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# CuO-NiO-TiO<sub>2</sub> bimetallic nanocomposites for catalytic applications

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Keywords: Heterogenous catalyst Oxidation of amine Reduction of nitrobenzene Cu-Ni-TiO2	CuO-NiO-TiO <sub>2</sub> nanocomposites with of 0.01–5.0 wt.% of Cu:Ni (1:1) supported on TiO <sub>2</sub> were prepared by a decomposition method. The catalysts structure and chemical composition were studied by means of XRD, SEM, EDX, TEM, FT-IR, UV–DRS, BET-analysis and compared for direct sunlight photo-degradation of methylene blue with commercial P25 catalyst. These studies revealed that the catalyst efficiency solely depends on the percentage of Cu-Ni dopants. The catalyst with low metal dopants displayed better photocatalytic activity. The optimum doping concentration for photo-degradation was 0.05 wt.%. The nanocomposite with higher metal loading (5.0 wt.%) was effectively employed as heterogenous catalyst for selective reduction of nitro benzene to aniline using sodium borohydride and for air oxidation of tertiary amine functionality to a tertiary amide.

#### 1. Introduction

Nanosized titanium dioxide (TiO2) based materials are widely investigated in recent decades for their photocatalytic and other applications. Being a wide band-gap semiconductor TiO2 has its limitations in harvesting natural light. Numerous studies have been undertaken to enhance its photocatalytic activity. These include incorporating metal/s or non-metal/s in the catalyst or on the surface of the catalyst [1-5]. In spite of several advantages, non-metal doping shows a major drawback of decreasing dopant concentration during the annealing process, which results in the decreased photocatalytic activity of these materials [6]. Transition metals Cu, Co, Ni, Cr, Mn, Mo, Nb, V, Fe are effective in improving the photoactivity of  $TiO_2$  [7–14]. Metal dopants widen the light absorption range, increase the redox potential of the photo-generated radicals and increase the quantum efficiency by inhibiting photo-generated electron-hole recombination. Transition metals introduce new energy levels below the conduction band in TiO<sub>2</sub> shifting the light absorption region from UV to visible light. The shift occurs due to the charge-transfer transition between the d-electrons of the transition metals and the valence band of TiO<sub>2</sub>.

The transition metal dopants mainly exist in their oxide clusters rather than metal atoms within the surface of Ti cation matrices, in contrast to non-metal dopants, which exist as isolated atoms within the surface. This is attributed to the difference in crystal nucleation behavior between dopants and  $TiO_2$  [15].

synergistic effect of the metals was confirmed by comparing the catalytic activity with individual metal dopings.

The optimum concentration of dopant metal ion plays a significant role in the catalytic activity of the host metal oxide. A remarkable shift in absorption wavelength is observed for M-TiO<sub>2</sub> with low doping concentration, while the recombination of photo-generated charge carriers is commonly observed at higher metal dopant concentrations [2,16]. The literature study demonstrates that, among the metal ion dopants of the first transition series, Cu, Mn, Fe, ions can trap both electrons and holes, thus avoiding their recombination and hence contributing for better activity, whereas Cr, Co, Ni, ions can trap only one type of charge carriers [17].

Coupling of narrow band-gap semiconductors with  $TiO_2$  has been proposed for potential application to induce an oxidation process under visible light. In this context, CuO with a bandgap of 1.4 eV having a high absorption coefficient can be effectively coupled with  $TiO_2$ . CuO- $TiO_2$ nanocomposites represent one of the most promising systems for the synergistic combination. This combination has demonstrated to be stable with improved photocatalytic properties [18,19]. Cu is found to be more effective with low dopant concentration (< 1%) for photocatalytic applications. For example, copper in 0.06 M % is reported to be optimum for the degradation of rhodamine B [20], 0.1 wt.% of CuO was proved to be the best for the degradation of methylene blue (MB) [21] and

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optimum loading of 0.5 M % copper ion in sulfated  $TiO_2$  for phenol oxidation [22]. Other than photo-degradation of toxic chemicals, it has found applications in hydrogen generation [23–26], antimicrobial activity [27], magnetism [28,29] and other studies [30–32].

Doping of NiO in the TiO<sub>2</sub> system has been studied for several properties, including photocatalytic reactions such as dye degradation and hydrogen production, since low valance Ni<sup>2+</sup> doping is generally considered to improve the photoactivity of titania [33–35]. For example, 0.5 wt.% of Ni-doped TiO<sub>2</sub> shows better photocatalytic degradation of MB [36]. In another study 1.5 M % Ni was found to be optimum for methyl orange degradation [37]. Room temperature ferromagnetism is also displayed by Ni doped TiO<sub>2</sub> [38].

