Synthesis carbon foams prepared from gelatin (CFG) for cadmium ion adsorption

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Abstract : In this paper, carbon foam from gelatin (CFG) was synthesized by acid-catalyzed carbonization of gelatin solution on mild condition by the simple method. Gelatin (Ge) were used as sacrificial template and source of carbon. Sulphuric acid was used as acid catalyst. Carbon foam CFG sample were characterized by scanning electron microscope (SEM), nitrogen adsorption desorption and FTIR for knowing textural and structural properties of the sample. Carbon foam CFG sample demonstrated macro pipes-channel like with pore size that varies between 30-40 μ and surface area m 60-100 m^2g-1. The carbon foams CFG sample were tested by using adsorption process for obtained their performance for decreasing Cd(II) ions from aqueous solutions. The adsorption capacities for cadmium was 46.7 mg/g obtained by using adsorbent dose 50 mg, initial concentration 50 ppm, contact time, 3 h; room temperature, stirring rate 150 rpm) which reached equilibrium at 55 min. Adsorption process fits using using Lagergren and Ho and McKay equation and measuring data

Keywords: carbon foam CFG, texture, structure, adsorption, cadmium ion, capacities

1. Introduction

Carbon foam as new generation of material applied in wider field such as adsorbent, catalyst, electrical material, radiator, fire resistant composite and electrodes [1]. Carbon foam have unique physical character such as high thermal stability, high thermal conductivity, large pore, large volume and high surface area. The high surface area of carbon foam playing urgently role as supporting part in catalysis and adsorption ter. The traditional technique for praparation of carbon foam using glassy and graphite step. The other method for carbon foam preparation explored by hard templating, carbonization, compression and soft templating. Some of source of carbon has been used on the previous paper such as coal, pitch carbon from petroleum aldehyde, sucrose, phenol, resin and polyimide, furfuril alcohol [2-3]. The using of gelatin as source of carbon foam very rarely investigated. Gelatin is alternative source of carbon foam due to the polymer contain with high of amine chain.

   The carbonization of carbon foam source produce the unique character as graphitisable material [2]. The carbon with glassy part, graphitisable and have insulation character obtain after carbonization step. The technology to produce carbon foam develope rapidly in last decade trough hard templating methode [2-4]. However, this technique unfavourable due to the high cost and less effisient. The other

side, the using soft templating method to replace hard templating method started to research in few years[3].

The present work aimed at producing carbonaceous porous matrices for hosting phase-change materials for seasonal heat storage, using a "green" precursor. Carbon foam from gelatin (CFG) was synthesized by acid-catalyzed carbonization. Characterization of Carbon foam CFG using scanning electron microscope (SEM), nitrogen adsorption desorption and FTIR Then were tested by using adsorption process which is fits using using Lagergren and Ho and McKay equation and measuring data. The adsorbate concentration is not influence the adsorption the desorption [9] but Ho and Mckay told that the adsorption rate is linearly related to the square of the number of adsorption vacant sites [10]. The equation of Lagergren and Ho and McKay describe in Table 4.

2. Experimental section
2.1 Materials
All chemicals including sulfuric acid, deionized water, gelatin and cadmium ion solution were purchased from Sigma Aldrich used without any purification. Gelatin technical grade (medium molecular weight (200 kDa) was purchased from Gel-Pro Australian supplier.

2.2 Instrumentation
The investigation of carbon foam samples using Philips X'Pert-MPD diffractometer by radiation of Cu Kα (k = 1.5418 Å). The operation of Cu anode at 40 kV and 30 mA. The isotherms adsorption desorption nitrogen of carbon foam measured by AUTOSORB-1 instrument (Quantachrome Co.) at -196 ℃. The surface area and pore size of carbon foam sample measured by Brunauer–Emmet–Teller (BET) and Brunauer–Joyner–Halenda (BJH) method. The surface area were derived from nitrogen uptake from BET model at relative pressure 0-0.99. The pore size distributions were derived from the adsorption branches of the isotherms by using the Barett–Joyner–Halenda (BJH) model. The total pore volumes (Vt) were obtained from the amount of nitrogen uptake at P/P0 of 0.99

The images of carbon foam sample recorded by scanning electron microscope (SEM, Hitachi H800) combine with Electron Dispersive Spectrometer (EDX) to verify the presence of elemental inside the carbon foam samples. The analysis of functional group conducted at range 400–4000 cm^{-1} by Fourier transform infrared spectroscopy (FTIR) (Shimadzu spectrometer 2800).

