Designing Nanostructured Transition Metal-Doped TiO_2 Photocatalysts by a Low Cost and Versatile Gel Process

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Abstract

Crystalline metal doped TiO_2 nanoceramics were produced through a process that utilized the formation of monolithic gels. TiO_2 was doped in atomic percentages from 0% to 8% with different first row transition metals, such as Mn, Fe, Cu, Ni, Cr, and Co.

The resulting nanoceramics were characterized by X-ray powder diffraction (XRD), surface and porosity analysis, Raman spectroscopy and transmission electron microscopy (TEM). Their photocatalytic properties were tested in the degradation of various organic dies, such as methyl red. The crystal structures of the prepared samples showed that the substitutional doping can be achieved by the gel method, which successfully created metal-doped TiO_2 nanoceramics.

Other characterization results showed variations between samples with different dopant types and molar ratios of metals, which could suggest differences in photocatalytic properties.

Introduction

- For decades, TiO_2 has been known as a photocatalyst under ultraviolet light. Because of this, it is added to paints, textiles, glasses, tiles, sunscreens, and other products. By doping with other metals, the band gap of TiO_2 can be engineered, thereby allowing it to become an efficient photocatalyst under visible light.

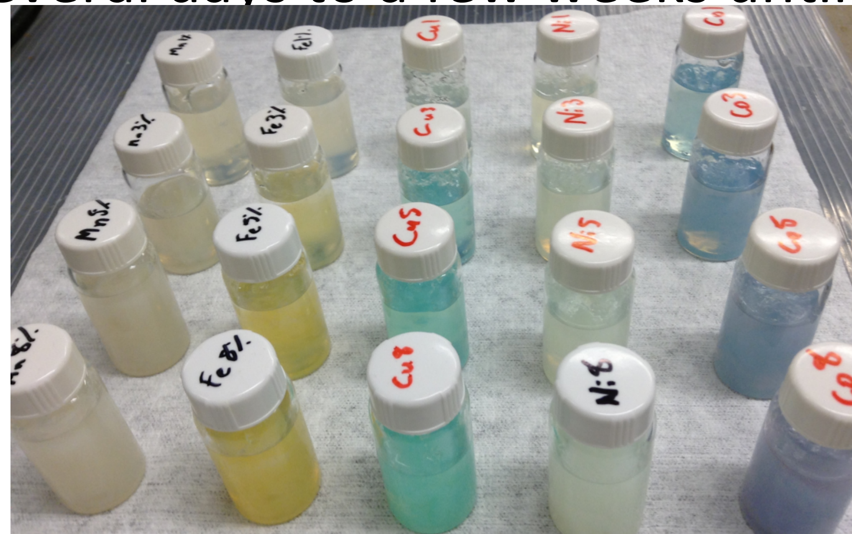
- Characterizations were carried out for several different metal-doped TiO_2 samples in order to compare the photocatalytic activity and crystal structure of different atomic percentages of different doping metals in a compound.

Experimental

Preparation of M-doped TiO_2 Samples

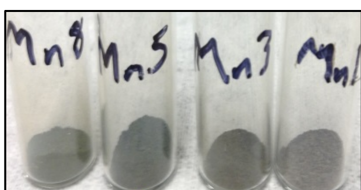
- Add ethanol into a beaker.
- Add the reagent consisting of your doping metal. The reagent is typically a chloride or nitrate, and the amount is adjusted based on the intended atomic percentage of doping metal.
- Add aqueous KCl.
- Add titanium tetraisopropoxide.
- Stir solution with magnetic stirrer for about 10 minutes.
- Remove magnetic stirrer from the solution.
- Partially cover the beakers with laboratory film.

- Let the solutions sit from several days to a few weeks until the solution turns into a gel.
- Dry the gels in a hooded airflow system until completely dry.
- Grind the dried gels into a powder.

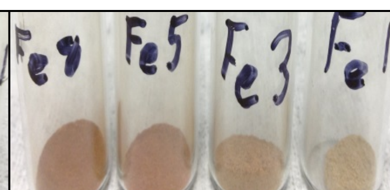


Gels before drying.

