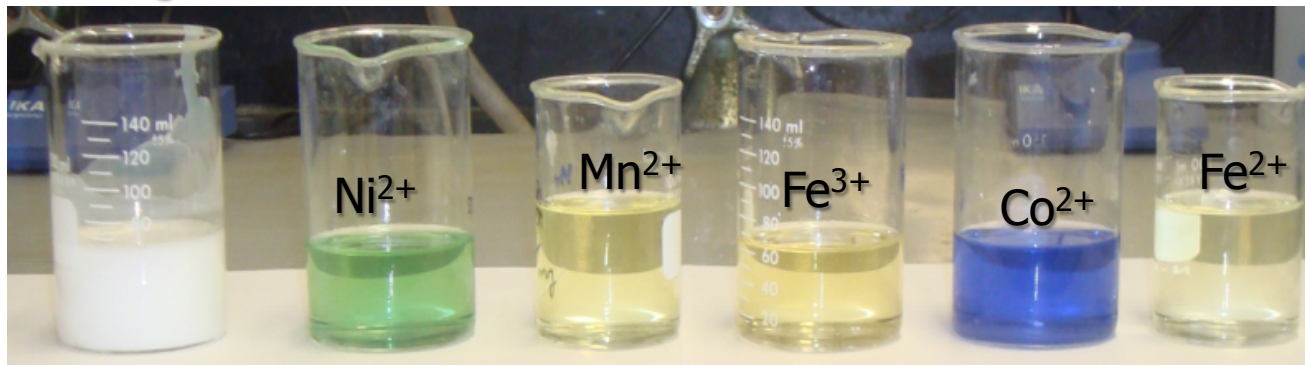
# Materials and Methods

- Synthesis of the metal-doped titania systems through sol-gel chemistry involved addition of titanium tetraisopropoxide ( $\text{TiOC}_3\text{H}_7$ ) to ethyl alcohol, potassium chloride, and various metal chlorides to generally produce an 1-8% concentration of metal-doped systems.
- The gels were then dried in an oven, ground into a powder, and annealed at 600 degrees.
- X-ray diffraction patterns were obtained using a XRD Rigaku MiniFlex II and X'Pert Pro PANalytical diffractometers.