2.3 Procedure: Preparation of Carbon foam from Gelatin (CFG)
Carbon foam from gelatin, designated as CFG, was prepared using gelatin as a structure-directing agent and carbon precursor. Gelatin CFG was synthesized by modified Pechini method [8]. At first, 0.01 mol sulfuric acid and 100 mL distillation water were mixed carefully. The solution of gelatin prepared by adding 1.5 g gelatin into sulfuric acid solution followed by stir process 60 min. The first mixture prepared by adding, 1.0 g gelatin into the solution of gelatin. The first mixture homogeninized at 150 rpm and heated at around 90 °C for 45 min. The foam like gel obtained by heateding process at 150 °C in oven for 15 h. Then, the next process followed by calcination at 900 °C with argon gas flow for 3 h. The synthesized CFG obtained by filtration with deionized water, and drying over night in oven at 100 °C.

2.4 Adsorption of cadmium ion into Carbon Foam of Gelatin (CFG)
The adsorption evaluation of cadmium ion as pollutant model using carbon foam from gelatin (CFG) as adsorbent was investigated by using the fixed-bed reactor. The test prepared by continuous flow term using column with a diameter and a length of 2.5 cm and 15 cm, respectively. The weight of adsorbent was 30 mg of carbon foam from gelatin (CFG) completed with paper filter in bottom of column(Whatman, USA) The cadmium ion as pollutant model was prepared by mixing the initial solution of cadmium ion and the effluent. The cadmium ion as pollutant model was adsorbed through the column at room temperature. The sampling effluent was obtained at range 5 to 800 minute (1 mL/5 minute) followed byn filtration step. After filtration, cadmium concentrations analyze using Atomic Absorption Spectrophotometry (AAS, Shimadzu AA-6300). The relationship between the dissolved K concentration in cadmium solution ($C_{solution}$, mg K L^{-1}) and the cadmium sorbed K concen- tration

(C_{Cd}, mg K kg^{-1}) can be described by either using Lagergren and   Ho and McKay equation and measuring data

3. Result and Discussion

Figure 1 shows the typical picture of a single broken carbon foam from gelatin (CFG) that clearly has a foam-like structure by the simple camera and SEM. The SEM graph showed that carbon foam from gelatin (CFG) have foaming part after calcination step as first prediction. These phenomenon represented by sulfuric acid role that catalysis foam forming in gelatin chain during high temperature treatment. The resulting SEM image of carbon foam from gelatin (CFG) containing hard texture, soft line surface and disordered puzzle-like shape. The three dimension images of foam shape and texture exhibited by photograph are shown in Fig. 1. The photograph result show that the diameter size of CFG an average of ~100 μm, are match with sulfuric acid as catalyst factor. For a sum, the morphology of CFG is a mixture of puzzle-like pipe, disordered soft surface, and paralelical shapes. The texture of CFG surfaces not only exhibited by photograph but also SEM micrograph as shown in Fig 2. Water on gelatin vaporated by heat treatment and foaming process generate crack pore with diameter up to 10 μm within whole surface.

