

# PHOTOCATALYTIC REMOVAL OF COPPER AND SELENIUM FROM WASTEWATER UNDER VISIBLE LIGHT

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## Abstract

*Zirconia and silica mixed titanium oxides were synthesized by modified sol-gel method in presence of a surfactant (CETAB). Materials were characterized by surface area, XRD, SEM and UV-Vis spectroscopy. Materials are found to be in uniform size and mostly spherical when synthesized in presence of CETAB. Effect of surfactant concentration on the particle size, shape and the catalytic activity is also evaluated. Calcination temperature plays an important role on the phase stability and catalytic activity of the materials. It is well observed that without any hole scavenger the efficiency of photocatalytic metal removal is quite low for both the metal ions within 30 minutes of reaction. However, addition of hole scavenger increases the activity many folds and hence complete removal of Se and Cu was possible in 30 minutes of reaction. Among all the organic hole scavengers used, sodium formate is found to be the most active one for selenium whereas for copper EDTA is the most suitable one. Reaction pH also plays an important role in the efficiency of the metal removal. Above all synthesized materials are found to be efficient catalyst for visible light reaction. The same catalyst is found to be reusable at least for 5-6 times with 4-5% decrease in the activity.*

## Introduction

Since the discovery of photo-induced water cleavage on titanium dioxide electrodes by Fujishima and Honda [1] in the early 70s, the interest in applying  $\text{TiO}_2$  as heterogeneous photocatalyst to purify water and wastewater has been increasing rapidly. Compared with conventional water treatment approaches, such as chlorination, ozonation, UV radiation and advanced filtration processes;  $\text{TiO}_2$  as a durable semiconductor has a number of advantages including high oxidation efficiency for complete decomposition and mineralization of organic waste, reductive removal of toxic metal ions, cost effectiveness and minimal disinfection byproducts [2, 3]. In particular solar light induced photocatalytic process can be comparatively low cost and hence much attractive for larger use. In this context so many modified catalysts were developed in recent years for potential use as photocatalyst in visible light. The incorporation of transition metal into the anatase phase of  $\text{TiO}_2$  has been frequently studied as a way to extend the spectral response to the visible range [4]. In addition, certain  $\text{Ti}_{1-x}\text{M}_x\text{O}_2$  phases show an enhancement of the photoactivity due to structural and electronic modifications induced by the dopant. In this respect, the inclusion of  $\text{Sn}^{4+}$  in the rutile and the anatase structures leads to a significant increment of the rate for the photocatalytic oxidation of acetone [5] or methylcyclohexane vapor. In the recent years many mixed oxide systems were reported as potential photocatalyst due to the different nature of the binary oxide systems over pure titania [6, 7]. In particular addition of  $\text{ZrO}_2$  was found to be beneficial as it inhibited the anatase to rutile phase transformation [8, 9]. Similarly addition of silica also increases the catalytic activity particularly in presence of UV light. Anderson and Bard [10,

11] reported that a mixed oxide powder of  $\text{TiO}_2$  and  $\text{SiO}_2$  can be more efficient photocatalyst than pure  $\text{TiO}_2$  powder. On the other hand nonmetal doping of  $\text{TiO}_2$  rekindled a great interest in visible light catalysis since the report of the work of Asahi et al [12]. It is observed that doping with nonmetals like N[12], C[13], F[14] etc can increase the visible light absorption of the photocatalyst. Here we report the visible light mediated photocatalytic removal of selenium and copper over synthesized silica and zirconia mixed titania materials.

## Experimental

### *Material synthesis*

Titanium isopropoxide, zirconium butoxide and tetraethyl orthosilicate (Aldrich) were used as starting material. Materials were synthesized according to the earlier reported method [15]. Pure titania and silica, zirconia mixed titania were prepared by controlled hydrolysis of corresponding isopropoxide in presence of surfactant (cetyltrimethylammonium bromide, CETAB) in n-propanol water mixture. Silica and zirconia (10 and 20 wt%) mixed titania samples were prepared by using calculated amount of corresponding alcoxide mixture in n-propanol so as to maintain the ratio of 10:90 and 20:80 in the binary oxides. Required amount of surfactant (2mol%) was added to the reacting mixture before hydrolysis. Hydrolysis was carried out by drop wise addition of n-propanol and water mixture from a burette under magnetic stirring condition in 30min time period. The gel so obtained was maintained in the same stirring condition for another 4h. Subsequently the gel was filtered and washed with distilled water several times, dried at  $100^\circ\text{C}$ , calcined at 500, 700 and  $900^\circ\text{C}$  for 4h and kept for further use. Silica mixed titania and zirconia mixed titania are denoted as TiSi and TiZr, respectively. Number after the sample indicates the weight percentage of silica or zirconia mixed with titania.