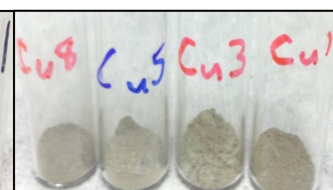
- Anneal the powders at 600°C for 12 hours.



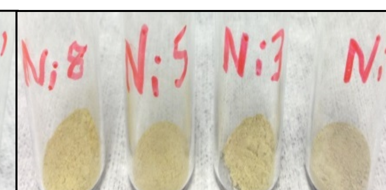
Mn-doped TiO_2



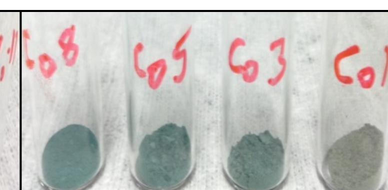
Fe-doped TiO_2



Cu-doped TiO_2

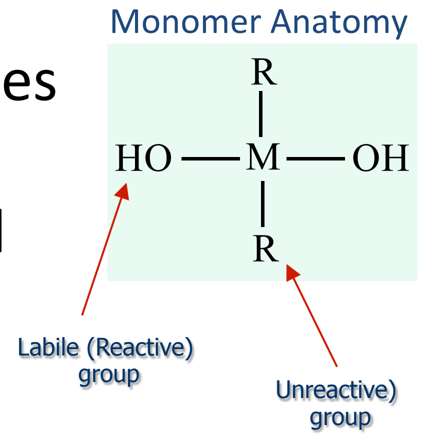


Ni-doped TiO_2



Co-doped TiO_2

Mechanism of Inorganic Gel Formation



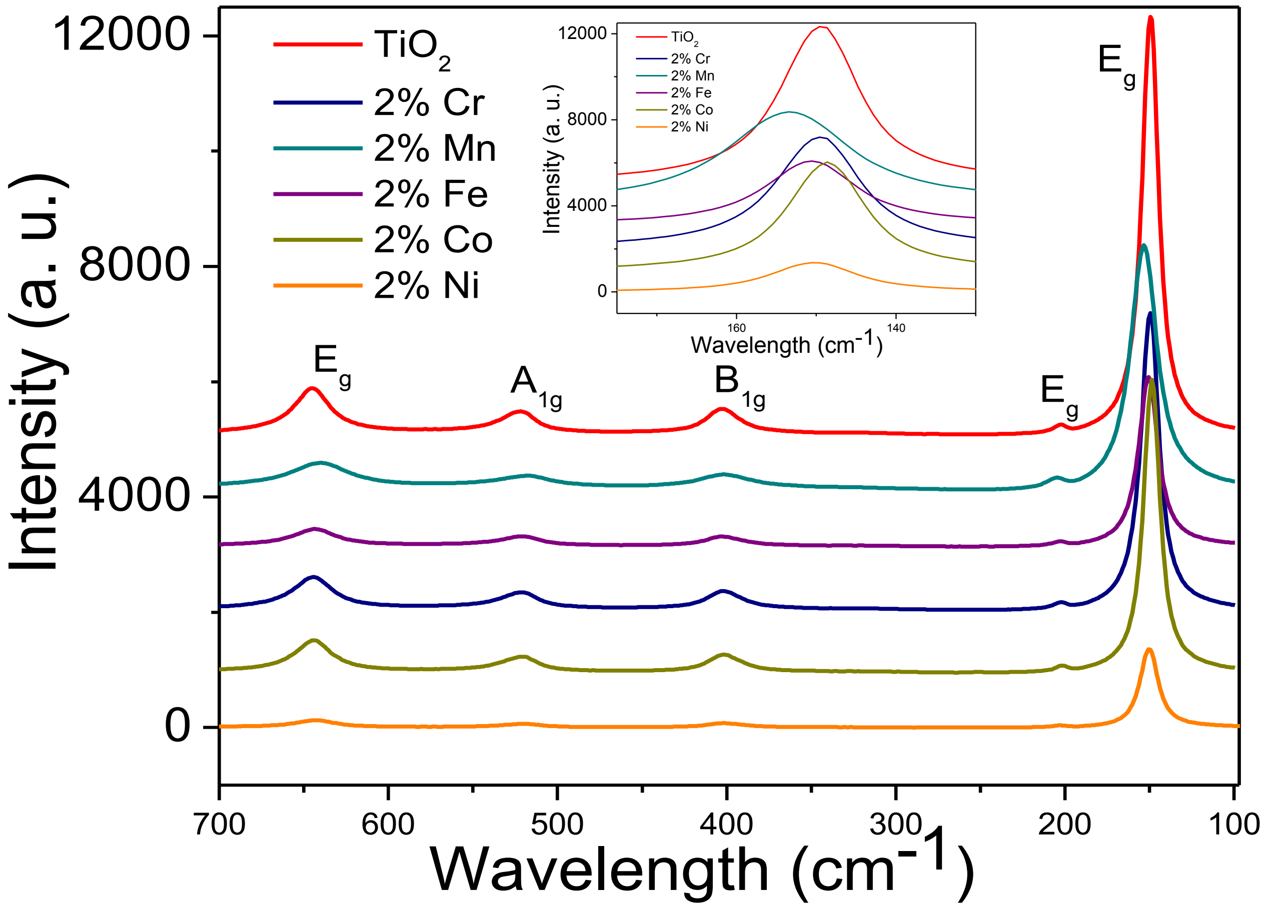
- The successful doping of a metal in TiO_2 causes the dopant to replace Ti in some monomers. These monomers undergo condensation and polymerization during hydrolysis.
- The addition of a chloride or nitrate reagent into the solution containing ethanol allows the formation of acid, typically hydrochloric acid.