Considerable effects are shown in improving the properties of  $TiO_2$  by copper and nickel doping. Comparative studies of copper and nickel doping reveal that Ni-TiO<sub>2</sub> display slightly better photocatalytic efficiency and also a higher shift in visible light absorption than that of Cu-TiO<sub>2</sub> [8,39], though Cu-TiO<sub>2</sub> individually exhibit higher photo-activity and a better shift in wavelength than the undoped material.

Recently co-doping systems with complementary dopants are studied and found to be rewarding. Various combinations with metal-metal [40–43], metal-non-metal [44,45], or of two non-metals [46–49] are studied in this regard. Such metal composites are more effective due to the synergistic effect of dopants which can lead to increased visible light absorption by narrowing band-gap and also acting as electron-hole trapping sites, thus decreasing the rate of recombination. Nanocomposites of such systems are reported to improve the charge separation effectively.

Among the metal combinations studied, Cu-Ni doping to  $TiO_2$  is gaining interest in recent years in the photocatalysis field due to their relative scavenging effect on photo-generated charge carriers.

Bimetallic Ni-Cu-TiO<sub>2</sub> was first reported by Gao et al. in 2004 [40] for the reduction of nitrate. They employed various mono-metallic, Cu-TiO<sub>2</sub>, Ni-TiO<sub>2</sub>, Pd-TiO<sub>2</sub> and Pt-TiO<sub>2</sub>, and bi-metallic, Ni-Cu-TiO<sub>2</sub>, Pd-Cu-TiO<sub>2</sub>, Pt-Cu-TiO<sub>2</sub>, combinations for this reaction. Among all these catalyst systems studied, Ni-Cu-TiO<sub>2</sub> was found to show the maximum photocatalytic activity. The promoting effect of bimetal was attributed by the authors to the more effective separation of photo-generated spatial charges in tiny TiO<sub>2</sub> semiconductor particles. For tiny metal-modified TiO<sub>2</sub> semiconductor particles, supported bimetal Cu and Ni behaves as short-circuited photoelectron chemical cell, where both cathodic and anodic reactions can occur at the same particle.

In the year 2009, Li et al. described *in situ* preparation of Ni-Cu/TiO<sub>2</sub> bimetallic catalysts [50]. Later this system was studied for dye degradation, solar hydrogen production from water, as an electrode for lithium-ion batteries and reduction studies [51–60]. It is also claimed that Ni in a combined system of Cu-Ni-TiO<sub>2</sub> acts as a supportive metal dopant to promote Cu-reactivity, to further enhance its properties. The enhancement was proposed to be due to the strong interaction between Ni and TiO<sub>2</sub>, which reduces the concentration of Ni at the catalyst surface and thus serves as an anchoring site for Cu on TiO<sub>2</sub> to enhance its stability [57].

In most of the studies, the preparation involved the use of commercial Degussa P25 as a support material. In continuation to our work on TiO<sub>2</sub> [61–64], we thought that co-doping TiO<sub>2</sub> with Cu and Ni might have a good potential to develop a catalytic system which not only can be used for photocatalytic studies but also could be used for other applications. As diverse observations regarding the optimum percentage of metal doping for effective photocatalytic activity were reported, we planned to vary the percentage of metal doping systematically from 0.01–5 wt.% with both the metals in equal molar proportion. In order to get uniform distribution different percentage of precursors (1:1) were mixed with titanium precursor and then gelled to form powders which were further calcined at 500 °C as shown in Scheme 1.

### 2. Experimental

## 2.1. Materials

Titanium tetraisopropoxide (TIP) (purity, 97 %),  $Ti(OC_3H_7)_4$ ,  $Cu_2(CH_3COO)_4$ ,  $Ni(CH_3COO)_2.4H_2O$ , were purchased from Spectrochem and MB from Merck. Isopropyl alcohol (IPA), supplied by Loba Chemicals, was used as a solvent medium.