### *Material characterisation*

XRD patterns of all the synthesized samples calcined at different temperatures were recorded on a Siemens (model: D-500) semiautomatic diffractometer using  $\text{Cu-K}_\alpha$  radiation source and Ni filter in the range of 10 to 70 degree.

BET surface area was determined by  $\text{N}_2$  adsorption desorption method at liquid nitrogen temperature using Quantasorb (Quantachrome, USA). Prior to adsorption desorption measurements, the samples were degassed at 393K at  $10^{-4}$  Torr for 5h.

SEM micrographs of powdered samples were recorded on scanning electron microscope (JEOL 840A, Japan) after gold coating.

FT-IR spectra of different samples were recorded with Nicolet 750 FT-IR spectrometer using KBr palate at room temperature in the range of 400 to  $4000\text{cm}^{-1}$  with scanning rate of  $4\text{cm}^{-1}/\text{min}$ .

### *Photocatalytic activity*

Prepared materials were used as photocatalyst for the reductive removal of selenium and copper ions in acidic pH. Stock solution of selenium and copper was prepared by dissolving required amount of sodium selenite and cupric chloride respectively, in double distilled water. All the photocatalytic experiments were carried out in a 200ml capacity three necked glass reactor fitted with 125w visible lamp under magnetic stirring condition. Constant reaction temperature was maintained through water circulation in the outer jacket of the glass reactor. All the experiments were performed in presence of air at atmospheric pressure. Initial

concentration of metal ions was maintained at 100ppm in each experiment. Sodium formate (200ppm) was used as the hole scavenger for all the experiment. After the reaction, metal deposited solid catalyst was separated by centrifuge. Metal ion concentration in the solution after and before reaction was estimated by AAS.

## Result and Discussion

Materials calcined at 500°C shows low crystallinity of anatase phase. The crystallinity on the materials increases with the increasing calcination temperature. It is observed that pure titania completely transform to rutile phase even at 700°C calcination. However, the other four binary oxide materials show the presence of clear anatase phase after calcination at 700°C. This justifies the phase stabilization effect of silica and zirconia even at low concentrations. Broad peak of 101 reflection conforms the nanocrystalline nature of the anatase phase. However, with the increase in the calcination temperature the peak became sharper indicating the increase in the crystallite size. Peak sharpening is clearly marked incase of pure titania with the increase in calcination temperature. Crystallite size calculated from the XRD line broadening technique is tabulated in Table-1 which also supports our argument.

**Table-1: Textural properties of synthesized TiO<sub>2</sub> and binary oxides.**

Sample code	Titania (Wt%)	Silica (wt%)	Zirconia (wt%)	BET Surface area (m <sup>2</sup> /g)			CS (nm)
				500°C	700°C	900°C	
TiO <sub>2</sub>	100	-	-	91	58	43	14.8
TiSi-10	90	10	-	126	106	85	10.2
TiSi-20	80	20	-	138	108	88	9.98
TiZr-10	90	-	10	105	89	76	12.6
TiZr-20	80	-	20	96	84	71	15.3

SEM micrographs of all the materials calcined at 500°C temperature are presented in Fig-1. At 500°C calcination all the materials maintain spherical shape with average particle diameter within 0.8-1.2µm. Increasing silica content in the material favored the smaller particle formation as observed in Fig-5. Unlike silica mixed samples zirconia mixed samples shows mostly uniform particle size. The average particle size increases to 1100nm due to zirconia addition. All the materials show maximum BET surface area at 500°C calcination. Subsequently the surface area decreases (Table-1) with the increasing calcination temperature up to 700°C. However a remarkable decrease is noticed in case of pure titania. Probably the phase transformation to rutile also decreases the surface area through particle aggregation forming larger crystallite size as observed in the Table-1. Moreover, the decrease in surface area is less in case of silica and zirconia mixed titania samples. Therefore, the presence of

silica or zirconia not only helps in anatase phase stabilization but also controls the sharp decrease in surface area by restricting the particle aggregation.

