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To cite this article: He Zhang & Jinglei Yang (2018) Hollow glass bubbles etched with tunable sizes of through-holes, Journal of Microencapsulation, 35:2, 192-203, DOI: [10.1080/02652048.2018.1452992](https://doi.org/10.1080/02652048.2018.1452992)

To link to this article: <https://doi.org/10.1080/02652048.2018.1452992>



Accepted author version posted online: 14 Mar 2018.
Published online: 26 Mar 2018.



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ORIGINAL ARTICLE



Hollow glass bubbles etched with tunable sizes of through-holes

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ABSTRACT

Hollow glass bubbles (HGBs) with through-holes at micron level were fabricated by etching them using diluted 1% hydrofluoric acid (HF) solution in a specially designed reaction system. In this study, the function of each component in the system was carefully investigated and improved to realise the controllable etching process. Various parameters were investigated to explore the optimal etching condition. Highest gross yield of about 85% and effective yield of about 50% were obtained at the optimised etching condition. A separating method was proposed to separate the etched HGBs with different hole sizes with the help of reduced pressure. After separation, HGBs with hole size at sub-micron level, less than 10 μm , and bigger than 10 μm , were achieved. The well-etched HGBs can be used as universal containers to store both reactive and inactive chemicals for applications in self-healing materials, biochemical engineering, and energy industry.

ARTICLE HISTORY

Received 13 December 2017
Accepted 12 March 2018

KEYWORDS

Hollow glass bubbles (HGBs); etching; through-hole; yield; separation

1. Introduction

Hollow glass bubble (HGB) is a newly developed material with low density, low thermal conductivity but high strength and good chemical stability. They can be readily dispersed into resins to render the matrix with lower weight, good sound-insulation, heat-resistance, as well as other improvements (Verweij *et al.* 1985, Park *et al.* 2005, Ashton-Patton *et al.* 2006, Yung *et al.* 2009, Aruniit *et al.* 2012). Due to the feature of high cavities, HGBs also find their ways as gas carriers for simple and small molecules besides the traditional applications as fillers. In 1994, Akunets *et al.* (1994) realised storage of hydrogen in HGBs with relatively thicker shell to bear the huge pressure inside. They can also be applied to laser fusion area when they are filled with neon (Ma *et al.* 1998), deuterium (Qiu *et al.* 2002), etc. However, the filling condition is very harsh even for these small molecules because of the dense and thick shell without any ready through-channels. Taking storing the simplest molecule, hydrogen, for an example, high pressure up to 100 MPa and high temperature up to 300 °C are necessary for their diffusion into the microsphere through the dense glass shell (Akunets *et al.* 1994).

Given the good properties of HGBs, they could also be employed as potential micro-containers for other purposes, like delivery and controlled release for drugs, catalysis, micro-reactors, and protection of reactive species. However, before being applied so, the shell permeability should be guaranteed because the load and release of the carried substances within the HGBs should be much more difficult than the small gaseous molecules even under high temperature and high pressure for long time. To date, various techniques have been explored to fabricate porous-wall HGBs, like spray-dry methods (Discher *et al.* 1999), layer-by-layer self-assembly methods (Caruso 2000, Ai *et al.* 2003, Liu and He 2007), templating methods (Wang *et al.* 2010, Xu *et al.* 2010, Liu *et al.* 2012), surface living polymerisation processes (Schmid *et al.* 2009), and modification of HGBs with dense shell (Newell *et al.* 2009). Due to advancement of fabrication techniques, size of through-pores can vary from nano-scale to micro-scale for different purposes. Li *et al.* (2010) synthesised porous-wall HGBs with pore size smaller than 10 nm by first directly fabricating the HGBs from glass powder and then leaching the sodium- and boron-rich phase in the dense shell by 4 M hydrochloric acid. This kind of porous wall

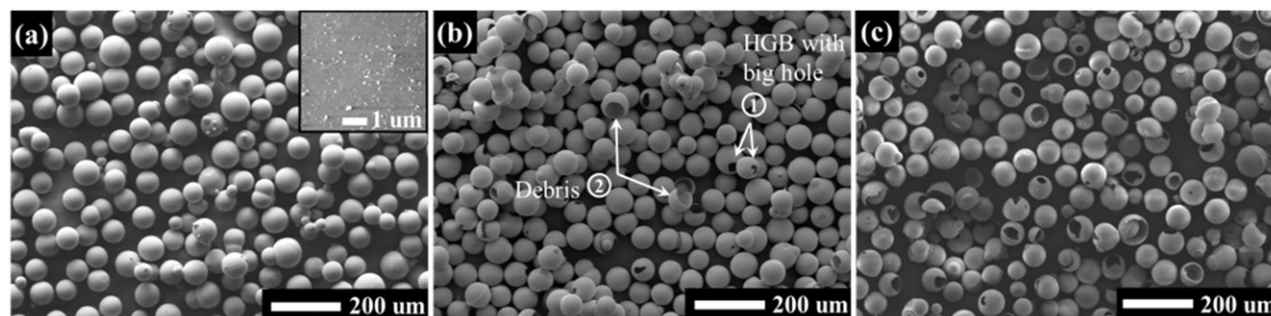


Figure 1. (a) HGBs with diameter of $67.5 \pm 7.4 \mu\text{m}$ used in this study after sieving and water-deposition. Inset at top right shows the loosely attached glass nano-particles; (b) Etched HGBs by Mixer I before water-deposition. Arrow ① indicates the etched HGBs with relatively big through-hole, and arrow ② indicates the debris in etched HGBs and (c) Etched HGBs by Mixer II before water-deposition. The etching condition for both cases is 160 ml HF solution with feeding rate of 35–40 drops/min for 2.0 g HGBs in 12 h.