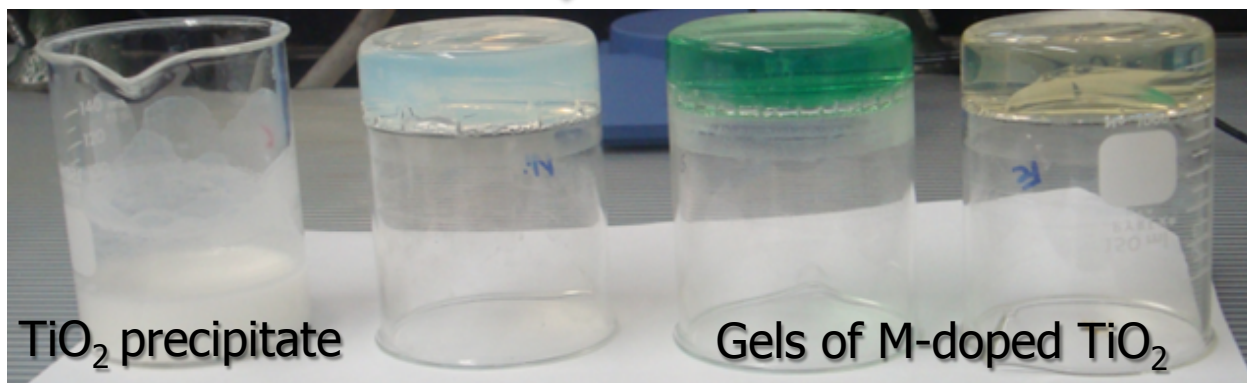


# Synthetic Procedure

## Starting Solutions



Gelling at room temperature

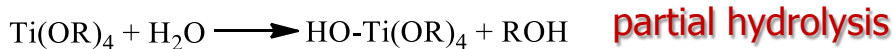


Heat treatment

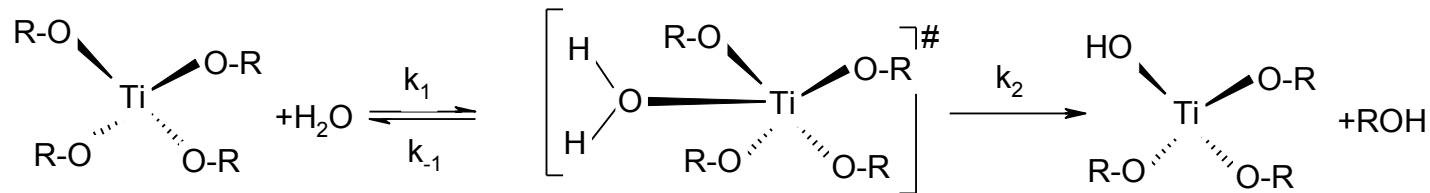
M-doped  $\text{TiO}_2$  Nanopowders

# Mechanism of Formation of Inorganic Gels

## 1. Hydrolysis of metalorganic precursors : a 2-stage reaction



## 2. Associative Mechanism



$$\ln k_{obs} = n \ln[H_2O] + \ln k_{exp}$$

Kivinen's Equation

$$\Delta H^\ddagger = 58.2 \text{ kJ/mol}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

Arrhenius's Equation

$$\Delta S^\ddagger = -83.7 \times 10^{-3} \text{ kJ/mol}$$

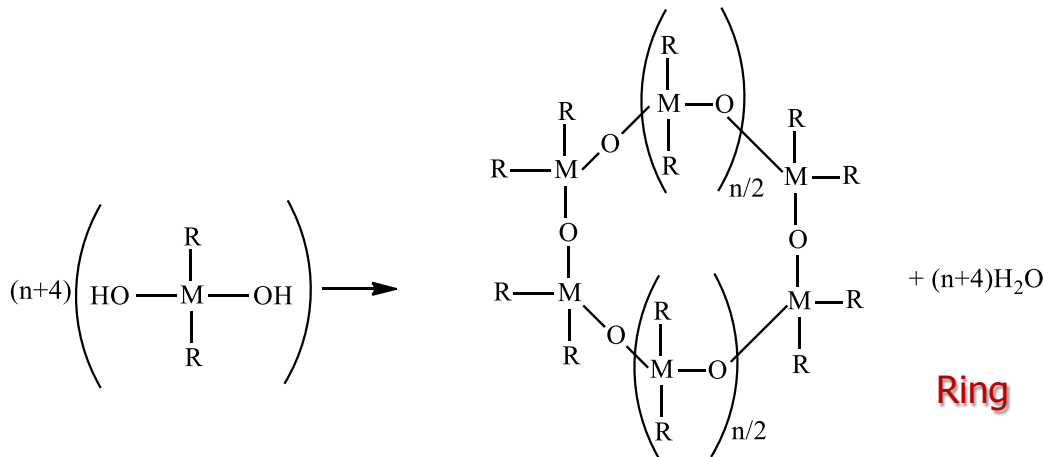
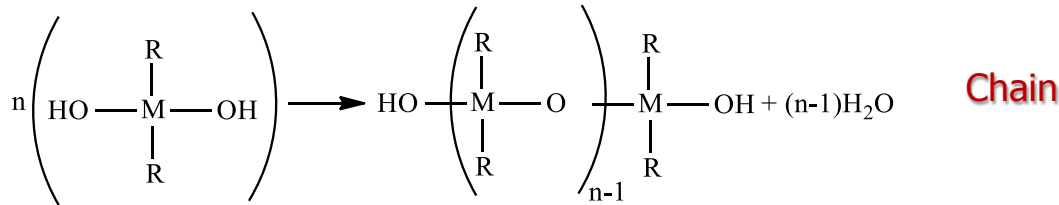
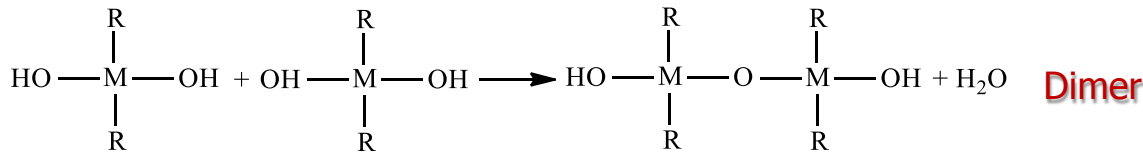
$$-T\Delta S^\ddagger = 24.9 \text{ kJ/mol}$$

$\Delta H^\ddagger$ ;  $-T\Delta S^\ddagger$  related to the bond weakening of the leaving group and bond forming of the entering group