$$MCl_z + zROH \longrightarrow M(OR)_z + zHCl$$

- The presence of an acid catalyst retards the rate of condensation in the solution, allowing a slow gelation process to develop instead of an instant precipitation process.

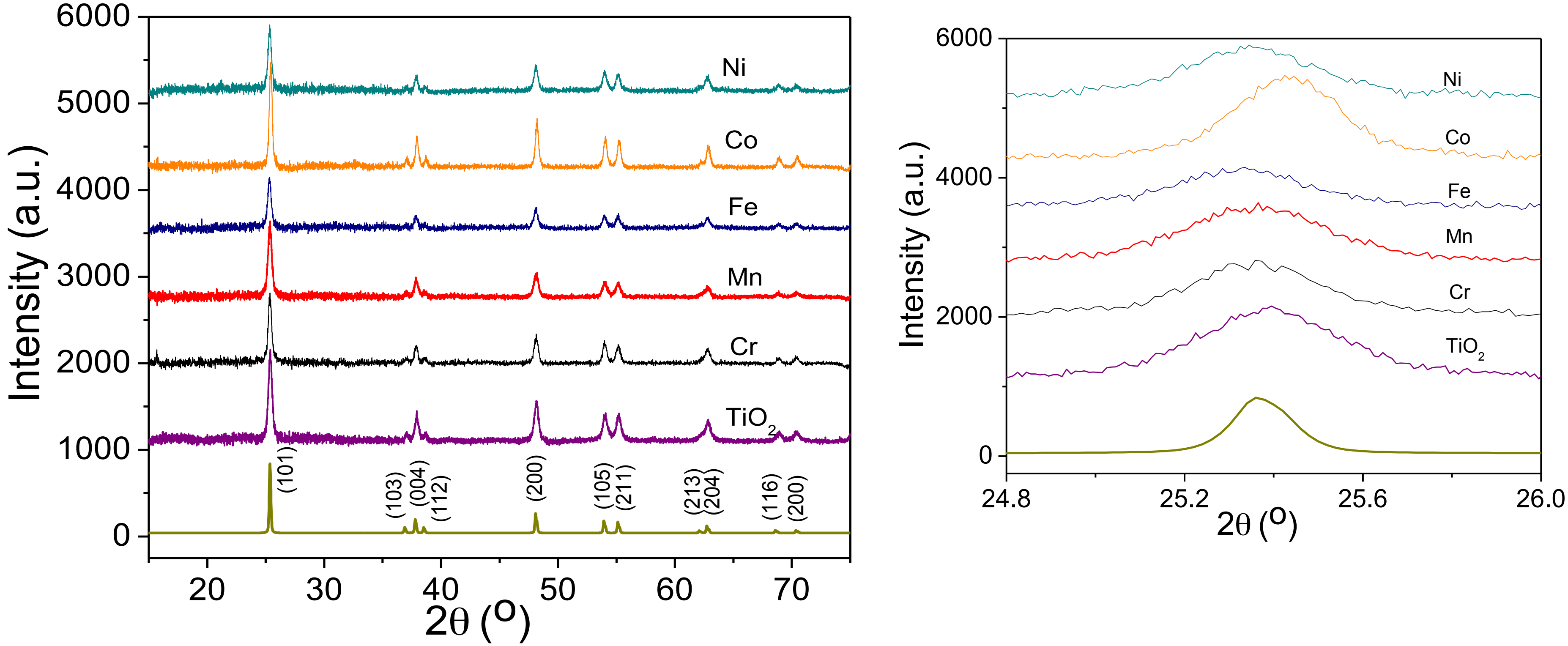
Experimental Results