## 2.2. Preparation of CuO-NiO-TiO<sub>2</sub> nanoparticles (Series B)

A mixture of copper acetate and nickel acetate in a 1:1 M ratio was dissolved in isopropyl alcohol by heating to 60 °C, and this solution was then added dropwise to a solution of titanium isopropoxide in isopropyl alcohol with constant stirring. A colloidal gel with a greenish tinge was obtained. The intensity of the green color was found to deepen with increased metal concentration. The gel was heated to 100 °C to get a precursor powder which was then calcined at 500 °C for 3 h. TiO<sub>2</sub> nano powders with colors ranging from pale green to dark green were obtained (SI, Fig. \$1). The samples were labeled as series B (Table 1). Similar procedure was followed for preparing of CuO-TiO<sub>2</sub> and NiO-TiO<sub>2</sub> samples.

## 2.3. Characterization techniques

The crystal phase composition and crystallite size of TiO<sub>2</sub> nanoparticles were recorded using Bruker D8 ADVANCE X-ray diffractometer with Cu K $\alpha$  radiation (1.5406 Å) in the 2 $\theta$  scan range of 10–80°. Morphology of the sample was investigated by using Zeiss Avo18 scanning electron microscopy (SEM) along with Energy-dispersive X-ray Spectroscopy (EDX), which was further confirmed by transmission electron microscopy (TEM), which is also used to investigate the particle sizes of the sample. TEM images equipped with selected area electron diffraction (TEM/SAED) were obtained by using TECHNAI F30 and

Table 1
Sample labeling

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(Cu + Ni)/Ti ratios (%)	Method 1			
0.01	B1			
0.05	B2			
0.10	B3			
0.50	B4			
1.00	B5			
2.00	B6			
5.00	B7			



Scheme 1. The synthetic scheme of Cu-Ni/TiO<sub>2</sub>.

PHILIPS CM 200 field emission transmission electron microscope operating at 200 kV.

Nitrogen adsorption/desorption isotherms and surface area ( $S_{BET}$ ) were obtained with a surface area and porosity analyzer (Micromeritics ASAP 2020 V3..00 H) and Quantachrome ASiQwin Instruments (ASIQC0100-4), at the temperature of liquid nitrogen. Before the analysis, samples were degassed at 150–300 °C for 0.5–12 h with a continuous flow of nitrogen gas.

Band-gap energy,  $E_g$ , and absorption edges of all the samples were determined using UV–vis diffuse reflectance spectroscopy (UV-DRS) (Shimadzu UV-2450). BaSO<sub>4</sub> was used as a background standard. Spectra were recorded at room temperature in the wavelength range of 200–800 nm. The IR studies were carried out on a Shimadzu IR Prestige-21 FTIR in the range of 4000–400 cm<sup>-1</sup>. Thin-layer chromatography (TLC) was carried out on silica gel 60 F254 aluminum plates purchased from Merck. <sup>1</sup>H NMR (400 MHz) spectra were recorded on a Brucker AVANCE 400 instrument. Chemical shifts are expressed in  $\delta$  relative to tetramethylsilane (TMS) which is expressed in ppm.

#### 2.4. Photocatalytic activity testing

The photocatalytic activity was assessed by monitoring the photodecomposition of MB. For comparison, commercial Degussa P25 was used as a reference material.

In a typical degradation experiment, 10 mg of catalyst was suspended in 25 mL of the aqueous dye stock solutions (0.010 g/L), prepared in deionized water, and were allowed to equilibrate for a given time (usually 15–30 min) in the dark before irradiation. The solution was then exposed to sunlight for 120 min between 10:00 am to 12:00 noon with intermittent swirling. Following the exposure of light at specified intervals of time, the decolorization of dye was recorded at its absorption maximum (650 nm), as a function of time against appropriate blanks.

The experiment was repeated three times for all samples, and the average of three readings was considered. The extent of photodegradation of dye was calculated using a calibrated relationship between the measured absorbance and concentration. The recyclability studies were also done for three cycles. The kinetic studies of the same were carried out from which the rate of dye degradation was determined.

## 2.5. Reduction of aromatic nitro compound

The catalytic performance of the sample with the highest CuO-NiO dopant (B7, 5 wt.%) and corresponding 5 wt.% CuO-TiO<sub>2</sub>, NiO-TiO<sub>2</sub>, and Degussa P25 samples was tested for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of sodium borohydride as a reducing agent. In a typical catalytic test, 100 mg catalyst was first sonicated in 10 mL ethanol. To that, 100 mg of the substrate (4-NP) was added, followed by 50 mg NaBH<sub>4</sub>. The yellow color of 4-NP was seen disappearing and changing to black. The progress of the reaction was monitored by TLC, and the formation of 4-AP was confirmed by proton NMR spectroscopy. The catalytic activity was further tested for 3 consecutive cycles.