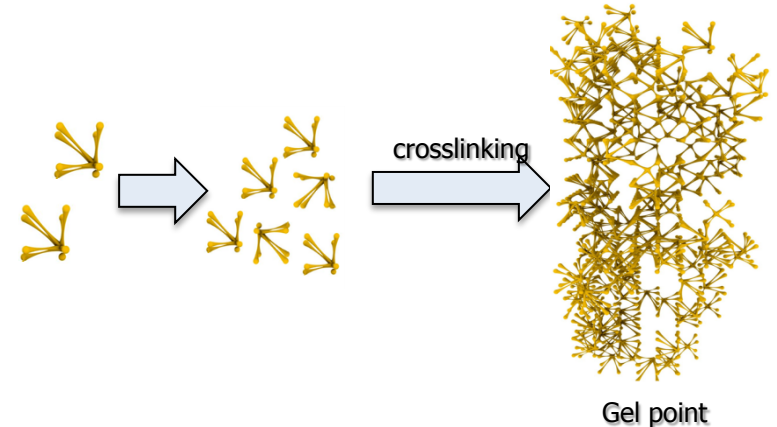
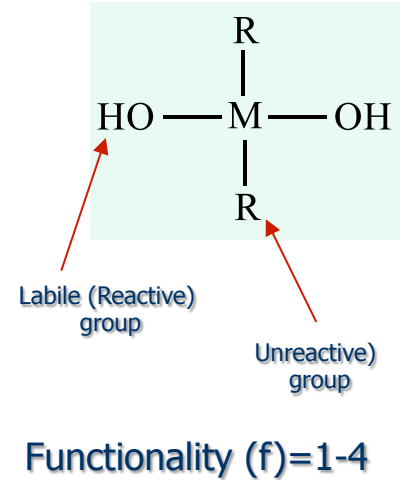
$$n = 3.4$$

# Mechanism of Formation of Inorganic Gels

## 3. Condensation and inorganic polymerization