HGBs can controllably uptake and release of molecule in 3–8 nm size, like anti-cancer drugs. By using a one-step method in a water/oil/water (W/O/W) ternary-phase emulsion system (Fujiwara *et al.* 2004, Pan *et al.* 2013), hollow HGBs with tunable through-holes from 250 to 560 nm can be fabricated. The authors reported that they are excellent support for polystyrene hydrogenation catalysts (Pan *et al.* 2013). Several big through-holes at micron level can be achieved via modifying the commercialised dense-wall HGBs by just putting them into diluted 1% hydrofluoric acid (HF) solution and then shaking them for a few minutes (Newell *et al.* 2009). The fabricated porous HGBs can be used as additives in lead-acid batteries to improve the poor ionic conductivity.

If properly modified, HGBs might be promising micro-containers for highly reactive healants for self-healing materials. Dense-wall HGBs with one or very few small through-holes is beneficial for this application considering ease of loading and long-term storage of healants. However, the above-mentioned porous HGBs either only have quite a number of nano-channels, which is adverse to the loading process, or have quite a few big holes at micron level, which is detrimental to the long-term storage. How to modify HGBs suitable for self-healing materials is attractive to advance this area.

In our previous study, we have reported etching of HGBs using diluted HF solution by a specially designed reaction system (Zhang and Yang 2013) and application of the etched HGBs as healant carriers for self-healing materials (Zhang and Yang 2014a, 2014b, Zhang *et al.* 2014). Although it works as designed, the etching quality and etching yield are relatively low, because of complexity of the reaction device and the etching process. In this study, first characteristics of the specially designed etching device were described

and improved. Later investigation about influence of the various factors was carried out to achieve an etching process with high etching quality, high yield, high efficiency, as well as high economy. The studied factors include the minimum volume of HF required for given amount of HGBs, stirring speed of propeller, feeding rate of HF solution, and finally amount of HGBs etched in one batch.

2. Experimental

2.1. Etching of HGBs

HGBs for etching with diameters in $63\text{--}90 \mu\text{m}$ ($67.5 \pm 7.4 \mu\text{m}$), as shown in Figure 1(a), were sieved from a commercialised HGB from 3M. Prior to being etched, the HGBs were water-deposited to remove debris. Water-deposition here means to immerse the HGBs in large amount of water in a separation funnel (Figure 2(a)) for about 4 h and dispose the deposited part. The floating HGBs on water top were collected and dried completely at room temperature (RT $\sim 22\text{--}25^\circ\text{C}$) for about 24 h for further usage. The details of procedure to etch HGBs using the specially designed mixer (Mixer I in Figure 2(c)) were reported in our previous work (Zhang and Yang 2013) and described briefly as below.

First, the collection zone was fully filled with deionised (DI) water through the outlet at bottom. M g pre-treated HGBs and enough DI water were added into the two top zones (reaction zone and separation zone) in the main mixer, and V ml 1% HF solution as etching agent was charged into the feeder. While the mixture was gently stirred at S rpm in reaction zone, the HF solution was slowly added into the mixture with feeding rate of F drops/min. With progress of the etching process, HGBs will deposit onto the bottom in the collection zone if their shell is etched through and the