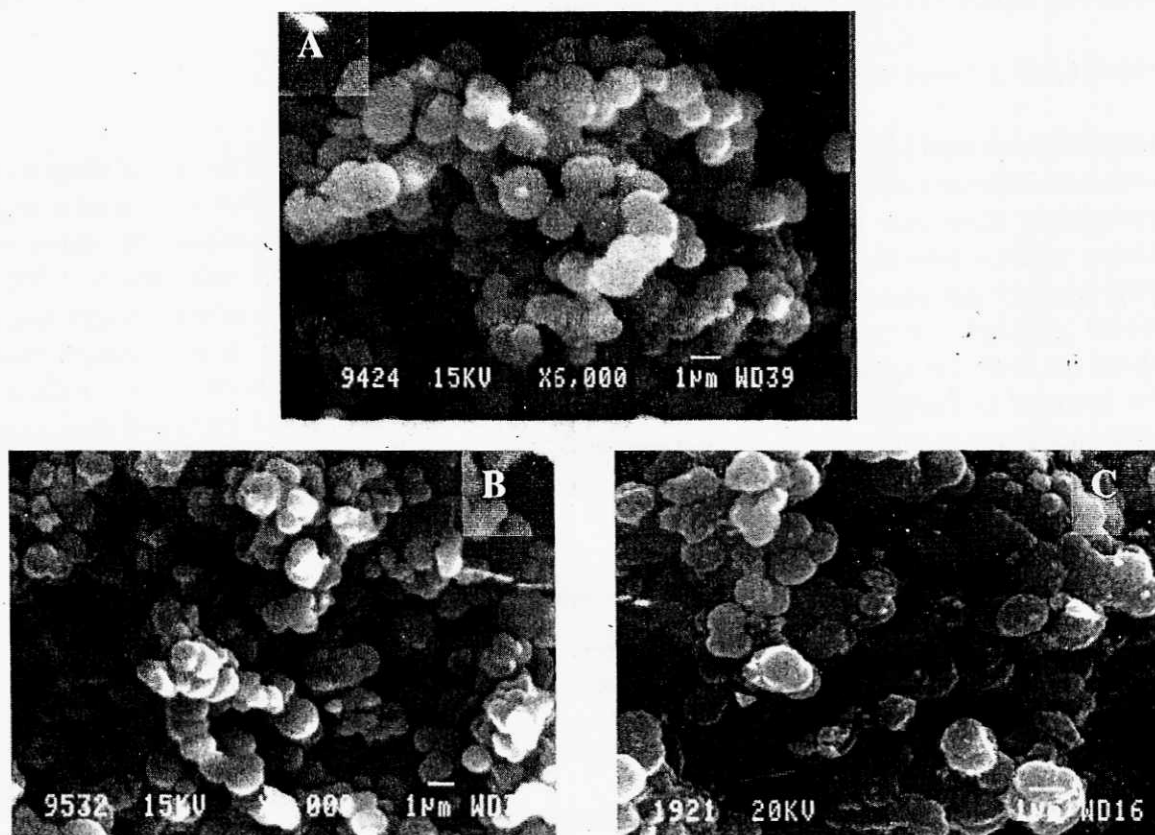


Fig-1:SEM micrographs of (A) Ti, (B) TiSi-10 and (C) TiZr-10 after calcination at 500°C.

#### *Nitrogen doping*

UV-vis absorption spectroscopy had been carried out to investigate the optical property of various synthesized materials. There is a clear red shift in the absorption band of all the materials (Fig-8) prepared in presence of CETAB in comparison to the  $\text{TiO}_2$  prepared without CETAB. Even with the silica and zirconia mixed materials the absorption band is extended to the visible range. Visible light absorption is highest in case of TiZr-10 sample. Since the  $\text{TiO}_2$  prepared without CETAB absorbs only UV light, the visible light absorption in case of other samples must originate from doping of nitrogen or carbon from CETAB into the materials during heat treatment. Therefore, it is understood that the presence of CETAB also favours the nonmetal doping of the samples and hence the enhanced visible light absorption.