## Anatomy of an Inorganic Monomer



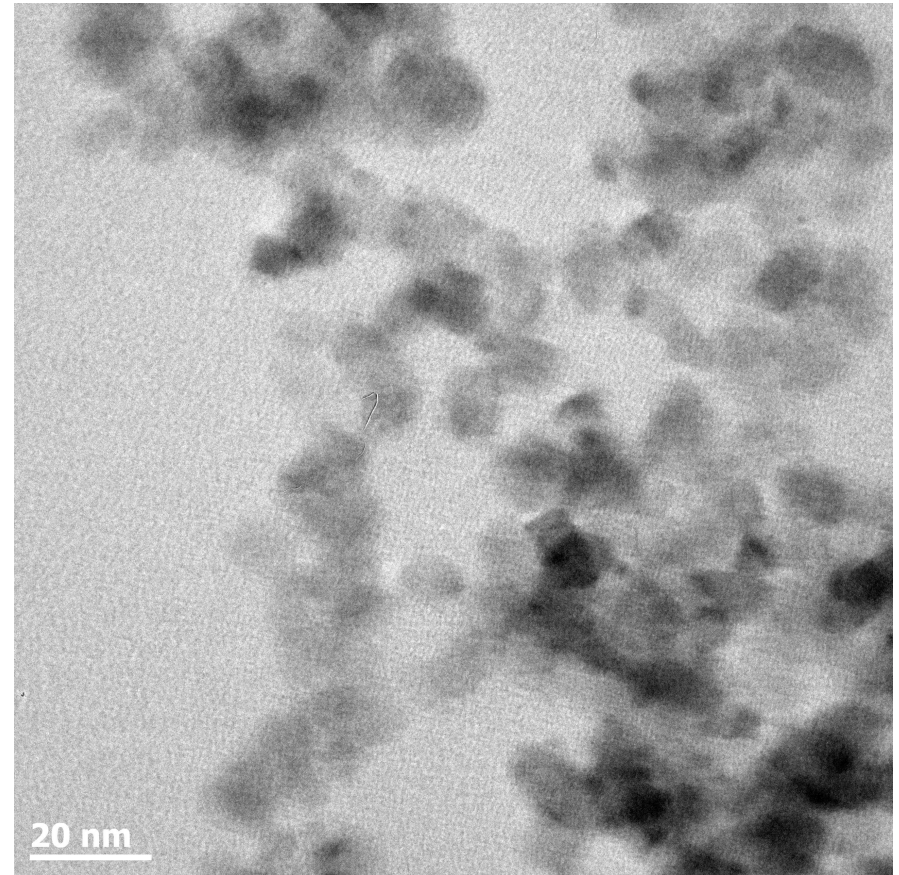
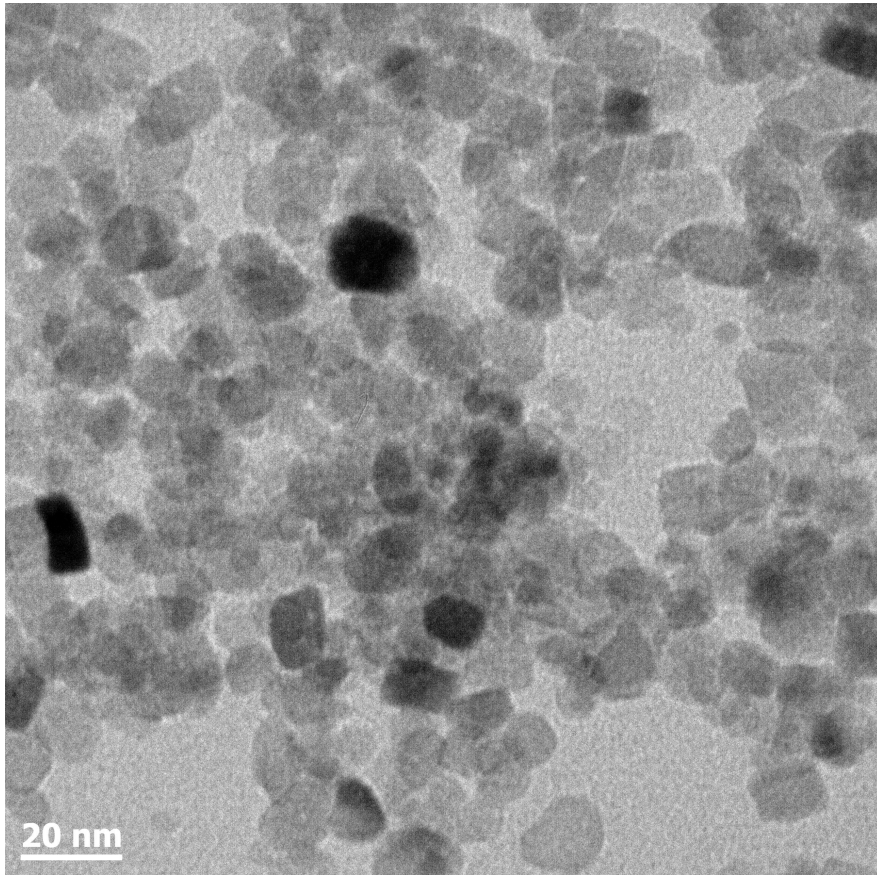
# Precipitation vs. Gelation in the Hydrolysis of Ti Alkoxides