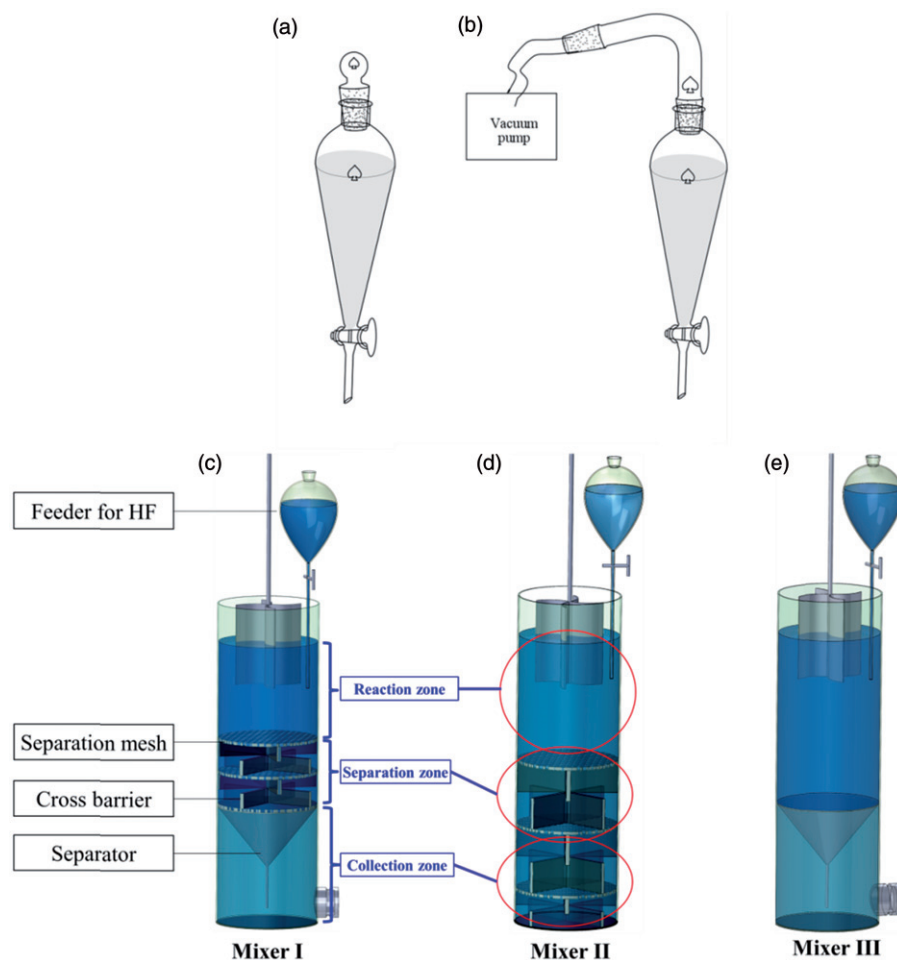


Figure 2. (a) Apparatus for water-deposition to remove debris in original HGBs and etched HGBs; (b) Apparatus for separation of etched HGBs with different hole sizes under reduced pressure of 250 mbar and 25 mbar. Etched HGBs with relatively bigger size of through-hole precipitate faster than these with relatively smaller size under the same reduced pressure. (c–e) Three different mixers adopted to study the function of separator, separation meshes and cross barriers: (c) Standard mixer (denoted as Mixer I) consisting of reaction zone for etching of HGB, separation zone for separation of etched HGB from intact HGB, and collection zone for collection of etched HGB. It has separation meshes and cross barriers in the separation zone, and separator between the separation zone and collection zone; (d) Control mixer (denoted as Mixer II) with separation meshes and cross barriers in collection zone to test the function of separator. The cycles just roughly show the regions for separation zone and collection zone and (e) Control mixer without separation meshes and cross barriers in the separation zone to test their function.

solution infiltrates into them. The process was ceased when all the HF solution was exhausted and the mixture further reacted for about 1–2 h. The etched HGBs collected from collection zone were rinsed for 3–4 times to remove residual HF, separated, and finally completely dried at RT for about 24 h.

In order to check functions of the key components, i.e. separator between separation zone and collection zone, and separation meshes and cross barriers in separation zone, other two control mixers (denoted as Mixers II and III as shown in Figure 2(d,e), respectively) were adopted for the etching process for comparison. As shown in Figure 2(d), Mixer II has more separation meshes and cross barriers to replace the separator. And in Mixer III shown in Figure 2(e), the separation meshes and cross barriers were absent. In the etching

process, the parameters, i.e. M , V , S , and F , were unknown and need to be optimised to give the best etching quality and highest etching yield. Etching quality was qualitatively determined by visually checking SEM images of the collected etched HGBs. Better quality means more etched HGBs with small through-holes at micron or sub-micron level but less etched HGBs with big through-holes (arrow ① in Figure 1(b)) and debris (arrow ② in Figure 1(b)) before the water-deposition process to remove them. The yield was defined and measured as described below in section 2.3. The parameters for etching adopted in the experiment are given in Table 1. As feeding rate of HF solution decreases gradually with the decreased HF solution in feeder during the etching process, the listed feeding rates in Table 1 are the initial feeding

Table 1. Etching conditions adopted in the experiment to optimise the etching process.

Amount of HGBs used in one batch (M/g)	Added HF solution (V/ml)	Stirring speed (S/rpm)	Feeding rate ^a (F/drops/min)
2.0	140	45	36.7 ± 0.6
2.0	150	45	36.0 ± 0.4
2.0	160	45	35.9 ± 0.6
2.0	170	45	36.6 ± 0.6
2.0	180	45	36.5 ± 0.5
2.0	160	40	36.5 ± 0.9
2.0	160	45	35.9 ± 0.4
2.0	160	50	36.6 ± 0.6
2.0	160	55	36.8 ± 0.3
2.0	160	45	27.8 ± 0.4
2.0	160	45	32.4 ± 0.6
2.0	160	45	34.3 ± 0.6
2.0	160	45	36.6 ± 0.6
2.0	160	45	39.0 ± 0.5
2.0	160	45	44.8 ± 0.7
2.0	160	45	53.1 ± 0.6
1.0	80	45	35.9 ± 0.7
1.5	120	45	35.9 ± 0.4
2.0	160	45	36.6 ± 0.6
2.5	200	45	36.0 ± 0.5
3.0	240	45	35.6 ± 0.3

^aThe averaged feeding rates with standard deviations were calculated based on the feeding rates of three independent repeats.

rates at the very beginning of etching process. As it is impossible to hold the feeding rate at exactly the same value in this system, the feeding rates vary a little bit among different runs.

2.2. Separation of etched HGBs with different hole sizes

Since HGBs with small through-holes are the desired part for our purpose, water-deposition was applied to the etched HGBs to remove debris generated during the etching process. Briefly, etched HGBs were added into a separation funnel (Figure 2(a)) with large amount of water. The mixture in the funnel was shaken by hand for about 5 min to immerse the HGBs in the water followed by being kept still for about half an hour for settling of debris. Deposition, i.e. debris, was removed through the bottom switch. In order to remove most of the debris, the process was repeated for 3–4 times. And finally, HGBs floating on water top was collected and dried for further separation.

The device in Figure 2(b) was adopted to narrow down size distribution of the through-holes on etched HGBs. The etched HGBs after removal of debris were added into the funnel with enough water. Under being shaken continuously by hand to immerse the HGBs in water, the mixture in the funnel was subjected to a reduced pressure of about 25 mbar for about 1 min to precipitate HGBs with relatively bigger through-holes. And then the reduced pressure was

removed to force infiltration of water into chambers of the etched HGBs, leading to the increase of density and finally precipitation of these HGBs. In order to remove them as many as possible, the process was repeated for 3–4 times. And finally, the HGBs floating on water top and the HGBs precipitating to the bottom were collected and dried separately. For the collected deposited HGBs, they were further separated to narrow down the through-hole size with the same process under a reduced pressure of about 250 mbar for 3–4 times. The HGBs floating and precipitating were collected and dried separately as the final products.