   Gelatin structure as carbon precursor is very important to control characteristic of the carbon foam pore system. The Large pore of carbon foam obtained by reduction process of gelatin molecule which is hydrocarbons convert to elemental via losing of hydrogen, oxygen, and nitrogen atoms. The loss of this element from gelatin molecule describes the mass loss of gaseous species. The carbonization process cause mass loss of these gasses such as hydrogen, water, ammonia. Gelatin as organic material at high temperature decompose to be small molecul and element that generate microporous part with hard texture and easy broke in large dimension. However, the large molecules such water and amonia will be quickly decomposed by carbonization then can create macroporous part in CFG. The fact about microporous and macroporous part geenrated after gelatin decomposition shows that CFG could be a new carbon matrix woth unique molecular size and shape. The size and shape of porous carbon CFG predict appeared by the weight loss of water and ammonia as huge polar molecules in gelatin which is showed at table 1.
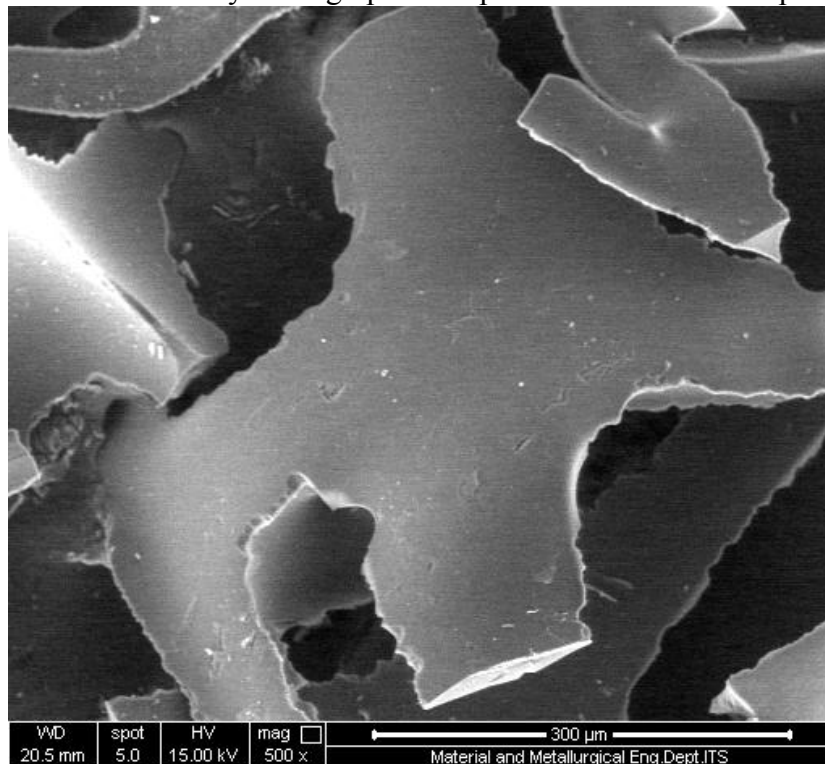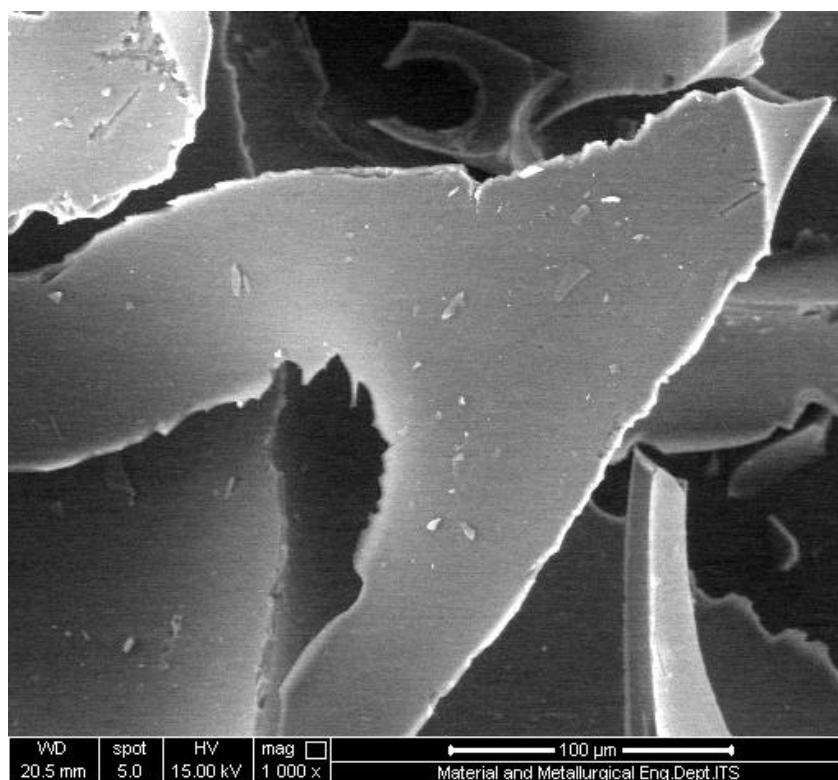

a.

b.

Figure 1 Carbon Foam by Photograph a. Perpendicular view and b. paralel view

a.

b.