Raman Spectroscopy



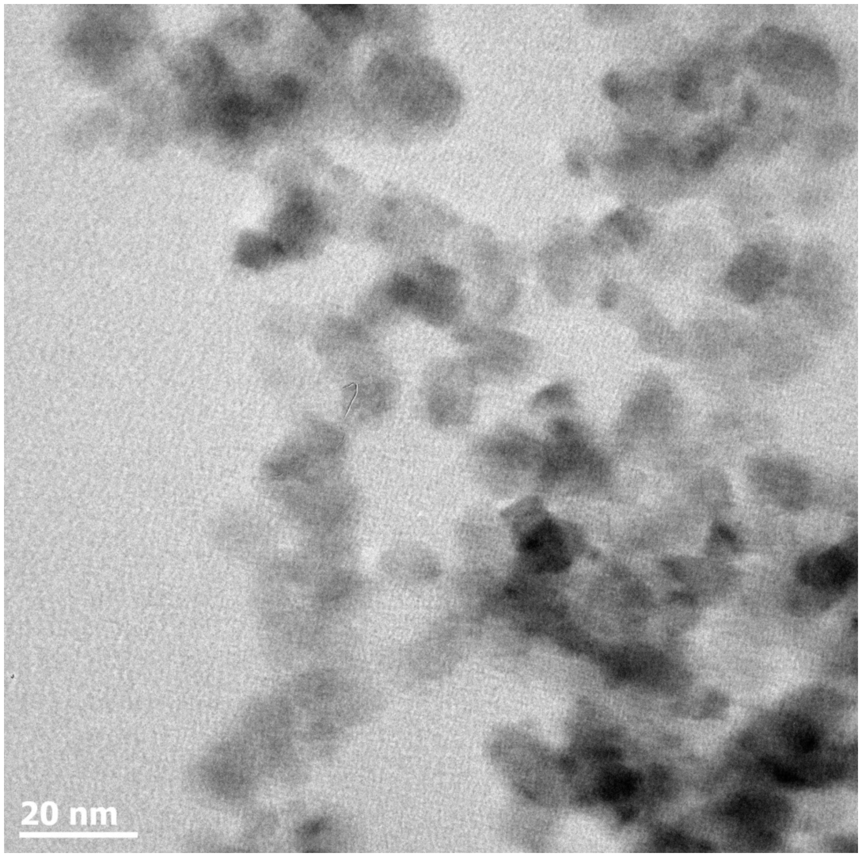
Raman spectroscopy data show striking similarities of the spectra of the metal doped powders with that of the undoped sample. This strongly suggests that transition metal ions substitute the Ti^{4+} in the host ionic lattice