2.3. Yield measurement for etching process

The yield of the etching process for HGB is a key factor. Usually, mass ratio before and after treatment is widely adopted for calculation of yield. However, during the etching process, some of the mass is etched away by its reaction with HF. If using this definition, the measurement will be seriously underestimated. Due to this, the volume ratio before and after the etching process should be a better estimate of the gross yield, as expressed as:

$$Y_{Gross} = \frac{V_{Gross}}{V_{Input}} \times 100\% \quad (1)$$

where Y_{Gross} means gross yield, V_{Gross} and V_{Input} mean volumes of the collected etched HGBs before water-deposition and input original HGBs, respectively.

Given the fact that there is some debris in the collection, effective yield of the process was defined as volume ratio of the collected HGBs after water-deposition to the input original HGBs, as shown in Equation (2):

$$Y_{Effective} = \frac{V_{Effective}}{V_{Input}} \times 100\% \quad (2)$$

where $Y_{Effective}$ means effective yield and $V_{Effective}$ means volume of collected etched HGBs after water-deposition.

Volume of HGB was measured using measuring cylinder as described below. After the measuring cylinder (capacity of 10 ml or 25 ml) was filled with HGB, it was gently tapped to minimise the space between the added HGBs. The tapping process was repeated until there is no volume change in the cylinder. The final constant volume was recorded for the calculation of the two yields. In order to obtain an averaged value with standard deviation, three independent

measurements were carried out based on three repeats in each set of parameters.

3. Results and discussion

3.1. Function of components in the fabricated practical system

3.1.1. Separator

As stated in [section 2](#), Mixer II, which does not have a separator between the middle separation zone and the bottom collection zone, was used to etch HGBs to test its function. Since both separation zone and collection zone are inserted with separation meshes and cross barriers, they connect with each other without clear boundary. The ovals in [Figure 2\(d\)](#) only schematically show the approximate regions of the three zones. This mixer can also realise the controllable etching process. [Figure 1\(b,c\)](#) shows SEM images of the obtained HGBs etched in Mixer I and Mixer II before water-deposition. The etching condition for the imaged HGBs is that 2.0 g HGBs were etched by 160 ml HF solution with feeding rate of 35–40 drops/min when they were stirred at 45 rpm for 12 h. Compared with the etched HGBs collected from Mixer I, these collected from Mixer II have more HGBs with relatively bigger through-holes (arrow ①) and glass debris (arrow ②). Quantitative measurement shows that the gross yield and effective yield for the etching process in Mixer II under the optimised etching condition are about 51% and 25%, respectively, which are much lower than these by Mixer I (about 85% and 50%, respectively, as mentioned later). The difference can only be explained by the better isolation of collection zone from separation zone introduced by the inserted separator. Attributed to this, circulation and over-etching by the conveyed HF to collection zone of the well-etched HGBs deposited in collection zone can be minimised or even totally avoided by the separator with small connection channel.

3.1.2. Separation meshes and cross barriers

The original purpose of the inserted separation meshes and cross barriers is to form the separation zone to slow down the water flow as well as the HGBs inside. However, besides forming the quasi-static zone, these barriers have some other special promotion for the immersion of HGBs in the solution for etching reaction. [Figure 3\(a,b\)](#) shows digital images of the etching processes in Mixer I and Mixer III without barriers, respectively. With the inserted barriers, more HGBs were

immersing in the solution during stirring and correspondingly less HGBs were floating on solution top. At the end of the etching process when the reaction was ceased, very few HGBs remained in the top zones. However, things are totally different for Mixer III when all the parameters were held unchanged as used in Mixer I. Majority of the HGBs was floating on solution top rather than immersing in solution. And at the end of the etching process, there were quite a lot floating HGBs keeping unetched. [Figure 3\(c,d\)](#) separately shows SEM images of the collected HGBs etched in Mixer I and Mixer III. The etching condition for the imaged HGBs is that 2.0 g HGBs were etched by 160 ml HF solution with feeding rate of 35–40 drops/min when they were stirred at 45 rpm for 12 h. Evidently, poor etching quality with more debris was found with the absence of barriers. Quantitative study by measuring the yield also gives the same result that low gross yield of about only 11.5% was obtained, which is much lower than that by Mixer I under the same etching condition, as mentioned later.

3.1.3. Feeder for HF solution

The addition of HF solution using a feeder with an extension tube into the mixer is of great significance for the whole etching process. It is necessary to modify the plastic feeder with a thin extension tube which is able to be immersed into the solution in the mixer. Among all the stirring speeds adopted in this system (40–55 rpm), there are a lot of intact HGBs floating on solution top ([Figure 3\(a\)](#)) because of their low density and the relatively small driving force generated by the low-speed agitation. The reaction is very fast if a big drop of HF solution falls directly onto the floating HGBs, leading to their non-uniform etching. Besides that, diameter of the extension tube should be small enough (about 1–2 mm) so that the circulating HGBs in mixer cannot flow up into or even block it.

