Self-initiated Photocatalytic Polymerization of Tough and Flexible Polyacrylamide Hydrogel/Polymeric Semiconductor C_3N_4 Composites

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Polyacrylamide (PAM)/g- C_3N_4 composite materials were prepared by the self-initiation of C_3N_4 via its photocatalytic activity. Radical species were produced during illumination of g- C_3N_4 and can initiate the formation of the PAM/ C_3N_4 composite. The effect of charcoal composited to C_3N_4 was also investigated. The physical properties of the PAM/g- C_3N_4 and PAM/g- C_3N_4 -charcoal composite materials were analyzed using SEM technique. Photocatalytic reduction of chromium (VI) to chromium (III) was validated using the composites.

Keywords: Polyacrylamide, g- C_3N_4 , Chromium(VI) reduction, Photocatalysis

1. Introduction

Hydrogels are a 3D crosslinked polymeric material that contains a hydrophilic group that can swell and retain a large amount of water or biological fluid within the structure without dissolving [1]. This ability to swell under biological conditions makes hydrogels an ideal material for biomedical applications, such as tissue engineering [2,3] and drug delivery [4,5]. Hydrogels can be synthesized by synthetic polymers or natural polymers. One of the recently used synthetic polymers is polyacrylamide (PAM), which is a non-toxic, biologically inert compound with a long chain length. PAM has a capacity for preserving its shape and mechanical strength, with conveniently adjustable mechanical, chemical and biophysical properties, allowing for its wide use in tissue engineering applications. Hydrogels can be synthesized via different polymerization methods [6]. Radical polymerization is one of the most attractive methods to prepare hydrogels because of their low cost and convenience. Free radical polymerization is a method of polymerization where a polymer forms as the successive addition of a free radical to the monomer [7,8].

Radicals generated during photocatalytic processes play an important role in the photocatalytic reaction. Therefore, these radicals

might be a promising candidate as a photo-initiator for utilization in radical polymerization processes [9,10]. The photo-initiator is one type of initiator in radical polymerization. It normally uses metal iodides, metal alkyls, peroxide and azo compounds as initiators. Recently, semiconductors have been found to generate radicals using a heterogeneous photocatalysis process. It has gradually gained attention but is rarely used in the polymerization process. In fact, not only semiconductors can generate radicals, but they can also improve the mechanical properties of the synthesized polymer. Polyacrylamide hydrogels have used semiconductors, such as TiO_2 , ZnO , SnO_2 , $CdSe$ and Fe_2O_3 , as initiators and found that the hydrogel exhibit excellent mechanical strength and high elasticity [11,12].

Recently the g- C_3N_4 photocatalyst has been extensively studied because it is active under visible light [13,14]. The photoactivity of the g- C_3N_4 catalyst has been examined for several purposes, including NO_x photocatalytic activity under UV and visible light irradiation [15,16], water splitting, and CO_2 photoreduction [13]. Moreover, the band gap of g- C_3N_4 is narrow, approximately 2.5-2.7 eV [13,14], and visible light can be utilized to activate the catalyst. PAM/g- C_3N_4 composite materials might be of interest for several applications, e.g.

provide the transport of analytes through inter-particle channels, gel density controllable and enhance the efficiency of protein separation in gel electrophoresis. Moreover, g-C₃N₄ modified with charcoal may also improve some properties of the hydrogel because charcoal is widely known to be a good absorber. A high surface area of charcoal would benefit the adsorption stage of the photocatalytic process. Charcoal can adsorb almost all reactants, such as water-soluble ions, organic compounds, inorganic compounds and heavy metals [17], which provides more active sites for the reaction between photo generated active species and reactants.

This work reports the novel fabrication of PAM/g-C₃N₄ and PAM/g-C₃N₄-charcoal composite hydrogel via a self-initiator of photopolymerization. The strong and good distribution of g-C₃N₄ in hydrogel was expected from this method, making it advantageous over other methods. The structure morphology and functional group of these self-initiated composite hydrogels were investigated. The photocatalytic activities were investigated by photoreduction of chromium (VI) to chromium (III). The photoreduction reaction has environmental significance because chromium (VI) is a common pollutant that is highly toxic to human health [18-20].