- Polymeric Gels instead of a precipitate form when the rate of hydrolysis has been slowed
- The average length of the polymeric chain *increases* with *decreasing* the hydrolysis rate
- Gelation can be triggered upon addition of an acid catalyst
- In very small amounts of water and the presence of an acid catalyst, gelation becomes dominant compared to precipitation

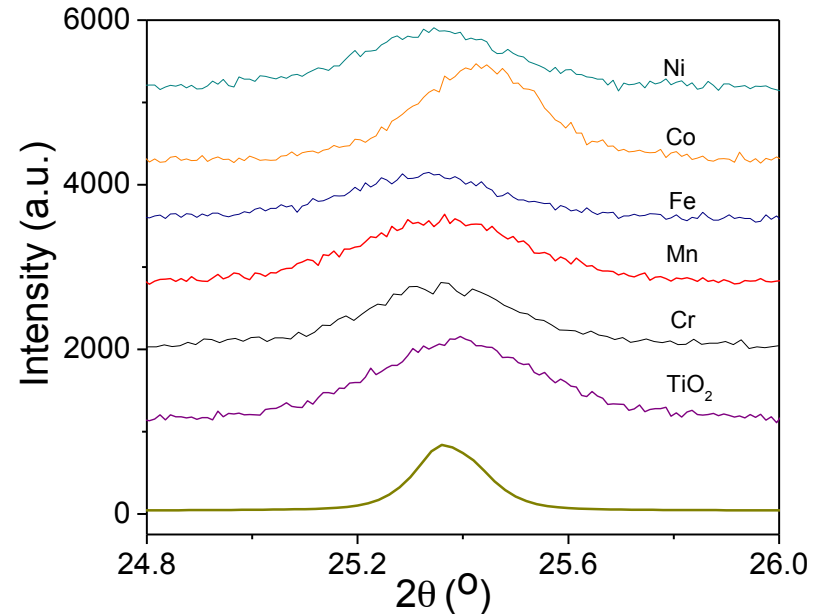
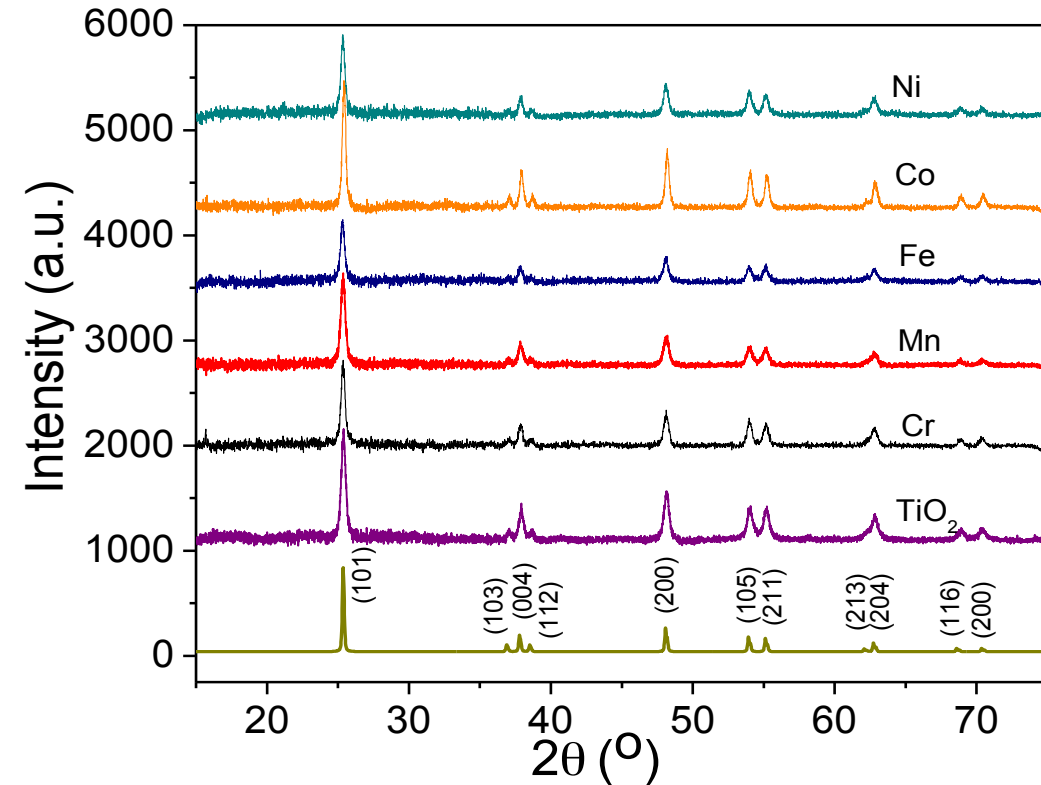


- The acid catalyst retards the rate of condensation of the intermediate aquo—hydroxo-complexes  $[Ti(OH)_x(OH_2)_{N-x}]^{(4-x)+}$
- Factors influencing the gel time: mole ratio of water/acid; size of the alkoxy group, total volume of the solution