Figure 2 – SEM images of Carbon Foam of gelatin nanoparticles with magnification (a)
300μm and (b) 100μ

Table 1. The Trend of Weigth loss obtained by DTG Intrument on carbon foam sample

Temperature (ºC)	% Wt	% Total Wt loss	Molecule assignment
0	100	-	-
0-100	88	12%	Water
100-150	75	25%	Water, amine
200-500	65	35%	Water, amine, oxygen, hydrogen
500-1300	5	95%	Water, amine, oxygen, hydrogen, carbon

Different thermogravimetry (DTG) measurements Table 1 and energy dispersive instrument exhibit that carbon and oxygen are the major elements of CFG. In the other side, gold element generate from Au grains that increase conductive and eletric character after coating step. In the major peak of C(79.9%) and O (18.9%) on carbon foam sample, indicating that the resulting carbon foam composed of carbon and oxygen phase as same as the previous research by Ge [8]. The mass loss of nirtogen from CFG shows decomposition process from gelatin during carbonization step. In addition, natrium peak in EDX spectrum show that preparation of gelatin using NaOH can create small presence of natrium still keep in gelatin chain during carbonization. The result of the elemental analysis shows that nothing sulfuric residue on CFGsuggests the presence of interaction between gelatin and sulfuric acid only on the preparation step but nothing on carbonization. The morphology of CFG describes of large numbers of hydroxyl groups presenting in gelatin inevitably interact with the negative charge of sulfuric acid by hydrogen bonding. That is the gelatin molecules should dominantly locate at the interface between sulfuric acid and gelatin chain (shown in Fig. 1). Some gelatin molecules may interact with sulfuric acid then sulfuric acid penetrates through the side chain of amino acid on whole gelatin molecule.

The CFG were examined by thermal gravimetric analysis (TGA) under nitrogen atmosphere. The TGA Table 1 exhibits a peak of large endothermic part at 110 °C that represent of water mass loss. These endothermic part was not only represent loss of twenty percent of water but also the deformation of helical structure and other bonding between gelatin molecules and catalyst. The melting temperature exhibit at 230 °C indicate the endothermic part appears [13]. The tranformation of tertiary structure of gelatin occured at range of oxidation and melting step. The splitting of peptide linkages of proteins starts at above 290 °C, and is indicated by several the exothermic peaks at 290 °C represent the peptide linkaged split within whole protein [7]. DSC information (not shown) shows the total weight loss at range 20 wt% up to 200 °C due to the water mass loss. In the other part, the weight loss of about 95 wt% from 200 °C to 1300 °C was associated the mass loss of majority of molecule and element high thermal treatment that generate carbon with high stability. As a sum, Table 1 explain about the huge change structure of during carbinization step that create some unique texture as SEM information due to the mass loss of water, amine, hydrogen and plenty of carbon as predicted before.

The FTIR reflectance spectrum of the CFG is showed in Table 2. The C–H vibrations showed by bands at 698, and 935 cm^{-1} with small intensity. The carboxylic groups, CH2 and CH3 wave number observe at 1154 and 1454 cm^{-1}The bands at 1524, 1541 and 1590 cm^{-1} represented to C=C and C=O vibrations in carbonyl groups respectively. The vibrations of –CH2 or –CH3 groups observed at at 1154 and 1454 cm^{-1}. The C–O stretching vibrations are represented by band at wave number 100–1300 cm^{-1}[14-16]. The difficulties of assign the bands in the range of 100–1300 cm^{-1} due to the overlapping of functional groups. The C–O–C stretching vibrations observed at at 1172 and 1268 cm^{-1} can indicated presence some functional group of alcohol, phenol and carboxyl. The band at 1103 cm^{-1} may be due to O–H. For a sum, the oxygen presented by spectra infra red explain about the mass loss of water which is match with TGA information