2. Experimental

2.1. Materials

Melamine was purchased from Sigma Aldrich (99%). Acylamide and *N,N'*-methylenebis acrylamide used for synthesis were purchased from Merck. Ammonium persulphate was purchased from Calbiochem.

2.2. Preparation of g-C₃N₄ and g-C₃N₄-charcoal

g-C₃N₄ was prepared by a condensation of melamine; whereas, g-C₃N₄-charcoal was prepared via a one-step thermal condensation of melamine and charcoal (100:4, wt/wt). Calcination of the powders was performed at 500 °C under air atmospheres for 2 hr. with a heating and cooling rate of 10 °C /min, respectively.

2.3. Preparation of self-initiated PAM/g-C₃N₄ and PAM/g-C₃N₄-charcoal composite hydrogel

The suspension of g-C₃N₄ or g-C₃N₄-charcoal in aqueous solution of acrylamide and *N,N'*-methylenebisacrylamide was similar to the conventional method but without initiators. Next, the suspension was placed into a 15-watt UV-LED

homemade reactor and left until gelation occurred. The synthesized products were washed with water and freeze dried for a day for further characterization.

XRD data were collected using a Rigaku Mini Flex II X-ray diffractometer. The specific surface area of the powder samples was measured by nitrogen adsorption at 77 K using the Brunauer-Emmett-Teller (BET) method (Micromeritics TriStar II). Scanning electron microscopy and transmission electron microscopy were performed using a JEOL JSM-6335F microscope and JEOL JEM-2010 electron microscope, respectively.

2.4. Evaluation of photocatalytic activity

The photocatalytic ability of PAM/g-C₃N₄ and PAM/g-C₃N₄-charcoal under visible light were evaluated by suspending the composites in 50 mL of K₂Cr₂O₇ solution. The suspension was first kept in the dark for 24 hours to reach an adsorption equilibrium at room temperature. Then, the suspension was illuminated with a homemade 30 watts visible LED lamp. A change in absorption of Cr⁶⁺ diphenylcarbazide complex measured at 542 nm in acid solution was monitored every 1 hour using a UV-Vis spectrophotometer.

3. Results and discussion

Self-initiated photocatalytic polymerization reaction highly depends on surface area, particle size and morphology of the photocatalysts. Table 1 shows a BET surface area and C:N ratio of the synthesized g-C₃N₄ and g-C₃N₄-charcoal. The BET surface area of the powders plays a major role for a radical generation by photocatalytic activity. It was found that g-C₃N₄ and g-C₃N₄-charcoal showed a moderate surface area. The g-C₃N₄-charcoal had a little bit higher surface area than naked g-C₃N₄. This is likely due to a higher inner porous area of charcoal produced under an oxidizing air atmosphere [9]. The C:N ratio of g-C₃N₄ obtained by EDS was consistent with those of other works [19,20]. Whereas C:N ratio of g-C₃N₄-charcoal samples showed higher content of carbon and lesser content of oxygen, indicating a composite of g-C₃N₄ and charcoal.

SEM images of charcoal, g-C₃N₄ and g-C₃N₄-charcoal are shown in Fig. 1. Smooth surface agglomeration of charcoal and rough surface with some agglomeration of g-C₃N₄ were observed. The characteristic surface of charcoal and g-C₃N₄ are useful in an analysis of the composite of g-C₃N₄-charcoal. Charcoal has a smooth surface because of

the agglomeration of individual amorphous powders; whereas, g-C₃N₄ is a graphene-like sheet, so that a rough surface was observed.

Table 1. The BET surface area and C:N:O ratio of the synthesized powders

Material	BET surface area (m ² /g)	EDS of Weight %		
		C	N	O
g-C ₃ N ₄	44.92	31.13	59.44	9.42
g-C ₃ N ₄ -charcoal	46.25	44.74	53.79	1.47

Fig. 1. SEM and HRTEM images of charcoal, g-C₃N₄ and g-C₃N₄-charcoal.