# TEM Micrographs of M-doped TiO<sub>2</sub> Nanopowders



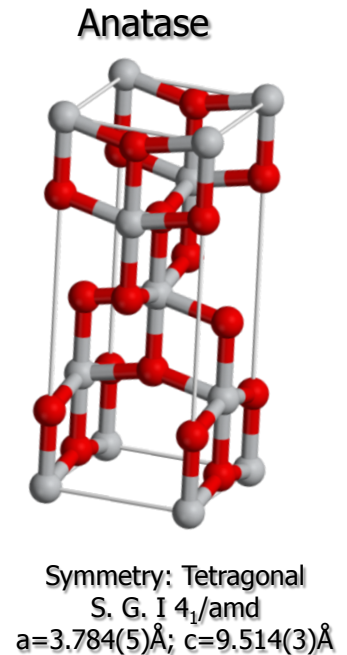
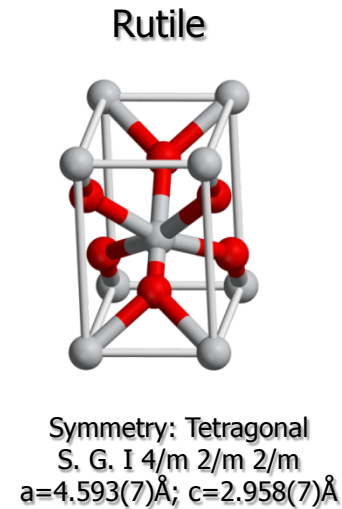
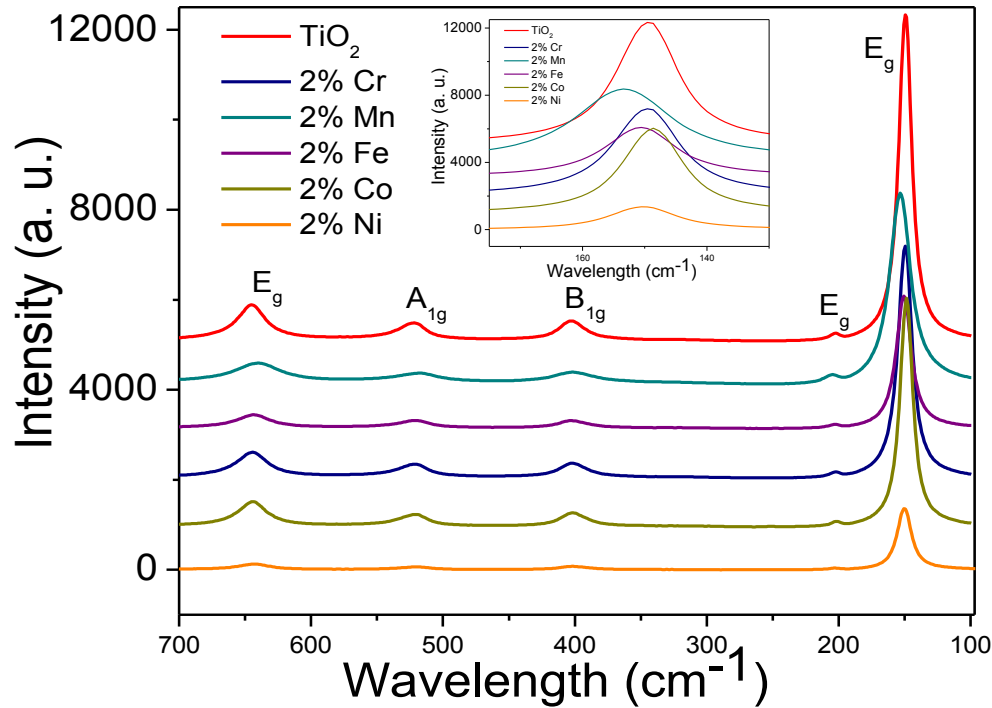
# Crystal Structure of M-Doped TiO<sub>2</sub> Nanoceramics



	Bulk Anatase	TiO <sub>2</sub>	2% Cr	2% Mn	2% Fe	2% Co	2% Ni
a (Å)	3.872(2)	3.775(6)	3.783(3)	3.783(5)	3.781(1)	3.780(2)	3.783(5)
c (Å)	9.616(5)	9.499(7)	9.507(4)	9.502(9)	9.512(8)	9.491(2)	9.502(7)
V (Å <sup>3</sup> )	144.18(9)	135.38	136.1	136.02	136.04	135.65	136.03
r(Å)	0.68 (IV)	0.87 (II) 0.75 (III)	0.87 (II) 0.75 (III)	0.81 (II) 0.67 (IV)	0.92 (II; HS) 0.78 (III; LS)	0.88 (II; HS) 0.75 (III, HS)	0.83 (II) 0.7 (III)