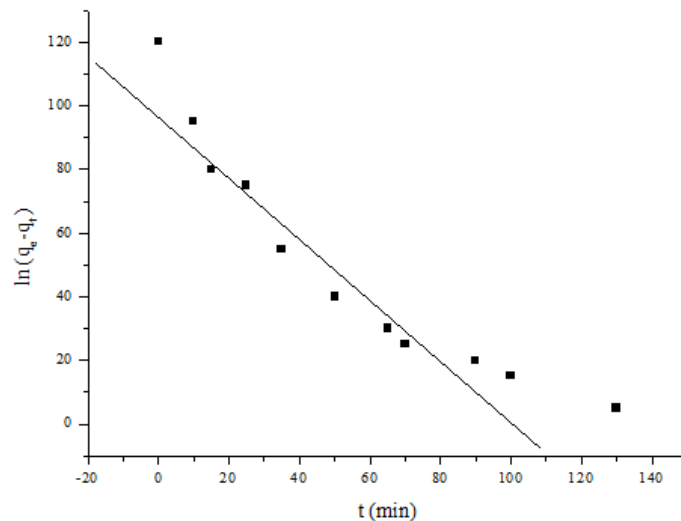**Table 2.** Peak assignment of FTIR spectra of carbon foam gelatin

Peak assignment	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area
C–H vibrations	316.33	29.004	11.929	324.04	293.18	11.629
C–H vibrations	347.19	11.632	62.832	362.62	339.47	12.123
C–H vibrations	478.35	25.331	2.041	555.5	424.34	75.774
C–H vibrations	648.08	28.457	0.244	848.68	640.37	106.355
C–H vibrations	925.83	32.588	0.98	972.12	856.39	55.734
carboxylic	1080.14	32.486	1.333	1249.87	979.84	129.438
C–O stretching	1350.17	32.944	0.162	1357.89	1257.59	47.545
C=C vibrations	1627.92	30.131	0.777	1643.35	1558.48	43.074
C=O vibrations	1851.66	31.547	0.286	1859.38	1820.8	19.172
CH2	2337.72	24.701	0.995	2353.16	1936.53	223.817
CH3	2862.36	22.666	0.082	2870.08	2399.45	283.104
C–O–C stretching	2931.8	21.742	0.356	2947.23	2870.08	50.386
vibrations of alcoholic	3425.58	14.668	0.125	3433.29	2985.81	327.453
vibrations of phenolic	3749.62	16.601	1.323	3788.19	3726.47	46.927

| Carboxylic | 3873.06 | 16.923 | 0.134 | 3880.78 | 3834.49 | 35.448 |

Table 3. Cadmium ion adsorption performance of carbon foam gelatin

Contact time (min)	C_0 (ppm)	The end Concentration (ppm)	Concentration adsorbed %
2	100	75 .1	24,9
10	100	69 .5	30.5
30	100	57 .5	42,5
60	100	21 .7	78,3
120	100	20.5	79.5
240	100	19.9	80.1
600	100	19 .9	80.1
840	100	19 .9	80.1

The surface area of CFG sample observed by nitrgen adsorption-desorption is 162.9 m^2/g dominated by 65% macroporous carbon, 20% microporous and 15% mesoporous part.. The pore size distribution of CFG sample is the combination of mesoporous (20-50 nm) and macroporous range (up to 60 nm) which is obtained as good correlation data with SEM data (Fig 2). The small pore of CFG due to the loss of water and ammonia during high-temperature treatment as good correlation with the theory [21]. This CFG sample shows a relatively multiform with maxima around 20-30 nm and up to 60 nm. The broken pipe sizes of pore systems (as observed from the SEM image) cannot be distinguished by the BJH analysis. The high adsorption at high pressures explain that CFG have a lot of macropores. The CFG exhibits considerably low surface area due to its macropore system and more rigid void spaces, which makes it be the efficient matrix as the hard template in the nanomaterial synthesis.
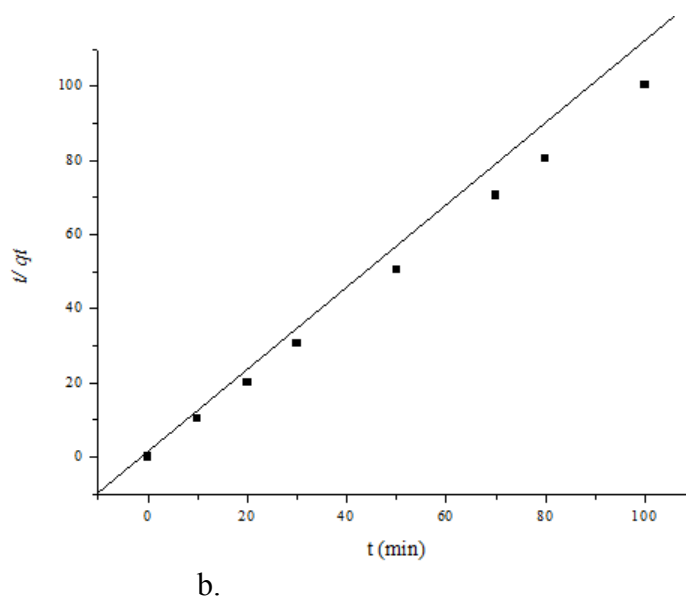

a.

b.