[Figure 4](#) shows the fed volume of HF solution into the mixer from the feeder as a function of time when 160 ml was added with initial feeding rate at about 36 drops/min. The feeding rate is relatively higher at the beginning because of the relatively higher pressure generated by the HF solution in the feeder, and decreases gradually due to the decreased water pressure by less HF solution in feeder. Since the early added HF only etches away the adhered nano-particles and thins the shell of HGB evenly rather than generates through-holes, a faster feeding rate can shorten the etching duration and therefore lower down possibility of breaking HGBs. While with a lower feeding rate during the through-hole forming stage, lower

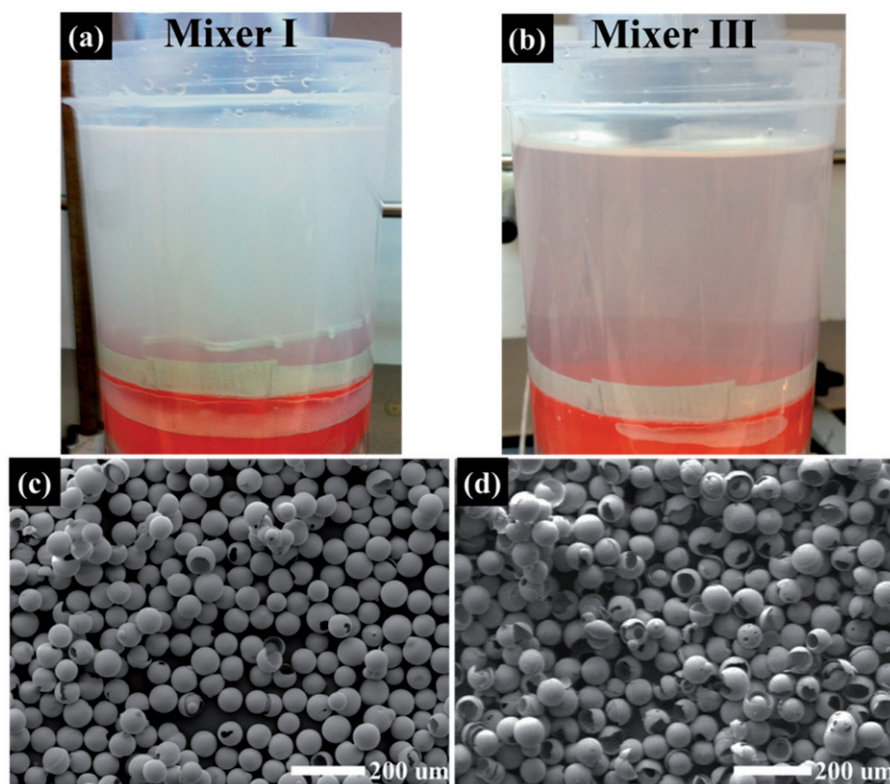


Figure 3. Digital images showing function of separation meshes and cross barriers in the separation zone, and SEM images of the collected HGBs from the corresponding mixers: (a) Mixing of HGBs in reaction zone and separation zone during the etching process in Mixer I with separation meshes and cross barriers, and (c) The corresponding etched HGBs; (b) Mixing of HGBs during the etching process in Mixer III without separation meshes and cross barriers, and (d) The corresponding etched HGBs. The etching condition for both cases is 160 ml HF solution with feeding rate 35–40 drops/min for 2.0 g HGBs in 12 h.

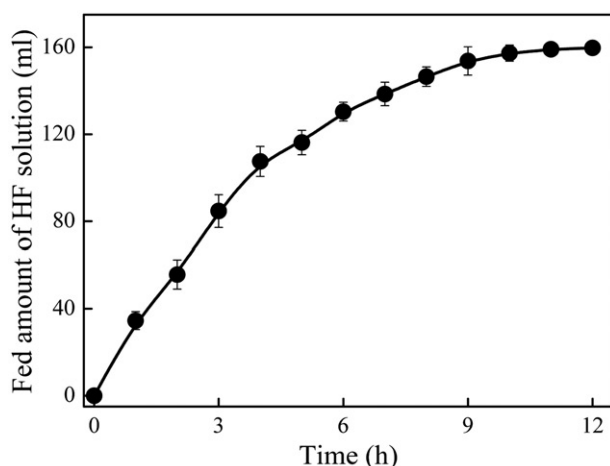


Figure 4. Fed volume of HF solution as a function of time into mixer for etching reaction. The total fed volume of HF solution is 160 ml, and the initial feeding rate is about 36 drops/min. The curve was plotted based on three independent repeats with feeding rate of 36.4 ± 0.8 drops/min. The feeding rate of HF solution is relatively higher at early stage of the feeding process, and slows down continuously.

residual concentration of HF in the mixer will alleviate over etching of the well-etched HGBs in the two top zones because infiltration of solution into the chamber and sinking of the well-etched HGBs take time.

The inverted pear-shape feeder also assures that most of etching agent is added into the mixer with a faster rate at the early stage.

3.2. Optimisation of etching process

3.2.1. Effect of added amount of HF solution

The required minimum volume of HF solution for given amount of HGBs is very important for the etching process, considering the yield and quality of etched HGBs. Figure 5(a) shows the yields of process with respect to the fed volume of HF solution. It can be observed that, for the adopted HGBs, the minimum volume for 2.0 g is around 160 ml. With decreasing the fed volume, the gross yield and effective yield decrease dramatically because the earlier fed HF mainly etches away the nano-particles on the shell and reduces shell thickness of all HGBs rather than generates holes in the shell due to the uniformly etching feature. While with increasing the fed HF solution from 160 ml, the yields decrease gradually. Theoretically, over-etching of the deposited HGBs in collection zone by the later added HF solution can be avoided by this specially designed mixer. However,