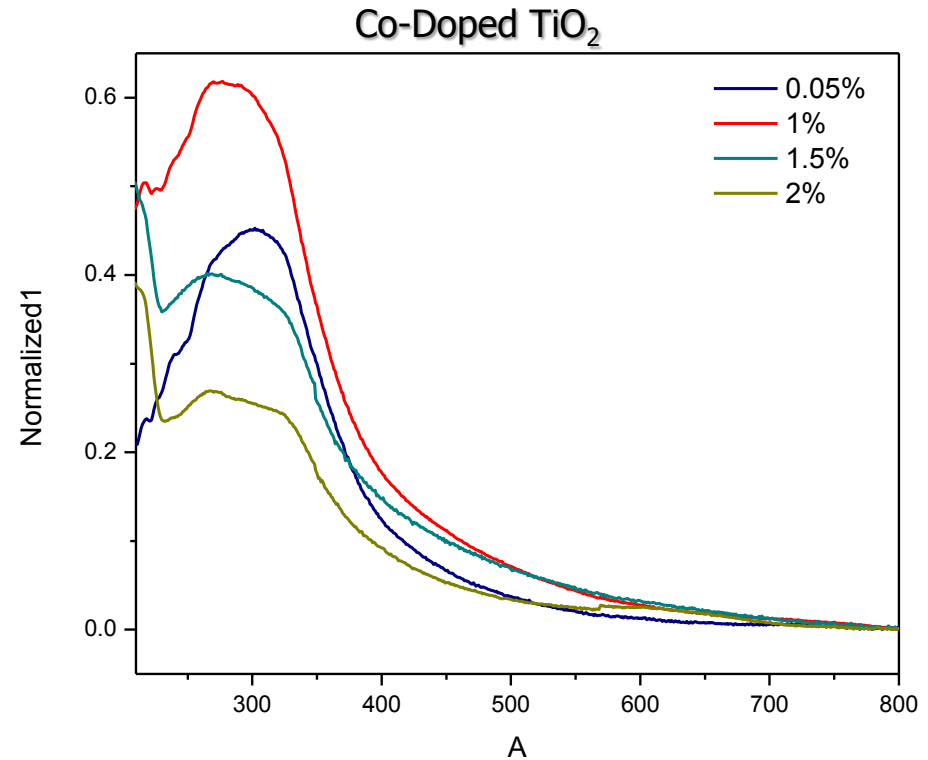
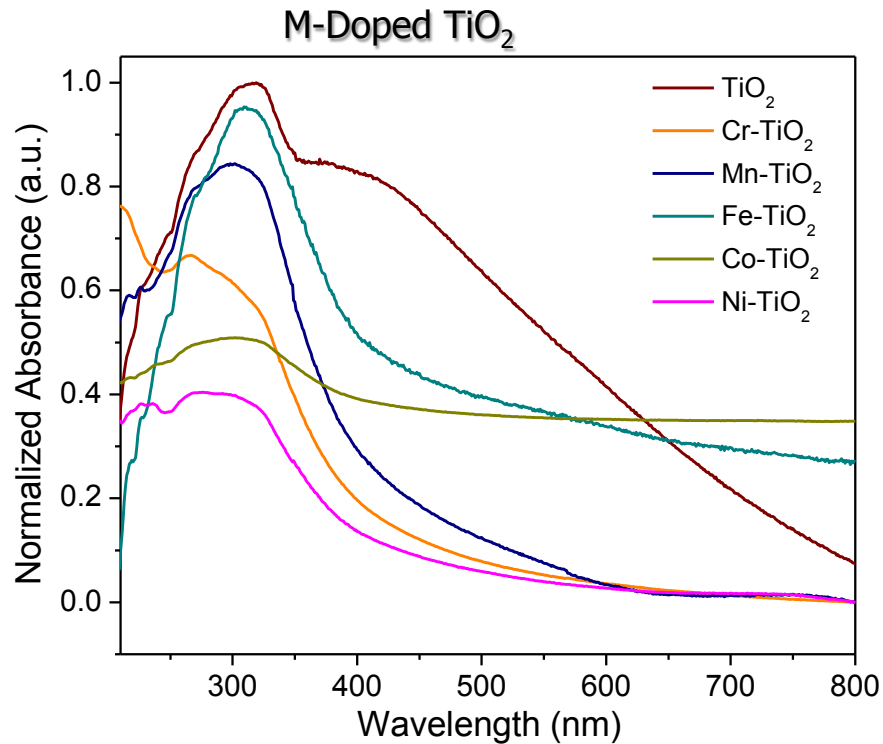


# Dynamic Lattice Analysis of M-Doped TiO<sub>2</sub> Nanoceramics



	Bulk Anatase	TiO <sub>2</sub>	2% Cr	2% Mn	2% Fe	2% Co	2% Ni
E <sub>g</sub>	144	149.1	149.6	153.7	150.2	148.7	150.4
E <sub>g</sub>	197	201.9	204.4	202.8	202.4	201.3	201.9
B <sub>1g</sub>	399	402.5	400.8	402.3	400.7	400.8	400.9
A <sub>1g</sub>	513	521.3	517.5	519.1	520.6	521.3	519
B <sub>1g</sub>	519	521.3	517.5	519.1	520.6	521.3	519
E <sub>g</sub>	639	644.9	639.5	641.8	643.4	644.1	641.0