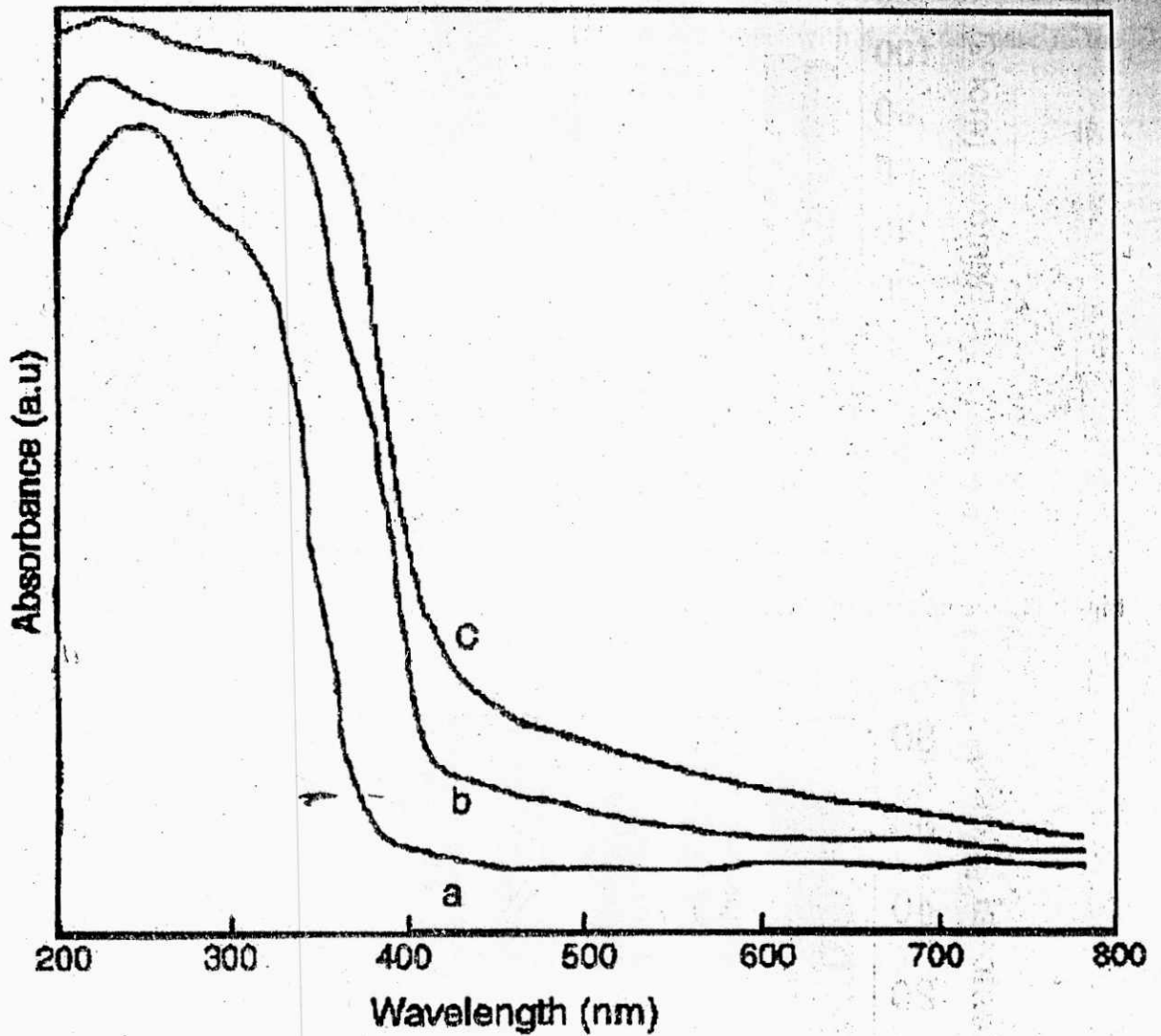


Fig-2: Diffuse reflectance spectra of (a) TiO<sub>2</sub> with out CETAB, (b) Ti and (c) TiZr-10.