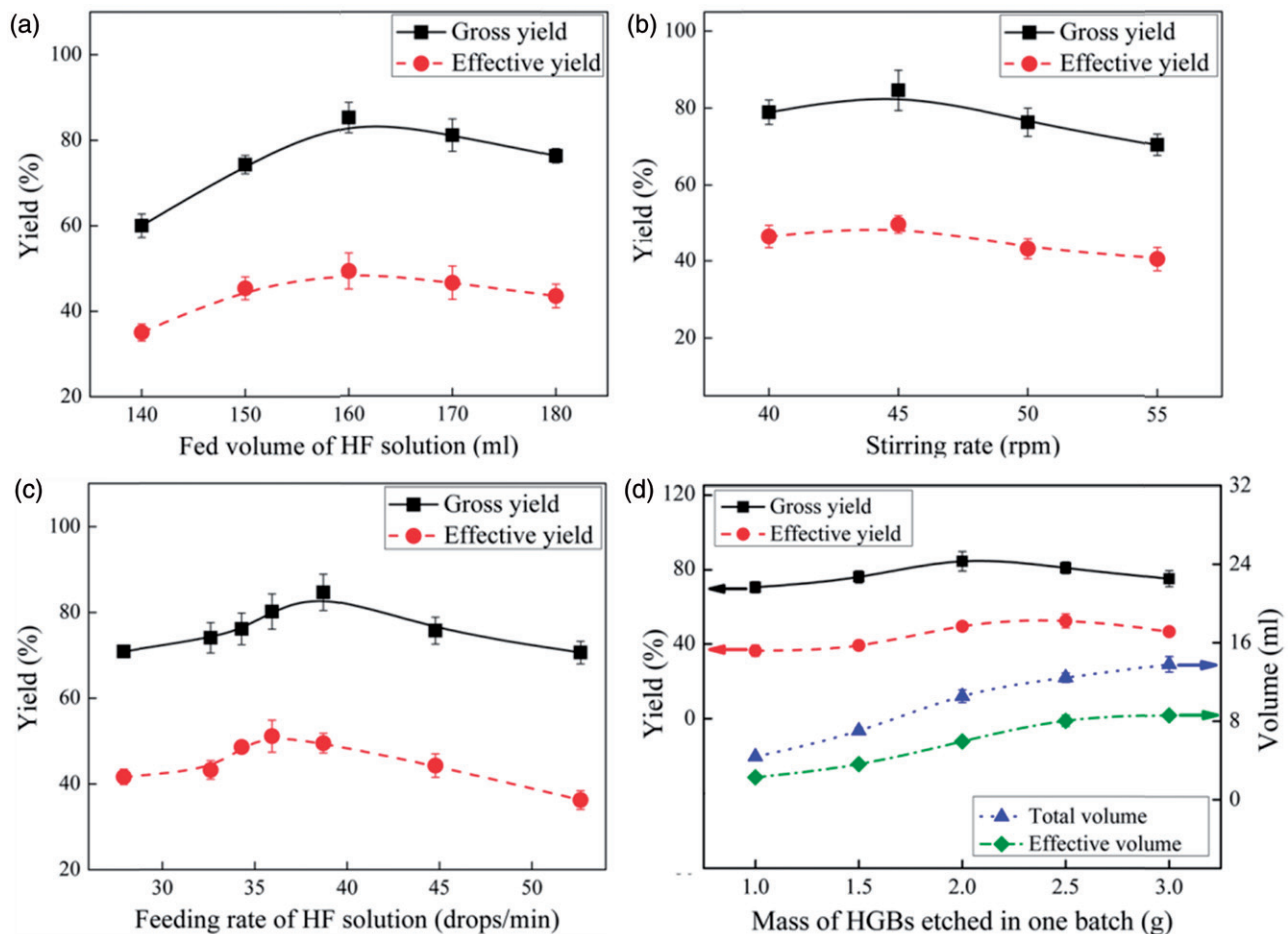


Figure 5. (a) Influence of the fed volume of HF solution on the gross and effective yields at feeding rate of 35–40 drops/min and stirring speed of 45 rpm for 2.0 g HGBs etched for 12 h. Highest yields were achieved when 160 ml HF solution was fed. (b) Influence of the stirring speed on the gross and effective yields when 160 ml HF solution was fed at 35–40 drops/min for 2.0 g HGBs for 12 h. Highest yields were achieved when 45 rpm was adopted for the agitation. (c) Influence of feeding rate of HF solution on the gross and effective yields when 160 ml HF solution was fed for 2.0 g HGBs stirred at 45 rpm for 12 h. Highest gross yield was achieved at feeding rate of 39.0 ± 0.5 drops/min, while highest effective yield was achieved at feeding rate of 36.6 ± 0.5 drops/min. (d) Influence of the mass of HGB etched in one batch on the gross and effective yields, and the collected gross and effective volumes when 80 Ml HF solution was fed at 35–40 drops/min and stirring speed of 45 rpm for M g HGBs etched for 12 h. Highest gross yield and effective yield were separately achieved when 2.5 g and 2.0 g HGBs were etched in one batch, although the collected total volume and effective volume increase with increasing mass of HGB etched in one batch.

given that the three different zones are not completely separated from each other, diffusion of HF from the two top zones to collection zone could take place during the etching process, especially when excess HF solution is fed at the end. Due to this, when the added HF solution exceeds the required minimum volume, over-etching of the deposited HGBs would occur, leading to decrease of quality and yields.