#### 2.6. Oxidation of tertiary amine

The highest CuO-NiO dopant (B-7, 5 wt.%) and corresponding 5 wt. % CuO-TiO<sub>2</sub>, NiO-TiO<sub>2</sub> and undoped TiO<sub>2</sub> samples were tested for the oxidation of *N*-phenyl-tetrahydroisoquinoline (THIQ) in open air using dioxane as solvent at 50 °C. In a typical experiment a mixture of 100 mg of *N*-phenyl THIQ, 60 mg of catalyst was refluxed in 2 mL of dioxane for 3 days. The progress of the reaction was monitored by TLC, and the formation of the product was confirmed by proton NMR spectroscopy. The catalytic activity was further tested for 3 consecutive cycles.

## 3. Results and discussion

### 3.1. IR spectroscopy

The IR spectra of all calcined  $TiO_2$  samples show the presence of surface hydroxyl groups and adsorbed water (Fig. 1) The characteristic stretching frequency of the –OH group can be seen between 3000-3500 cm<sup>-1</sup> and the corresponding bending vibrations at 1600 cm<sup>-1</sup>. The metal oxide bands seen at 500 cm<sup>-1</sup> are of Ti-O stretching. No bands are seen corresponding to the isopropyl group and also the acetate group suggesting, complete removal of the organic part.

IR spectra of precursor not calcined samples displayed distinct bands at  $3000-3500 \text{ cm}^{-1}$  and  $\sim 1600 \text{ cm}^{-1}$  of the metal hydroxide and water (Fig. 2). In addition to this, the bands at around  $1100-1600 \text{ cm}^{-1}$  were seen, clearly indicating the presence of organic functionality, i.e., an isopropyl group and an acetate group.

## 3.2. Optical studies

The absorption spectra samples are shown in Fig. 3. Significant absorption peaks in the wavelength region shorter than 400 nm can be assigned to the intrinsic band-gap of TiO<sub>2</sub>, while enhanced absorption in the visible region extending up to 800 nm can be attributed to the presence of CuO-NiO on TiO<sub>2</sub> matrix. It is observed that the red shift in absorption wavelength goes on increasing with the increase in dopant concentration, which suggests that the shift is clearly due to the presence of CuO-NiO in TiO<sub>2</sub>.

An additional peak is seen in this region from 550-800 nm for all the samples, which correlates with the corresponding peak for individual CuO/NiO doping, as reported in the literature. These weak absorption peaks can be attributed to the d-d transitions of the dopant ions in the crystalline environment of TiO<sub>2</sub> [31]. The intensity of this peak is observed to increase with increasing dopant concentration, except the sample with 0.01 wt.%, which display slightly higher intensity compared to samples with 0.05 and 0.1 wt.%. A considerable increase in the visible light absorption is attributed to the creation of new energy levels in the band-gap of TiO<sub>2</sub> and thus causes electronic transitions between the valence band and these intra-band energy levels [28].

The values of  $\lambda_{max}$ , absorption wavelength for all samples are summarized in Table 2. The minimum wavelength required to promote an electron depends upon the band-gap energy ( $E_g$ , eV) of the photocatalyst. The band-gap energy can be estimated by determining the absorption wavelength ( $\lambda_{max}$ , nm) of each UV–vis absorbance spectrum by the known relationship between the absorption band edge and the band-gap -  $E_g = 1239.8 / \lambda_{max}$ , where,  $E_g$  is the band-gap (eV), and  $\lambda$  (nm) is the wavelength of the absorption edges in the spectrum. The band-gap values are found to be in the range of 2.7–3.2 eV.

#### 3.3. Structural characterization

Analysis of phase composition, crystalline nature, and crystallite size of the prepared catalysts was carried out using X-ray powder diffraction



Fig. 1. IR spectra of calcined samples.



Fig. 2. IR spectra of precursor samples (uncalcined).



