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## Solid state route for synthesis of $\text{YFeO}_3/\text{g-C}_3\text{N}_4$ composites and its visible light activity for degradation of organic pollutants

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### ABSTRACT

$\text{YFeO}_3/\text{g-C}_3\text{N}_4$  composites with varying weight ratios were prepared following three different methods. The optimum weight ratio and the method of preparation for enhanced visible photocatalytic activity towards the degradation of organic contaminants were identified. The successful formation of the composites was proven by XRD and IR measurements. XPS analysis shows that the inactive  $\text{Y}_2\text{O}_3$  passive layer on the hexagonal  $\text{YFeO}_3$  (h- $\text{YFeO}_3$ ) disappeared during the composite formation, resulting in a direct and intimate contact of h- $\text{YFeO}_3/\text{g-C}_3\text{N}_4$  which is crucial for the photocatalytic activities. The loading of h- $\text{YFeO}_3$  varied from 1 to 20% and the highest activity was achieved at 2.4%. At the optimum loading 80% degradation of methyl orange (MO) was obtained under 5 h visible light illumination. The composite photocatalyst shows also modest activity for the photodegradation of 4-chlorophenol (4-CP). Additionally the synthesized composites were characterized by high resolution transmission electron microscopy (HR-TEM), Fourier transform infrared spectroscopy (FT-IR) and diffuse reflection UV–vis spectroscopy (DR-UV–vis). In order to determine the relative band positions of the composite photocatalysts their flat band potentials were estimated from Mott-Schottky analysis. Improved charge separation in the composite is mainly responsible for the enhanced photoactivity and supported by photoluminescence experiments.

### 1. Introduction

Finding effective and stable visible light active photocatalyst is still a challenge in the field of photocatalysis. Particularly such photocatalysts are of great interest in environmental remediation and decontamination of effluents. As most of the organic contaminants consist of stable aromatic rings their photocatalytic decomposition necessitates a photocatalyst with strong ability to generate holes which drive the photooxidation reaction at a reasonable rate [1]. Over the years several strategies were developed to extend the absorption edge of wide band gap semiconductors (e.g.  $\text{TiO}_2$ ) to the visible region of the light spectrum. Among them doping (cation or anion) is the most widely used method [2,3]. However, the shifting of the absorption edge to longer wavelengths obtained by doping is in most cases not accompanied by an enhanced visible light photocatalytic activity [4], since lattice strain and grain boundaries created by the dopant atoms lead to increased charge carrier recombination. The approach of composite formation with low band gap materials demonstrate enhanced photoactivity due to improved visible light absorption and or charge transport [5–7].

Another strategy is to prepare intrinsically low band gap

semiconductor oxide photocatalysts as they combine the properties of having a narrow band gap for visible light absorption and stability under illumination compared to III/V semiconductors which suffer from photo corrosion. Such classes of oxide semiconductors are mainly based on transition metals (e.g. Fe, Ni, Co, W, and Bi etc.) with partially filled d-orbitals [5,8,9]. Oxides of Fe are attracting great interest as they have suitable band gaps for visible light absorption and in most cases the valence band edges are more positive than  $\text{H}_2\text{O}/\text{O}_2$  leading to holes with strong oxidizing power [10]. Furthermore, for environmental decontamination of pollutants Fe based oxides are economically feasible as Fe is one of the most earth-abundant metals. The optical and charge transport properties, hence the photocatalytic activity and chemical stability of Fe based oxides can be tuned by forming binary metal oxides [11]. However, most iron based oxides suffer from fast charge recombination; as result strategies such as nanostructuring and composite formation are widely used to enhance their photocatalytic activities [12,13]. Metal-free semiconductors with extended  $\pi$  systems such as graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) [14] exhibit good charge carrier transport properties [15] and are attractive as photocatalysts for the removal of organic contaminants like dyes [16–18], and as