3.2.2. Effect of stirring speed

The adopted stirring speed should be able to excite circulation of HGBs while avoiding serious striking of HGBs with propeller during etching, due to the serious density mismatch of the mixture and fragility of the

thin-shell HGBs. Figure 5(b) describes the trends of the two yields when stirring speed changed from 40 rpm to 55 rpm. The highest gross yield of $84.6 \pm 4.2\%$ and effective yield of $49.4 \pm 2.3\%$ were found at the same time when stirring speed of 45 rpm was adopted. Under circumstance of lower speed less than 45 rpm, majority of the HGBs is floating on solution top rather than immersing in the etching solution because of the smaller driving force generated at lower stirring speed. With increasing the stirring speed from 45 rpm to 50 rpm, and further to 55 rpm, both the gross yield and effective yield of the etched HGBs decrease because more HGBs are broken due to the stronger hitting of HGBs in the mixer at higher stirring speed. Figure 6 shows SEM images of the collected etched

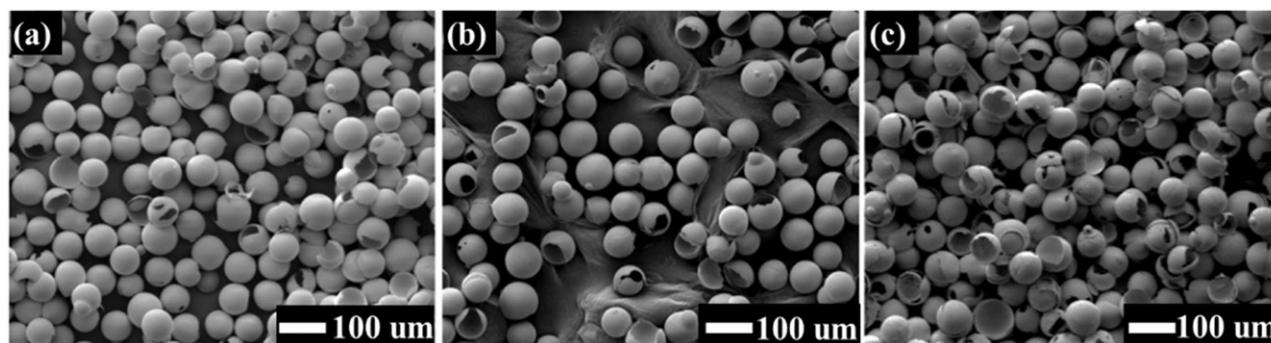


Figure 6. Collected HGBs before water-deposition at stirring speed of: (a) 45 rpm; (b) 50 rpm; and (c) 55 rpm. With increasing the stirring speed, debris and HGBs with large holes increase rapidly, leading to the lower etching quality and yields. The etching condition is 160 ml HF solution with feeding rate of 35–40 drops/min for 2.0 g HGBs for 12 h.

HGBs before water-deposition. From 45 rpm to 55 rpm, debris and HGBs with large holes increase rapidly, leading to the lower etching quality and yields at higher stirring speeds.

3.2.3. Effect of feeding rate of HF solution

Feeding rate of HF solution determines the residual HF concentration in the mixture and the etching duration for given amount of HGBs in the mixer. A lower residual HF concentration in the mixture is beneficial to the etching quality since the through-holes on HGBs are easier to be etched and enlarged in solution with relatively higher HF concentration due to their loose structure or thinner feature. And a longer etching duration is detrimental to the etching quality because it will lead to a higher chance for collision of HGBs in the mixer to become debris with low quality and the associated low yields. Figure 5(c) shows the trends of the two yields with regard to the feeding rate of HF solution. It can be observed that the highest gross yield of $84.6 \pm 4.2\%$ was found when the feeding rate was 39.0 ± 0.5 drops/min while the highest effective yield of $51.1 \pm 3.7\%$ was found when the feeding rate was around 36.6 ± 0.6 drops/min. Away from the peaks for both sides, the two yields decrease with the change of feeding rate. For a lower feeding rate, although the residual HF concentration is low in solution, the whole etching process will take a longer period, which has adverse effect on the etching quality and yield. While at a higher feeding rate, the residual HF concentration in the mixture will increase, possibly causing over-etching of the well-etched HGBs in the two top zones because filling and sinking of the well-etched HGBs take time. The shift of the peak of gross yield from that of effective yield to a higher feeding rate means there are more etched HGBs with relatively big holes, which form at a higher feeding rate of HF

and can be washed away during water-deposition. As these etched HGBs with big holes contribute more volume to the gross volume than debris generated by impact in the mixer, the higher gross yield at higher feeding rate of HF is understandable. Since the effective yield is the usable part and it does not vary too much when feeding rate of HF changes from about 35 drops/min to 40 drops/min, this range of feeding rate can be adopted in the etching process.

3.2.4. Effect of HGB mass etched in one batch

Efficiency of this etching process is determined by not only etching duration, but also how many HGBs can be etched in one batch. Figure 5(d) shows influence of HGB mass used in one batch on the collected volumes and yields of etched HGBs. As can be seen from the graph, the total volume obtained from one batch increases with increasing the input HGBs up to 3.0 g. Further increase of input HGBs is impossible due to the limited volume of the feeder and the main mixer. However, the highest gross yield was achieved when 2.0 g HGB were etched in one batch, while the highest effective yield was obtained at 2.5 g. Same as shown in Figure 5(c), separation of the two peaks appears here too. The reason is similar to the explanation for separation of the two peaks caused by feeding rate of HF solution. The residual concentration of HF per unit HGB decreases when more HGBs are etched in one batch with the same feeding rate of HF solution. Beyond their peaks at both sides, the two yields decrease gradually. The low yield caused by more HGBs etched in one batch can be easily understood since the collision between HGBs, especially the etched HGBs with thinner shell, would be more frequent when more HGBs are present in the given volume. However, it is very strange that the yields decrease with decreasing HGBs etched in one batch