Fig. 3. UV-DRS spectra of calcined samples.

technique. Fig. 4 presents the powder XRD pattern of calcined TiO<sub>2</sub> samples. Sharp and well-defined peaks indicate the highly crystalline nature of these catalysts. The peak positions and their relative intensities for all the samples suggest the presence of anatase as a major phase, as indicated by the consistent powder diffraction patterns (JCPDS card # 21-1272), with the main peak at  $25.27^{\circ}$  corresponding to the (101) plane. With the increase in metal concentration, two small peaks at 32.8° and 35.6° (marked with \*) are observed, corresponding to (110) and (111) respective planes of CuO monoclinic crystalline phase (ICDD file no. 80- 1916). No such peaks due to NiO crystalline phase are observed, though both the dopants are in equal concentration. This could be due to the higher ionic radius of  $Cu^{2+}$  (0.87 Å) than  $Ti^{4+}$  (0.74 Å) which causes a slight distortion of the perfect lattice of  $TiO_2$  when doped, while Ni<sup>2+</sup> being of the similar radius (0.72 Å) do not cause such a distortion [8,29]. These results are also supported by the literature reports for NiO-TiO<sub>2</sub>, which shows the absence of peaks due to Ni species, even at 12 wt.% of Ni doping [33], whereas for CuO-TiO<sub>2</sub>, CuO peaks were seen even for 2% Cu doping [30]. The absence of any of the segregate crystalline phases for various CuO or NiO species suggests the presence of highly dispersed metal oxide particles onto the TiO<sub>2</sub> surface.

The incorporation of CuO-NiO into TiO<sub>2</sub> lattice was further confirmed by studying the details of the intensity of peaks (004) and (200). Incorporation of Cu into TiO<sub>2</sub> is reported to cause preferential growth along (004) direction, thus increasing the intensity of (004) peak and a corresponding decrease in (200) peak, which in turn results in a decreased intensity ratio of  $I_{101}/I_{004}$  and  $I_{101}/I_{200}\text{,}$  with increasing Cu concentration [28]. Such variation of intensity ratio is observed, which

Table 2

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shows an initial increase from 0.1 to 1 wt.% of metal and later remains constant at a higher metal concentration indicating the lattice incorporation of metal species in this series. Slight fluctuations from the observed trend are seen for low metal concentrations (< 1 wt.%), which may be attributed to the combined effect of CuO-NiO species.

The average crystallite size was determined from (101) diffraction peak (the most predominant highest intensity peak), according to the Debye-Scherrer equation –  $D = K\lambda / \beta \cos \theta$ , where, K is the Scherrer constant,  $\lambda$  is the X-ray wavelength,  $\beta$  is the peak width at half maximum and  $\theta$  is the Bragg's diffraction angle. It is found to be in the range of 11-14 nm (Table 2). The synthesized samples were found to be smaller in size as compared to Degussa P25 (25 nm). A linear decrease in size with increasing metal content is observed. The fluctuations observed in sizes can be considered as the effect of the lattice strain produced during synthesis [38]. Strain and the number of dislocations are the influencing factors for the crystallite size of the sample. The lesser value of strain and dislocation density enhances free carrier mobility in the host lattice. The strain is inversely proportional to the crystallite size. The broadening due to lattice strain in the material is represented by the relationship -  $\varepsilon$  $=\beta$  / 4 tan  $\theta$ , where,  $\varepsilon$  is the strain in the material. Linear increase in strain is observed from 0.0113 to 0.0121 with increasing metal percentage (Table 2). The increasing value of strain indicates the increasing degree of imperfections with a corresponding increase in Cu-Ni % into TiO<sub>2</sub> lattice. The linear decrease in size or increase in strain suggests the incorporation of metal species into the TiO<sub>2</sub> lattice.

# 3.4. Surface properties

The typical plot of N2 adsorption-desorption isotherm and corresponding pore size distribution curves (inset) of the catalysts are shown in Fig. 5. The isotherm curves can be classified as typical of a mesoporous material of the type IV associated with capillary condensation taking place, as per the IUPAC classification. The hysteresis loops in the BJH adsorption analysis are observed to be of H2-type for samples B1-B4, with the leveling off the loop at saturation vapor pressure  $(P = P_0)$ for the sample B1 (0.01 wt.% CuO-NiO). While with the increasing metal % (B2, B3, B4), the loop does not level off even at saturation vapor pressure  $(P = P_0)$ , which is a characteristic of the mesoporous materials arising out of agglomeration of nanoparticles, with slit-shaped pores.



Fig. 4. XRD plots for calcined samples.

