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SiO$_2$-TiO$_2$-B$_2$O$_3$-BaO glass-ceramic system with Fe$_2$O$_3$ or CuO additives as photocatalyst

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ABSTRACT

Different amounts of Fe$_2$O$_3$ or CuO have been added over the glass batch composed mainly of SiO$_2$, B$_2$O$_3$, BaO and the photoactive TiO$_2$. The obtained glass samples were subsequently heat treated at the onset of nucleation temperature (490 °C) for 1–3 h followed by heating at 550 °C for the same period in order to obtain nanocrystalline glass-ceramic materials. X-ray diffraction analysis of the obtained materials revealed amorphous structure; however, tiny crystals could be detected under high-resolution electron microscope (HR-TEM). All samples showed absorption in UV with variable absorption in the visible light regions depending on the composition. The prepared glass-ceramic materials displayed photocatalytic efficiency for the degradation of Humic Acid, though Fe doping is much favorable than Cu doping. About 46% removal of humic acid could be achieved when using sample containing 0.5 wt.% of Fe$_2$O$_3$ and heat treated at 490 °C/1 h followed 550 °C/1 h.

1. Introduction

The most popular and promising photocatalyst is crystalline TiO$_2$ because of its high efficiency, low cost and wide gap which can be activated by UV light from solar or artificial radiation sources [1,2]. Two main criteria were investigated for improving the efficiency of TiO$_2$: minimizing photogenerated electron–hole recombination rates and expanding the range of operation into visible light wavelengths [3]. Both processes can be achieved by coupling TiO$_2$ with other materials such as semiconductor oxides that show a clear energy difference between their valence bands as well as between their conduction bands (the two differences-shifts being to the same direction) [2,3].

The strong absorptivity of Fe$_2$O$_3$ in the visible range, along with its abundance and low cost, narrow band gap (Eg $\approx$ 2.2 eV [4]) has stimulated considerable interest in its use as a photocatalyst and a photoelectrode [5]. But, the position of the valence band of Fe$_2$O$_3$ does not allow the generation of OH radical from water making it an ineffective photocatalyst for organics oxidation, when used by itself [6]. Therefore, its combination with other semiconductors (e.g. TiO$_2$) is obligatory [7]. TiO$_2$–Fe$_2$O$_3$ binary mixed oxides were reported to be a good catalyst with improved photocatalytic

properties and enhanced visible light response. Studies with TiO$_2$–Fe$_2$O$_3$ mixed oxide catalyst have shown an increased photocatalytic activity for dichloroacetic acid destruction at 450 nm [8]. Recently, Wodka et al. [9] synthesized Fe$_2$O$_3$/P25 composite containing 1 wt.% of the iron(III) oxide nanoparticles on the Evonic-Degussa P25 titania surface using precipitation method. According to their findings, doping with Fe(III) enhanced the activity of TiO$_2$ toward the removal of oxalic acid (OxA) and formic acid (FA) from water under UV or artificial sunlight (halogen lamp). Also, Liu et al. [10] prepared Fe$_2$O$_3$–TiO$_2$ composite photocatalyst using hydrothermal method, which showed excellent photocatalytic activity for the degradation of auramine under visible and solar light irradiation.

Cu$_2$O (and CuO) is also an abundant p-type semiconductor with band-gap energy of 1.8–2.5 eV (and 1.21–2.00 eV, respectively) [11] that absorb visible light. CuO/TiO$_2$ nanorods has been prepared via electrospinning process and showed excellent antibacterial abilities under visible light [12]. In a similar study, TiO$_2$/CuO electrospun nanofibers was successfully fabricated and displayed efficient concurrent photocatalytic organic degradation and clean energy production from dye wastewater [13].

Because photocatalysis usually occurs on the surface of photocatalyst, the higher the surface area is, the better is the efficiency of the photocatalyst due to presence of more active sites for the adsorption of water and contaminants as well as for the formation of hydroxyl radicals [14]. One method for increasing the

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surface area is to diminish the particle size as possible using surfactants and polymers as structure-directing agents [14]. However, this small particle size leads to difficulties in separation of the photocatalyst from the treated solution. Precipitation of photoactive crystals in a glassy matrix in the form of glass-ceramic ensures the confinement of crystal growth and hence small crystals could be obtained. In mean time, the glass-ceramic composite as a whole possesses large particle size which allows its separation by simple methods [15].

In this study, we propose a glass-ceramic composition in which TiO_2, as photocatalyst, was coupled with another low band gap semiconductor (Fe_2O_3 or CuO) to enhance TiO_2 activity. The glass composition is SiO_2, TiO_2, B_2O_3, Na_2O, K_2O, P_2O_5, Li_2O and BaO with either Fe_2O_3 or CuO. The prepared photocatalytic glass-ceramic materials were investigated for the degradation of Humic acid (HA) which is the major constituent of natural organic matter found in all surface waters [16,17] and represent the major precursor of the carcinogenic halogenated disinfection by-products (DBPs) [18].