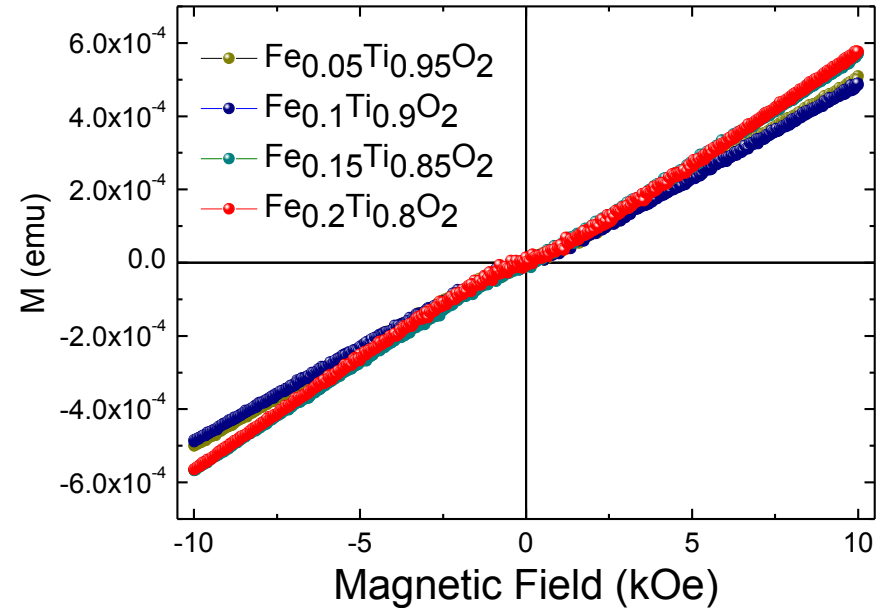
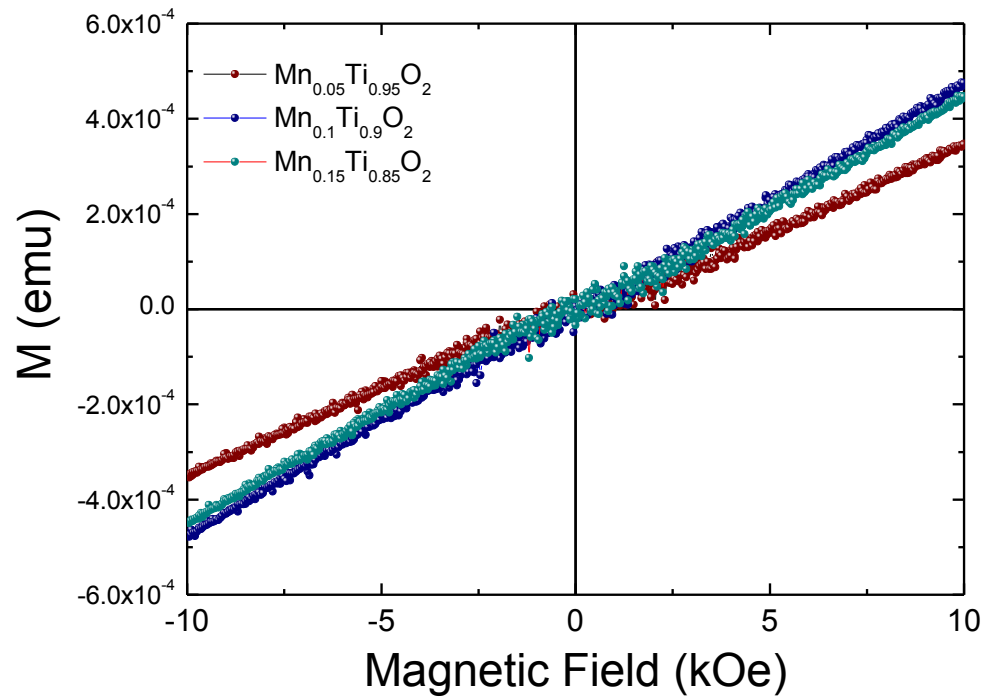
# UV-vis Spectra of M-Doped TiO<sub>2</sub> Nanoceramics



- A red shift of the absorption edge in Co-doped titania ascribed to the charge-transfer transition between the d-electrons of the dopant and the TiO<sub>2</sub> conduction band



# Magnetic Properties of M-Doped TiO<sub>2</sub> Nanoceramics



# Discussion and Conclusions

- We have successfully prepared transition metal-doped  $\text{TiO}_2$  nanopowders by a simple sol-gel process
- The presence of transition metal ions inhibits the hydrolysis of  $\text{TiO}_2$  with the formation of precipitate, leading to the formation of gels
- Within the gel, the transition metal ions are uniformly distributed; they replace partially the  $\text{Ti}^{4+}$  in the titania structure
- The resulting M-doped titania nanopowders retain a crystal structure described by that of anatase

# Discussion and Conclusions

- Magnetic measurements at room temperature revealed the presence of a paramagnetic behavior in all samples, which confirms the cationic substitution of the  $Ti^{4+}$  ions by transition metals
- Magnetic properties of the nanopowders also suggested the absence of clusters formed by dopant ions, thereby confirming the uniform doping of anatase by transition metals by the proposed experimental protocol
- The catalytic activity of these nanopowders towards the photochemical degradation of dyes will be investigated

# Acknowledgments

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