Summary of the properties of CuO-NiO-TiO <sub>2</sub> nanoparticles.								
Sample	Cryst. size (nm)	Lattice strain	Peak intensities $I_{101}/I_{004}$	ratio I <sub>101</sub> /I <sub>200</sub>	BJH surf. area (m <sup>2</sup> /g)	Pore vol. (cc/g)	$\lambda_{max}$ (nm)	Rate const. k (min $^{-1}$ )
B1	14.65	0.0113	6.905	4.302	43.50	0.059	392.2	0.0229
B2	14.38	0.0115	6.918	4.255	60.00	0.096	387.9	0.0296
B3	14.48	0.0114	3.601	3.977	93.95	0.156	395.6	0.0197
B4	12.93	0.0128	5.844	3.946	101.93	0.177	397.2	0.0176
B5	11.88	0.0139	6.181	4.413	70.70	0.097	427.9	0.0155
B6	11.15	0.0148	6.435	4.530	90.58	0.126	453.9	0.0174
B7	13.73	0.0121	6.357	3.831	72.23	0.191	464.2	0.0156
P25	25.00	_	_	_	56.00	0.250	370.7	0.0179



Fig. 5. Nitrogen adsorption-desorption isotherms and pore size distribution (inset) of CuO-NiO-TiO<sub>2</sub> nanoparticles.

The mesoporous nature of these samples is also confirmed by the pore size distribution curve extended up to 40 nm. With further increase in metal %, for sample B5 (1 wt.%), H3-type hysteresis loop with the absence of plateau at high relative pressure and starting at a slightly higher value ( $\sim 0.5 \text{ P/P}_0$ ) is obtained, designating the non-rigid nature of the mesopores, which is also supported from the broad pore size distribution. For the samples, B6 and B7, the intermediate of H2- and H3type hysteresis loops, with distinctly observed pronounced plateau region for sample H6, indicates the presence of ink bottle-shaped pores [65] and is reflected in their poor photocatalytic activity. The unusual shape of the pore size distribution curve is seen in these samples. The shape of isotherm and pores size distribution curves shows a direct impact on the photocatalytic activity. The BJH surface area and pore volume of these samples are given in Table 2. It can be seen that the surface area goes on increasing with metal concentration up to 0.5 wt.%, whereas it becomes random after that. A similar linear increasing trend is also observed for pore volume, which decreases at 1 wt.% metal insertion and again increases up to 5 wt.%.

## 3.5. Morphological studies

The surface morphology of these nanoparticles is studied by SEM analysis. SEM micrographs and corresponding EDX images are shown in Fig. 6. Fine granular and densely packed nanoparticles of spherical shape are seen in almost all the samples. Particles are seen to be uniformly distributed and are of similar morphology for varying metal concentrations. Slight aggregation of particles is also observed with a lesser degree of agglomeration. Slightly higher agglomeration is observed among the particles of the sample with 5 wt.% Cu-Ni loading.

The EDX images further confirmed the chemical composition of the prepared nanoparticles. From these images, Ti and O are observed to be major constituents with a slight presence of C, which may be due to the supporting material used. Traces of Cu and Ni species are also seen in all the samples signifying the incorporation of these species into the  $TiO_2$  matrix.

The samples with lower metal loading (0.01-0.1 wt.%), displaying higher photo-degradation rates, were further investigated with TEM analysis. TEM micrographs (Fig. 7) displayed well distributed tiny nanoparticles of nearly spherical shape. Slight agglomeration is observed for samples with 0.01 wt.% metal loading. The average particle sizes of these catalysts were obtained to be in the range of 13–14 nm. These values are consistent with the XRD results.

The corresponding SAED images (inset of Fig. 7) are used to study the polycrystalline nature of these samples, which shows concentric ring

patterns of small spots. The observed patterns are consistent with Bragg's reflections observed in the XRD pattern. The interplanar spacings could be indexed according to anatase  $TiO_2$  as (101), (004), (200), (211), (204), (220), and (215), matching with the XRD results (JCPDF no. 21-1272).

## 3.6. Photocatalytic activity

The photocatalytic activity of the samples was studied by the degradation of MB, which is the most studied azo dye for comparing catalytic activity. Fig. 8 displays the comparative catalytic activity under natural sunlight irradiation in comparison with Degussa P25 as a standard.

It can be seen that the samples B1, B2 and B3 display better photocatalytic activity compared to Degussa. The highest degradation rate is observed for sample B2 (0.05 wt.% Cu-Ni). Thus, we can say that the catalysts with lower metal insertion (0.01-0.1 wt.% Cu-Ni) are a suitable candidate for the degradation of MB. These samples (B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub>) though have bigger crystallite sizes with lesser absorption wavelengths values are more photo-active than the others. The random values of surface area and pore volume could be related to photo-degradation results. Hence the observed photocatalytic activity can be solely attributed to the low Cu-Ni dopant concentration of these catalysts. Earlier, we had reported complete photo-degradation of MB using nano TiO<sub>2</sub> and also LC–MS studies of the degradation process to show that MB does get demineralized [52,53].