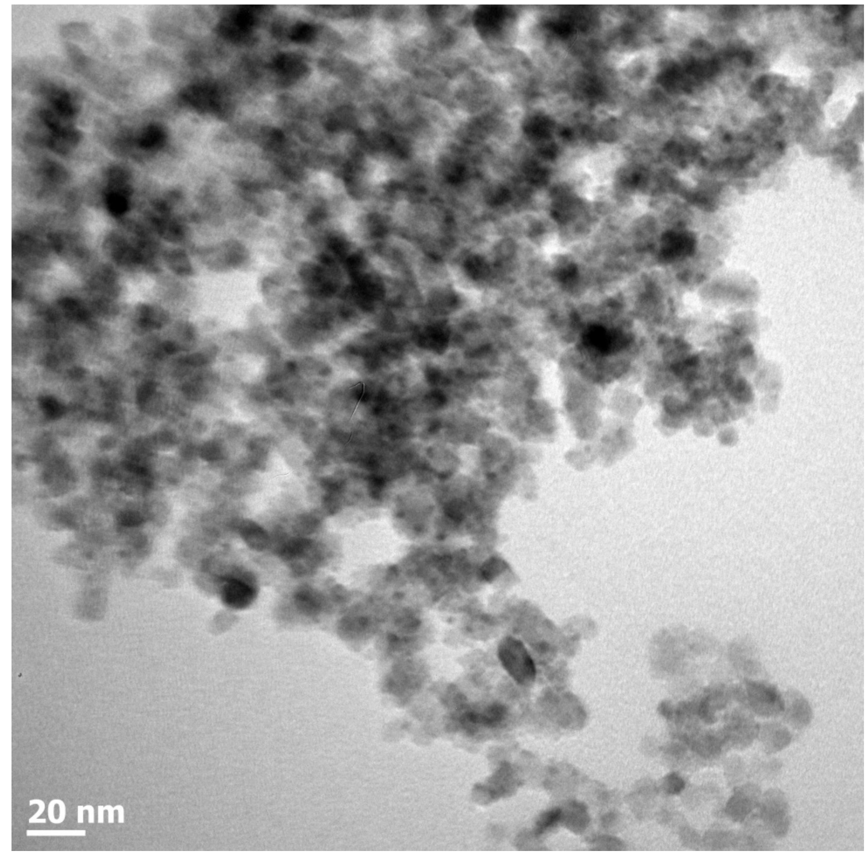
Crystal Structure



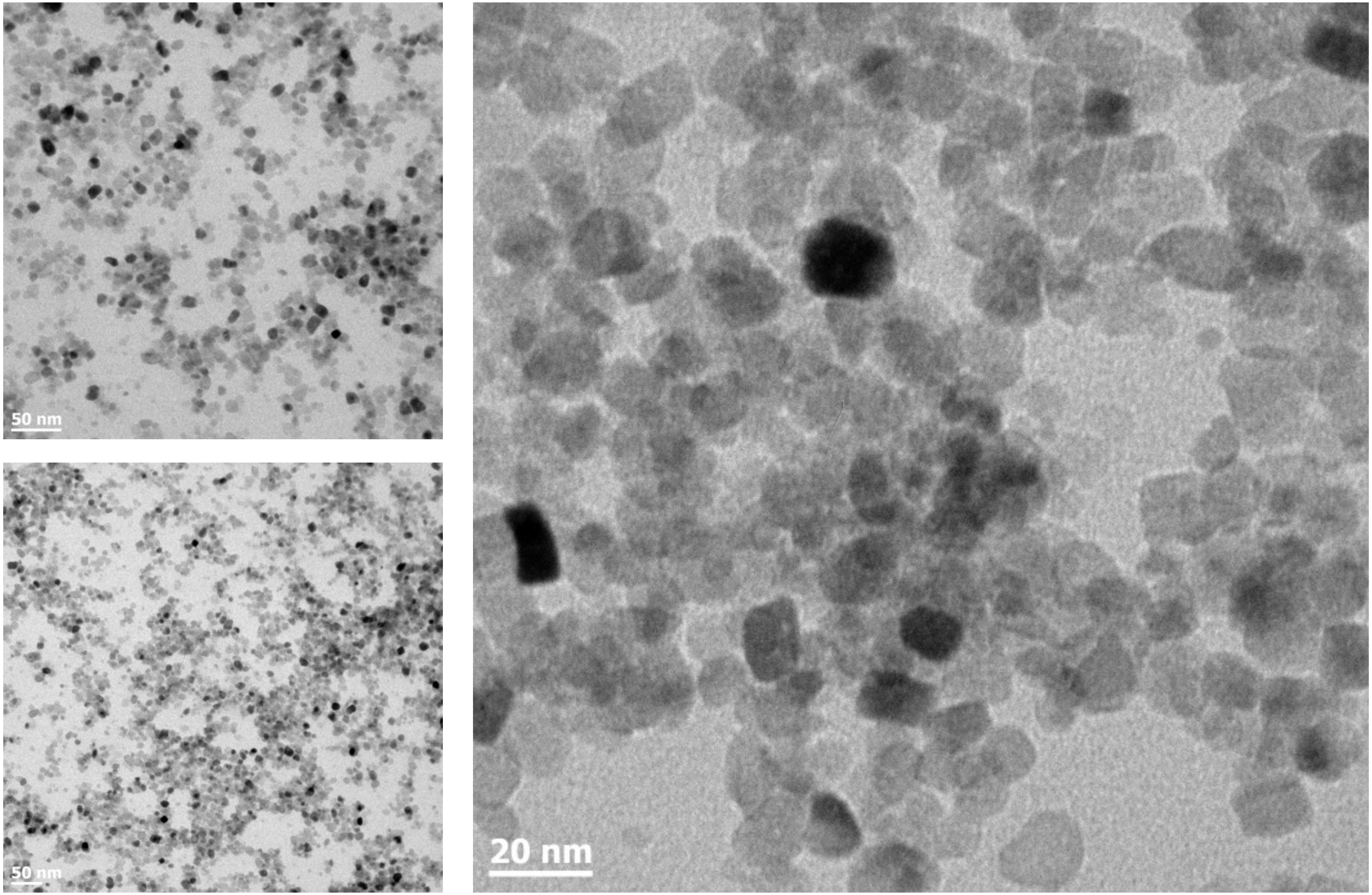
	Bulk Anatase	TiO_2	2% Cr	2% Mn	2% Fe	2% Co	2% Ni
a (Å)	3.872(2)	3.775(6)	3.783(3)	3.783(5)	3.781(1)	3.780(2)	3.783(5)
c (Å)	9.616(5)	9.499(7)	9.507(4)	9.502(9)	9.512(8)	9.491(2)	9.502(7)
V (Å^3)	144.18(9)	135.38	136.1	136.02	136.04	135.65	136.03
r(Å)	0.68 (IV)	0.87 (II) 0.75 (III)	0.87 (II) 0.75 (III)	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)