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heterogeneous catalysts [19]. It has been reported that different forms of  $\pi$ -conjugated material/photocatalyst composite show enhanced photocatalytic activities due to improved separation of the photo-generated charges [20,21]. The g-C<sub>3</sub>N<sub>4</sub> is nontoxic and can be prepared by thermal decomposition of readily available materials (e.g. melamine and hydrazine) under controlled atmosphere [22,23]. Furthermore, the position of conduction ( $-0.8$  V) and valence band ( $1.9$  V) edges of g-C<sub>3</sub>N<sub>4</sub> are suitable for the photo reduction and oxidation of water [14,15]. However, it has an optical band gap of  $2.7$  eV which limits the light absorption to below  $460$  nm. Recently, we have reported the low temperature synthesis of hexagonal yttrium ferrite (h-YFeO<sub>3</sub>) which shows high photoactivity for the degradation of MO [24]. The h-YFeO<sub>3</sub> exhibits conduction and valence band edges of  $0.23$  V and  $2.1$  V vs. RHE, respectively. In principle the composite photocatalyst between g-C<sub>3</sub>N<sub>4</sub> and h-YFeO<sub>3</sub> can benefit from (i) the good light absorption properties of hexagonal YFeO<sub>3</sub>, (ii) the excellent charge transport properties of g-C<sub>3</sub>N<sub>4</sub> and (iii) suitable band positions of both catalysts for efficient charge separation. In attempt to prove this concept, here we report solid synthesis route for the formation of h-YFeO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts. The surface area and morphologies of h-YFeO<sub>3</sub> were primarily optimized using different types of organic complexing agents namely, citric acid and ethylenediaminetetraacetic acid and their molar ratios in the sol gel synthesis. The optimized h-YFeO<sub>3</sub> samples were then used to form composite photocatalysts following three different solid state synthetic routes with varying h-YFeO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> precursor mass ratios. Their photocatalytic activities were tested for the photodegradation of 4-CP and MO and we found that the h-YFeO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite at specified ratio show high activity compared to the performance of the single photocatalysts alone.

## 2. Experimental

### 2.1. Materials

Iron (III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 99%), citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, 99%), ammonia water (NH<sub>3</sub>·H<sub>2</sub>O,  $\geq 25\%$ ) and 4-CP (C<sub>6</sub>H<sub>5</sub>ClO,  $\geq 99\%$ ) were purchased from Sigma-Aldrich. Yttrium nitrate hexahydrate (Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 99.9%), methyl orange (C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S, analytical grade) were purchased from Alfa-Aesar and ethylenediaminetetra-acetic acid (EDTA, C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>, ACS grade) from VWR-Prolabo. They were all analytical pure and were used without any further purification. De-ionized water was used during the experiments to prepare the required metal ion solutions.

### 2.2. Synthesis of catalysts

#### 2.2.1. Synthesis of YFeO<sub>3</sub>

The h-YFeO<sub>3</sub> was synthesized by sol-gel citrate route using a combination of two complexing agents [24]. In a typical synthesis procedure,  $0.01$  mol Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and  $0.01$  mol Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were separately dissolved in deionized water to obtain the required metal ion solutions of  $1:1$  molar ratio. EDTA and citric acid were dissolved in deionized water separately to obtain a  $1.05:1.5$  molar ratio of complexing agent to metal nitrate; NH<sub>3</sub>·H<sub>2</sub>O was added to assist the dissolution of EDTA. The metal ions solutions were added to the complexing agent solution under stirring, the molar ratio of the final solution was  $1:1:1.05:1.5$ . The solution was dark brown and was heated under stirring for  $2-3$  h at  $300$  °C to obtain a dark brown gel and heated further to  $400$  °C for  $1$  h yielding black flakes. The obtained flakes were ground to powder and calcined at  $675$  °C for  $10$  h in air to obtain h-YFeO<sub>3</sub>.

#### 2.2.2. Preparation g-C<sub>3</sub>N<sub>4</sub>

Direct heating of melamine at  $520$  °C for  $4$  h at heating rate of  $10$  °C/min<sup>-1</sup> in a top covered crucible was used to synthesis g-C<sub>3</sub>N<sub>4</sub> [16].