It is observed that the bimetallic dopant species, CuO-NiO, efficiently improves the properties of host TiO<sub>2</sub> material. The greater shift in absorption wavelength and decreasing crystallite sizes are seen with increasing metal concentration. The decrease in degradation rate with increasing metal concentration can be accounted for surface blocking of active sites of the catalyst at higher metal concentration. Also, Cu/Ni at higher concentration may themselves act as a recombination center, thus reducing the photocatalytic efficiency of the catalyst [32].

A plot of ln ( $C_0/C_t$ ) versus time (Fig. 9) represents a straight line which indicates the photocatalytic degradation follows pseudo-first-order kinetics. The rate constants derived from the plot are given in Table 2. The rate of degradation is observed to increase initially with increasing concentration (0.01 to 0.05 wt.%) and further goes on decreasing with increasing metal concentration.

Recyclability studies were done for three cycles after separating the catalyst by centrifugation. All the samples could be reused for degradation with negligible loss in activity (Fig. 10).

The leaching of the catalyst was studied using ICP-MS. After the



Fig. 6. SEM micrographs and corresponding EDX images of CuO-NiO-TiO<sub>2</sub> nanoparticles.



Fig. 7. TEM micrographs and corresponding SAED images (inset) of CuO-NiO-TiO<sub>2</sub> nanoparticles with lower metal % loading.

declorisation of MB solution the filtrate was subjected ICP-MS studies, where, it showed to contain Cu 10.641 ppb and Ni 80.631 ppb amount. This study showed that, though the leaching is negligible there is some trace quantity of catalyst lost during the recycling.

Further to check the synergistic effect both 0.05 wt.% CuO-TiO<sub>2</sub> and 0.05 wt.% NiO-TiO<sub>2</sub> were prepared in a similar way and the tested for photo-degradation studies (Fig. 11). These results clearly showed that there is synergy between the metals resulting in increase in



Fig. 8. Sunlight degradation plots for MB.



Fig. 9. Kinetic studies MB degradation.



Fig. 10. Recyclability studies of the catalyst B2 for photodegradation.

photocatalytic activity.

## 3.7. Plausible mechanistic pathway of photocatalysis

On exposure to sun light electron-hole pairs are formed on the individual surfaces of NiO, CuO and TiO<sub>2</sub>. The generated electron and holes can either recombine or involve in a photocatalysis reaction.  $TiO_2$ is a n-type semiconductor while NiO and CuO are p-type semiconductors. All the three semiconductor surfaces are in contact resulting



Fig. 11. Sunlight degradation of MB by 0.05 wt.% Cu-Ni-TiO<sub>2</sub>, Cu-TiO<sub>2</sub>, Ni-TiO<sub>2</sub>.

in cascade nano heterojunctions which facilitate electron and hole transfers (Fig. 12). This reduces the probability of recombination of the charges making the catalyst more effective for photo-degradation of dyes.

# 3.8. Catalytic reduction

The sample with higher metal loading (B7, 5 wt.%) was studied for the sodium borohydride mediated reduction reaction. 4-Nitrophenol (4-NP) is an industrial pollutant discharged by pesticide, herbicide, insecticide, and dve industries [66]. Hence, its reduction to 4-aminophenol (4-AP) which gets degraded faster, is very important in the effluent treatment strategies. Also, 4-AP is an industrially important raw material in many industries. Hence 4-NP was chosen as a substrate for the reductions studies. The efficient conversion of 4-NP to 4-AP was observed in 5 min using sodium borohydride (Scheme 2). The recyclability was studied up to 3 cycles, with an increase in reduction time for a subsequent reduction (Table 3). Further reductions were too slow to be useful. The reduction failed to take place with Degussa P25. In the case of 5 wt.% CuO-TiO<sub>2</sub> the reduction was complete after 30 min while in case of 5 wt.% NiO-TiO2 it took 120 min for completion of the reaction. During the reduction the colour of the catalyst was found to change to black indicating reduction of the metal oxides by NaBH<sub>4</sub>. Thus the active catalyst in this case is Cu-Ni/TiO2 and not the CuO-NiO/TiO2. The transformation was found to be completely selective with no trace of intermediate reduction products. Moreover the reduction was found to



Fig. 12. Schematic band diagram showing the facilitation of charge transportation processes for the synergistic effect of the metals for the photocatalysis reaction.



Scheme 2. Reduction of 4-NP to 4-AP.