Transmission Electron Microscopy Images



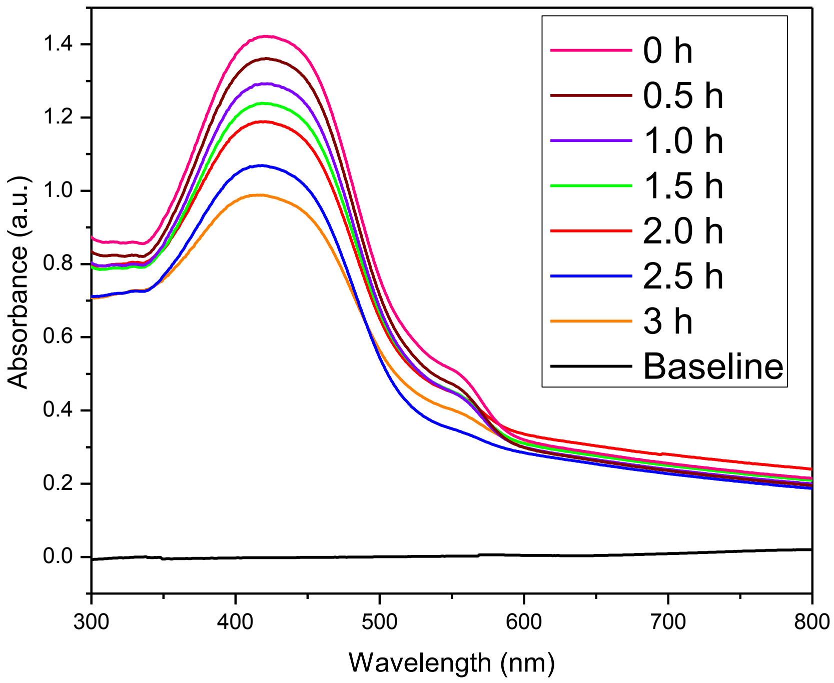


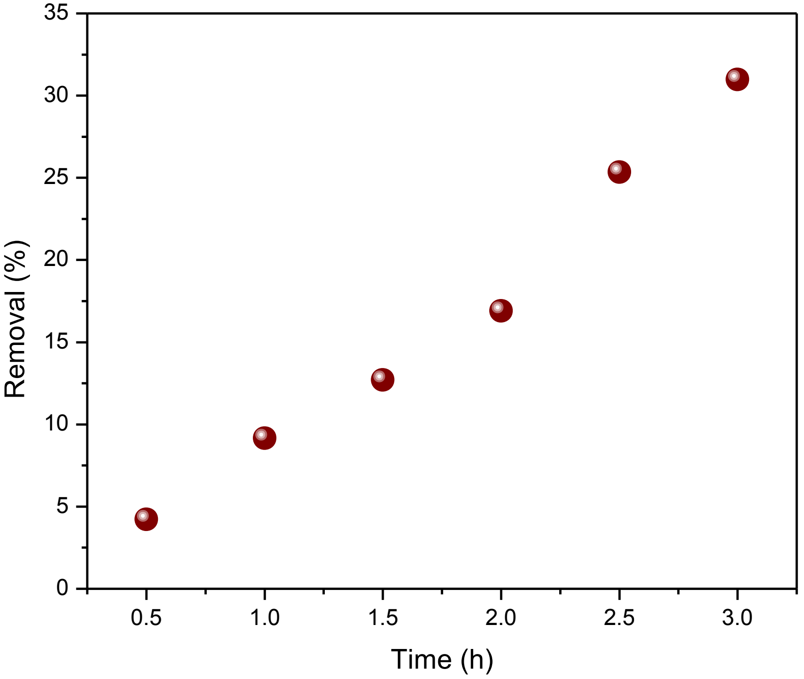
TEM Images of iron-doped TiO_2 nanoparticles



TEM images of chromium-doped TiO_2 nanoparticles

Photocatalytic Properties of Co-Doped TiO_2 Nanoparticles





The removal efficiency of methylene red by the Co-doped TiO_2 nanoparticles after 3h is 35%

Conclusions

- In this study, we prepared metal-doped TiO_2 nanoparticles using monolithic gels, rather than precipitants. This proved successful as the lack of impurities in the crystal structure of the samples confirmed the observation that the transition metal ions replace titanium in the host crystal.

- As evidenced by TEM pictures and Raman spectroscopy, nanoparticulate anatase samples doped with different metals and in different amounts are quasi-spherical and exhibit different sizes.

- These variations could allude to enhanced photocatalytic properties, allowing us to determine which characteristics maximize the efficiency of a photocatalyst.

Acknowledgements

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