#### 2.2.3. Preparation of YFeO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite

Three preparation routes are followed to form YFeO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts. In route (i) in situ formation of g-C<sub>3</sub>N<sub>4</sub> in h-YFeO<sub>3</sub> matrix was performed. In a typical synthesis  $0.1$  g h-YFeO<sub>3</sub> and  $4$  g melamine are mixed and ground (to obtain  $2.4$  wt.% of h-YFeO<sub>3</sub>) using mortar and pestle for  $20$  min. Then the sample was calcined at  $520$  °C for  $4$  h. This sample was named as C<sub>1</sub>. In route (ii)  $0.1$  g h-YFeO<sub>3</sub> and  $4$  g melamine are mixed together and then dispersed in methanol. The mixture was put in the ultrasonic bath for  $2$  h then filtered, dried and calcined at  $520$  °C for  $4$  h in covered crucible. This sample was named as C<sub>2</sub>. Route (iii) employed physical mixing of  $4$  g of g-C<sub>3</sub>N<sub>4</sub> and  $0.1$  g of h-YFeO<sub>3</sub>, which is then directly tested for the activity. This sample was named as C<sub>3</sub>. The heating rate for the preparation of C<sub>1</sub> and C<sub>2</sub> was  $10$  °C/min<sup>-1</sup>. Similarly,  $1, 3, 4.7$  and  $20$  wt.% YFeO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts were prepared by mixing  $0.1$  g YFeO<sub>3</sub> with  $9, 3.2, 2,$  and  $0.4$  g of melamine, respectively.

#### 2.2.4. Preparation of electrodes

The working electrodes were prepared on fluorine-doped tin oxide (FTO) glass slides ( $15$  Ω cm<sup>-2</sup>, Pilkington Germany). FTO slides with a size of  $2$  cm ×  $6$  cm were cleaned with  $0.1$  M HCl,  $0.1$  M NaOH, acetone, ethanol in ultrasonic bath, respectively. Then  $0.1$  g of the photocatalyst samples were dispersed in  $1$  ml ethanol in an ultrasonic bath for  $1$  h. Subsequently,  $200$  μl of the dispersion were placed on the FTO glass substrate and the doctor-blade technique was applied for coating. Finally, the FTO substrate was dried in a furnace for  $30$  min at  $80$  °C and calcined for  $3$  h at  $600$  °C, the heating rate was  $2$  °C/min.

## 2.3. Characterization of photocatalyst

### 2.3.1. UV-vis measurements

A Cary 4000 UV-vis spectrophotometer (VARIAN) equipped with an integrating sphere was used for DR-UV-vis absorption measurements. MgO was used as a white standard and the spectral range was  $200-800$  nm.

### 2.3.2. Fluorescence measurements

The fluorescence of 2-hydroxy terephthalic acid (Scheme S1) and photoluminescence of powder samples were measured on a VARIAN Cary Eclipse Fluorescence Spectrophotometer.

### 2.3.3. X-ray diffraction

A Xpert PRO X-ray diffractometer (PANalytical) with theta-2theta configuration equipped with a Cu K $\alpha$  radiation ( $\lambda = 1.540598$  nm) was used to determine the sample phases, crystallinity and purity. The diffractograms were recorded between  $10-80$  ° in  $\theta-2\theta$  configuration at operating voltage and current of  $40$  kV and  $40$  mA, respectively.

### 2.3.4. X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out in an ultra-high vacuum set-up, ESCALAB 250 Xi (Thermo Fisher) equipped with a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV). The high resolution spectra for the C 1s, O 1s, N 1s and Fe 2p photoelectron lines were recorded with a pass energy of  $20$  eV and a step size of  $0.02$  eV. The binding energy scales were corrected to the charge shift by referring to the most intense C 1s peak at  $284.8$  eV. The spectra were analyzed using Avantage software (version 5.951)

### 2.3.5. Fourier transform infrared spectroscopy (FT-IR)

Bruker FT-IR Tensor 27 Spectrometer with platinum ATR was used for functional groups determination of the catalysts.

### 2.3.6. Gas adsorption experiments

N<sub>2</sub> gas adsorption experiments were performed with an ASAP 2020 and a Tri Star II (Micromeritics) and the surface area is calculated using the Brunauer-Emmett-Teller (BET) approach. All the samples were

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