#### *Photocatalytic activity*

It is well observed that without any hole scavenger the efficiency of photocatalytic metal removal is quite low for both the metal ions within 30 minutes of reaction. However, addition of hole scavenger increases the activity many folds and hence complete removal of Se and Cu was possible in 30 minutes of reaction.

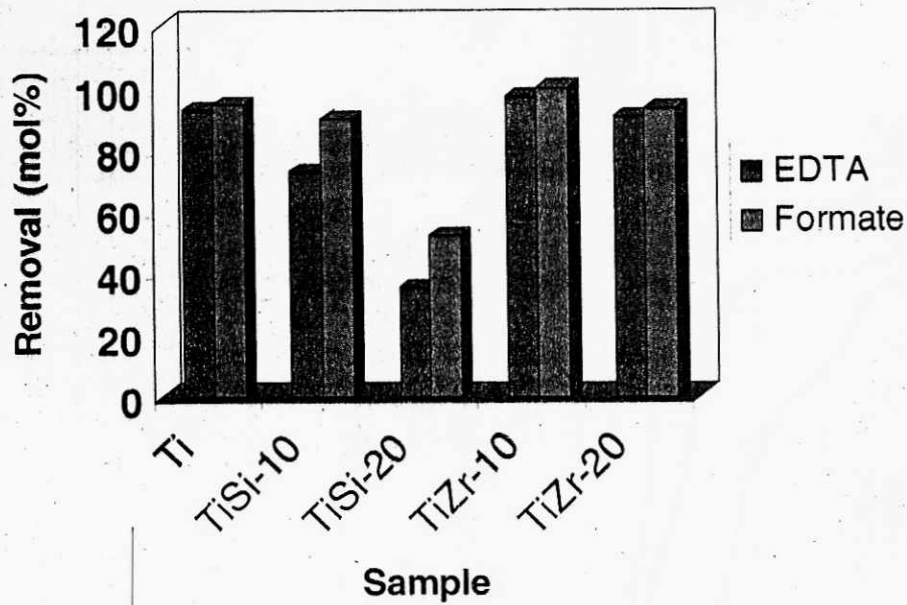


Fig-3: Photocatalytic removal of selenium in presence of EDTA and formate.

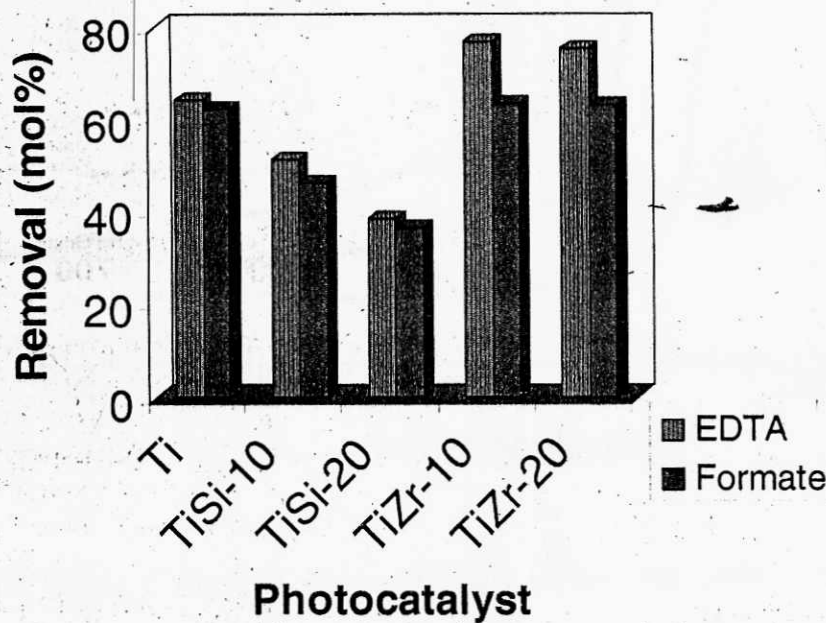


Fig-4: Photocatalytic removal of copper in presence of EDTA and formate.