 Table 3

 Recyclability data for nitro reduction.

Cycle no.	Time (min)
1	05
2	30
3	90

be very rapid taking only five minutes and at ambient conditions. The undoped  $\text{TiO}_2$  failed to reduce 4-NP suggesting that the metals are vital for this reduction process. However, the reusability of the catalyst was limited due to leaching of metals which could be observed from the fading of the color of the catalyst.

### 3.9. Plausible mechanistic pathway of nitro reduction

Sodium borohydride reduces the CuO and NiO to its corresponding metals which form a Cu-Ni alloy on the surface of  $TiO_2$  which act as a supporting matter. The hydrogen liberated by reaction of sodium borohydride with ethanol gets adsorbed on the alloy's surface which acts as hydride to reduce the nitro group to amine (Fig. 13). The synergy between the two metals in the alloy is responsible for higher reduction rate compared to the individual metals. The poor response for the recyclability is due to leaching of the alloy because of its stronger complexation with the product amine than to  $TiO_2$  and also due to its poor adsorbity on the surface of  $TiO_2$ .

### 3.10. Catalytic oxidation of tertiary amine

The sample B-7 (5 wt.%) was further tested for the oxidation of tertiary amine *N*-phenyl tetrahydroisoquinoline (THIQ) to its corresponding amide in open air (Scheme 3). The oxidation was found to be complete after 3 days with complete conversion to give *N*-phenyl-2-tetrahydroisoquinolone. The oxidation of amine to its corresponding amide is an important reaction in biochemistry and has recently attracted considerable attention in organic synthesis [67,68]. The



Fig. 13. Plausible mechanism of nitro reduction.



Scheme 3. Oxidation of N-phenyl THIQ.

recyclability studies were done for three cycles without much decrease in yield (Table 4). A trace amount of oxidation product was also observed with undoped  $TiO_2$  under identical reaction conditions.

For comparison, 5 wt.% NiO-TiO<sub>2</sub> and CuO-TiO<sub>2</sub> were tested for oxidation of *N*-phenyl-THIQ under similar conditions, where in, it was observed that use of 5 wt.% NiO-TiO<sub>2</sub> gave a trace amount of product, while in case of CuO-TiO<sub>2</sub> partial oxidation was observed.

## 3.11. Proposed mechanism for oxidation of tertiary amine

A speculative mechanism is proposed for the oxidation of tertiary amine in Scheme 4. The nano composite CuO-NiO-TiO<sub>2</sub> gets attached to nitrogen of the tertiary amine *via* its lone pair. The resulting complex intramolecularly removes the acidic benzylic hydrogen adjacent to the nitrogen resulting in formation of iminium ion and Cu<sup>+2</sup> getting reduced to Cu<sup>+1</sup>. The transient Cu<sup>+1</sup> donates one electron to oxygen to form metal peroxy intermediates which disproportionate to Cu<sup>+2</sup> and hydroperoxide anion. The hydroperoxide anion then attacks the iminium ion to form the organic hydroperoxide which further disproportionate to amide and water.

## 4. Conclusion

CuO-NiO-TiO<sub>2</sub> nanoparticles with 1:1 Cu:Ni ratio and varying M:Ti concentration, were synthesized by a decomposition method. The photodegradation studies reveal efficiency of these catalysts which solely depended on the percentage of Cu-Ni dopants, irrespective of the other properties, and catalysts with low metal dopants are observed to display better photocatalytic activity. The optimum doping concentration for photo-degradation is observed to be 0.05 wt.%. Further, the utility of the nanocomposite with higher metal loading (5 wt.%) as a heterogenous catalyst for nitro reduction and tertiary amine oxidation was demonstrated. For the reduction studies the actual catalyst was Cu-Ni/TiO<sub>2</sub> while for the photocatalysis and air oxidation of amine to amide was clearly demonstrated in all the three applications where in it was found that individual metal doping showed less effect compared to the combined one.

## Individual contributions

Pratibha V. Bakre. Synthesis, characterization, photocatalytic studies and manuscript writing.

Durga P. Kamat. Nitro reduction studies.

Ketan Mandrekar. Amine oxidation studies

Narendra Nath Ghosh. BET studies

Santosh G. Tilve. Designing, planning and overall supervision

Table 4	
Recyclability data for amine oxidation.	

Cycle no.	Yield (%)
1	63 60
3	59



Scheme 4. Proposed mechanism of oxidation of N-phenyl THIQ.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111193.

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