Figure 3 The plot uses a. the Lagergren equation and b Ho Mckay equation in cadmium ion adsorption on the carbon foam of gelatin (CFG)

Table 3 showed the shaking time effect during cadmium adsorption into carbon foam of gelatin (CFG). The shaking time effect cadmiun ion adsorption onto carbon foam gelatin (CFG) was observed by mixing 50 mg of carbon foam of gelatin (CFG) into 10 mL of 100 ppm of cadmium solution the stirr for 0-840 min at room temperatures.. The results indicated that the equilibrium adsorption amount (qe) of cadmiun ion onto carbon foam gelatin (CFG) slightly decreases with shaking for 20-60 minute indicating that the adsorption process is exothermic in nature. However, the value of qe slightly stable from by increasing sking time from 60 to 840 minute, showing that saturation of adsorbent for the adsorption of cadmiun ion onto carbon foam gelatin (CFG) in this range. The capacities of adsorption for cadmium was 46.7 mg/g obtained by using adsorbent dose 50 mg, initial concentration 50 ppm, contact time, 3 h; room temperature, stirring rate 150 rpm) which reached equilibrium at 55 min. The homogenous adsorption of cadmium ion into carbon foam of gelatin (CFG) using Lagergren and Ho and McKay equation and measuring data described in table below

Table 4. Lagergren and Ho and McKay equation

Model	Equation
Lagergren.	$ln\,(q_e - q_t) = \ln q_e - k_1\,t$
Ho and McKay	$\dfrac{t}{q_t} = \dfrac{t}{q_e} + \dfrac{1}{q_e{}^2 k_1}$

Table 3 shows the comparasion about Lagergren and Ho and Mckay equation. In the Lagergren kinetic model, the adsorbate concentration (A) is assumed to have no effect on the adsorption rate and the desorption rate is negligible. If q_t is an active site covered by adsorbat (A-S) at a given time and q_e is the adsorption capacity at equilibrium, the rate depends only on $(q_e - q_t)$ [9]. In the other side, Ho and Mckay approach appears based on the assumption that the adsorption rate is linearly related to the square of the number of adsorption vacant sites [10].

Broadly speaking, the whole coefficient of adsorption correlation of various models shows almost the same R value of 0.999 except the pseudo-order one model by Lagergren. The value of K Langmuir is closest to the value of K in the second order model of pseudo-Ho and McKay (1999), 1.82 and 1.72 g /mg respectively with a maximum value of 46.7 and 43.1 mg/g. This indicates that the adsorption of

cadmium ion on the carbon foam of gelatin (CFG) approaches a pseudo second order model in which the adsorption rate is linearly related to the square of the number of vacant adsorption sites. From these indications it can be concluded that the carbon foam of gelatin (CFG) adsorption capacity of 46.7 mg / g represents the value representing the material's ability to adsorb cadmium ion. Carbon foam of gelatin (CFG) performance in this study did not differ much with previously research.The result of adsorption process fits using Lagergren, and Ho and McKay adsorption model conclude that carbon foam gelatin (CFG) is new adsorbent with the high potential for maintain environmental problem.

4. Conclusion

Carbon foam CFG prepared by carbonization of gelatin as carbon precursor and sulfuric acid as catalyst. The pores of CFG materials generated by the release of water and ammonia molecule from gelatin. The pore type of CFG material was the macroporous system with average size is 20-30 nm and contain the huge size-disordered pipe up to 10 μm. The CFG material contains oxygen and carbon as the major element. The thermal stability of CFG was up to 1000 ºC indicating that CFG could be the new hard template candidate in the future. The adsorption performance summary describe that CFG material have high potential ability to adsorb cadmium pollutant in enviromental management.

Acknowledgements

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