Among all the organic hole scavengers used, sodium formate is found to be the most active one for selenium whereas for copper EDTA is the most suitable one. Probably EDTA attached with titania surface helps in the complex formation with copper ions and hence the higher photoreduction. Reaction pH also plays an important role in the efficiency of the metal removal as observed in the Fig-5. At lower pH selenium removal is higher whereas copper removal is highest at higher pH. It is understood that at pH within 1-3 copper has a tendency to remain in the soluble form. However selenium metal is not soluble in that pH. So pH

adjustment can help in the separation of pure selenium and copper from the mixed solution. Above all synthesized materials are found to be efficient catalyst for visible light reaction. The same catalyst is found to be reusable at least for 5-6 times with 4-5% decrease in the activity.

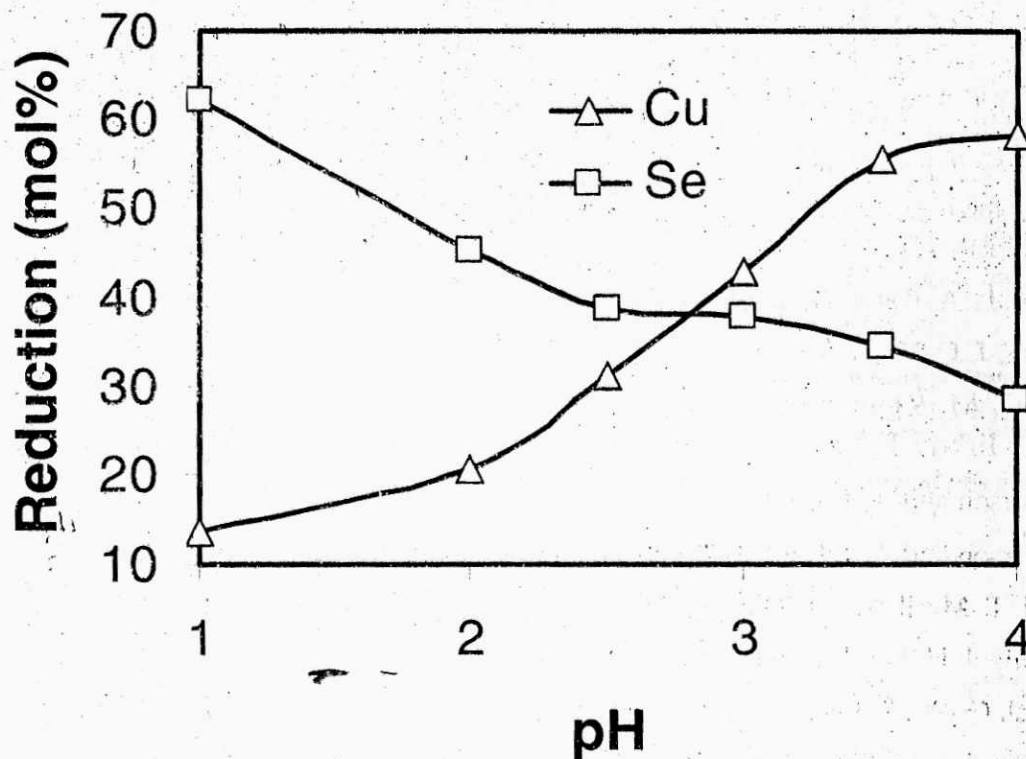


Fig-5: Effect of pH on the selenium and copper photoreduction.

### Conclusion

Spherical and uniform sized binary oxide materials were synthesized in presence of CETAB through sol-gel method. Synthesized materials showed visible light absorption and hence can be used as photocatalyst for solar light reaction. Catalytic removal of selenium and copper depends on the hole scavenger and pH of the solution. EDTA is found to be effective for copper removal whereas formate favors the high selenium removal in a similar reaction condition. Similarly low pH favors the high selenium removal. Copper removal increases with the increase in pH. So copper and selenium can be separated from a mixture solution only through pH adjustment.

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