The morphology of g-C₃N₄-charcoal (100:4, wt/wt) calcined under air atmosphere exhibited small separated flake morphology; this is possibly due to the moderate oxidation of charcoal. HRTEM images confirmed an existence of g-C₃N₄ embedded into charcoal. D-spacing of g-C₃N₄ in g-C₃N₄ and g-C₃N₄-charcoal were clearly seen.

Fig. 2. FT-IR spectra of charcoal, g-C₃N₄ and g-C₃N₄-charcoal.

Figure 2 shows the IR vibrational frequencies of charcoal, g-C₃N₄ and g-C₃N₄-charcoal. The IR spectra exhibited a characteristic band at 1,650-

1,500 cm⁻¹, which corresponds to the C=C and C-O functional groups of charcoal. The g-C₃N₄ charcoal sample showed a contribution band of similar several fingerprint bands of g-C₃N₄ and charcoal. Sharp bands at approximately 820 cm⁻¹ was corresponded to triazine units [15].

Figure 3 shows the SEM images of the PAM/g-C₃N₄ prepared by self-initiated photocatalytic polymerization. It was found that the self-initiated PAM/g-C₃N₄ had a good distribution of g-C₃N₄ into the hydrogel. The distribution is attributed to the radical produced at the surface of g-C₃N₄. Therefore, polymerization hydrogel would have happened at the surface of g-C₃N₄. This finding may contribute to the strong and tough of the composite hydrogel because g-C₃N₄ was distributed throughout the hydrogel. On the other hand, PAM/g-C₃N₄ composite hydrogel, prepared by conventional method using ammonium persulfate as initiator, have obvious boundary lines between the PAM hydrogel and g-C₃N₄. However, swelling ratio of the PAM/g-C₃N₄ composite hydrogel was rather smaller than the PAM hydrogel because the interconnect of g-C₃N₄ throughout the hydrogel inhibit a swelling of the hydrogel, which a mechanism may be proposed as shown in Fig. 4.

Fig. 3. SEM images of PAM/g-C₃N₄.

Fig. 4. The proposed mechanism of swelling ratio of the hydrogels.

Photocatalytic reduction of chromium (VI) to chromium (III) was also investigated.

The separation of a photoactivity effect from an adsorption effect was measured using an adsorption experiments for 24 hrs (Fig. 5). It was found that percent Cr (VI) sorption increases when using PAM, PAM/g-C₃N₄ and PAM/g-C₃N₄-charcoal as adsorbent, respectively. g-C₃N₄ seems to have adsorption capacity for chromium (VI) higher than naked PAM. However, existence of charcoal on g-C₃N₄ provide the highest adsorption capacity. Chromium (VI) adsorption was in equilibrium after keeping the suspension in the dark for 18 hrs.

Fig. 5. Adsorption capacity of chromium (VI).

Photocatalytic reduction of chromium (VI) to chromium (III) was evaluated after an equilibrium of adsorption as shown in Fig. 6. The naked PAM showed neglect activity. The photoactivity of g-C₃N₄ was moderate because of the narrow band gap energy of g-C₃N₄, which facilitated e⁻-hole pairs recombination. The hydrogel with higher surface area, PAM/g-C₃N₄-charcoal enhanced photoactivity; this confirms the effect of an increased surface area. Moreover, this is possibly due to the electron transfer between the conduction band of g-C₃N₄ to charcoal is beneficial in the suppression of e⁻-h⁺ pair recombination.

Fig. 6. Photocatalytic reduction of chromium (VI) to chromium (III).

4. Conclusion

A novel fabrication of PAM/g-C₃N₄ and PAM/g-C₃N₄-charcoal composite hydrogel is reported using a one-step method. Composite materials were successfully prepared using photoactivity of g-C₃N₄. The photocatalytic reduction activities chromium (VI) to chromium (III) were investigated. The PAM/ g-C₃N₄-charcoal showed good photoactivity, consisting with the hypothesis that charcoal acts as electron transfer surface.

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