2. Experimental

2.1. Preparation of glass samples

The glass samples were prepared using reagent-grade chemicals (Loba Chemie, India). All chemicals were used as received without further purifications. The composition (24.69 SiO_2, 24.29 TiO_2, 12.95 B_2O_3, 7.69 Na_2O, 4K_2O, 1.2 P_2O_5, 0.8 Li_2O, 24.28 BaO in wt.%) was selected because of its good transparency and photocatalytic activity according to our previous study [15]. Fe_2O_3 or CuO was added to the mentioned composition with 0.25, 0.5 and 1% over the batch to study their effects on the final glass-ceramic products. The prepared materials were labeled as TFx and TCx for Fe_2O_3 and CuO additions, respectively, where x refers to the addition percentage.

The glass samples were prepared by melting the composition batch in a platinum crucible. The furnace temperature was raised to 1200 °C gradually to avoid sputtering or splashing of the batch materials during melting. After complete melting, the molten batch was held for 2–3 h at constant temperature with occasional swirling to ensure homogenization of the melt. The melted samples were then casted onto hot steel moulds and then rapidly transferred to a muffle furnace adjusted at desired temperature for annealing to obtain strain-free glass samples. Photographs of the prepared materials, taken by Sony Cybershot DSC-H9 digital still camera (Japan), are presented in Fig. 1.

2.2. Characterization of prepared materials

Temperatures of crystallization and growth of the prepared samples were determined using differential scanning calorimetry (DSC) (SETRAM Instrumentation Regulation, LabsysTM TG-DSC16 under inert gas). The crystal structure was identified from the collected XRD patterns using Bruker diffractometer (Germany) with graphite monochromatized Cu-Kα radiation. Optical properties of polished glass and glass-ceramics slabs ($1 \times 0.3 \times 3\,cm^3$) were measured using JASCO spectrophotometer (Model V630, Japan).

2.3. Evaluation of photocatalytic performance

Photocatalytic experiments were carried out using one–liter photo-reactor. The reactor consists of two parts; the first part is an inner quartz double-wall jacket with inlet and outlet for the water circulation to maintain the temperature constant during the experiment. This jacket has an empty chamber at the center for immersion of a medium pressure mercury lamp (150 W, $\lambda_{max} \approx$ 365 nm). The second part is the outer borosilicate glass container (volume 750 mL after insertion of the inner part) in which the reaction takes place.

HA solution was mixed with the glass-ceramic materials (0.5–2 mm grain size), stirred for 60 min prior to experiment to allow adsorption equilibrium of HA on the glass-ceramic surface. Then, the UV lamp was switched on to start photodegradation process. After definite irradiation times, suitable volumes of the solution were sampled using a syringe and the glass-ceramic materials were allowed to settle down. After that, the solution was analyzed according to the UV–vis absorbency at 254 nm.

3. Results and discussion

3.1. Characterization of the prepared materials

Differential scanning calorimetry (DSC) is a rapid tool for studying the crystallization nature through the determination of temperature range of crystallization and the suitable heat-treatment schedule. This is achieved by finding out the onset of glass transition temperature (T_g), onset of first crystallization peak (T_p) and endotherm endpoint liquidus temperature (T_{liq}) [19].

Fig. 2 shows the DSC curves of TF glass samples containing various amounts of Fe_2O_3. It is obvious that adding Fe_2O_3 causes a marked shift on the DSC data to higher values, which is evidenced by the shift of the endothermic and crystallization peaks to higher temperatures. Specifically, the glass transition temperature (T_g) increased from 507 to 516 and up to 520 °C when the weight ratio of Fe_2O_3 were 0.25%, 0.5% and 1 wt.%, respectively. The increase in glass transition temperature can be ascribed to the increase in average coordination number with the addition of Fe_2O_3. According to Sun's bond-strength criterion for glass formation [20], the fundamental condition for glass formation is the existence of strongly bonded large networks or long chains for atoms in the liquid. The increase in iron oxide content creates strongly bonded networks which are responsible for the increase in thermal stability of the glass. Similar behavior was observed for the glass systems 35TeO_2–(65-x)V_2O_5–xFe_2O_3 [21] and 20ZnO–(80-x)TeO_2–xFe_2O_3 [22]. On the other hand, the peak of crystallization (T_p) appeared at 704 °C and 832 °C in case of 0.25 and 0.5% Fe_2O_3,
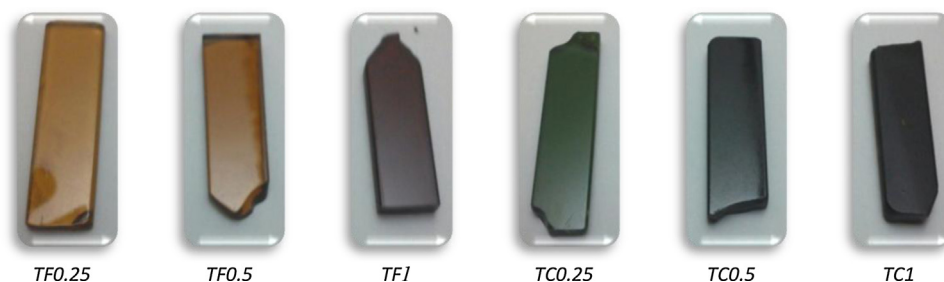

TF0.25 TF0.5 TF1 TC0.25 TC0.5 TC1

Fig. 1. Photographs of the prepared TF and TC glass samples.