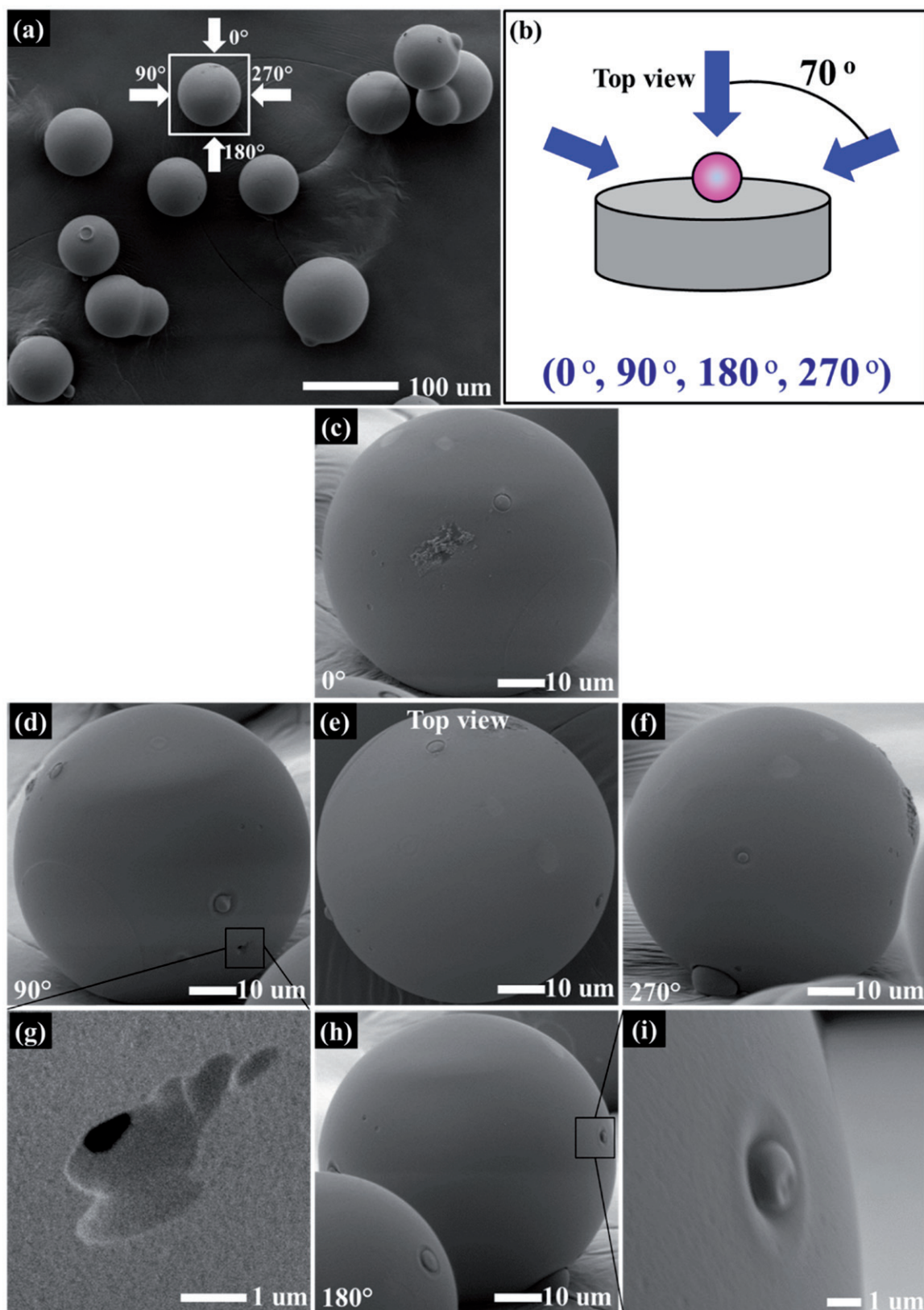


Figure 7. (a) Overview of etched HGBs with small through-hole at micron or sub-micron level floating under reduced pressure of 25 mbar; (b) schematic configuration of SEM imaging for observing one etched HGB from different views; (c–f and h) Corresponding SEM images from different views: (c) 0°, (d) 90°, (e) Top view, (f) 270°, and (h) 180°; (g) a through-hole at sub-micron level on the etched HGB enlarged from (d), and (i) A pre-defective area left unetched through after the etching process enlarged from (h).

from 2.0 g, given that collision among HGBs should be less in a small batch. Considering the fact that there are still quite a few floating HGBs keeping unetched at the end of etching process in the 1.0 g and 1.5 g batches, possible reason for this phenomenon might be that the occurrence of the etching process requires a minimum concentration of HF in the mixture. As a consequence of this, part of the earlier added HF solution is consumed to give the minimum concentration in the mixer rather than contributes to the etching process itself, leading to the low yields for the etching processes for the 1.0 g and 1.5 g batches.

3.3. Separation of etched HGBs with different hole sizes

The separation mechanism of etched HGBs with different through-hole sizes is much similar to that for separation of etched HGBs from intact ones during the etching process. When the device as shown in Figure 1(b) for separation is subjected to reduced pressure by evacuation, the air inside the etched HGB flows out due to the relatively high pressure inside the etched HGB. With the removal of reduced pressure thereafter, water around the etched HGB is forced into chamber

of the etched HGB due to the relatively high pressure outside. By repeating this process, density of HGB gradually increases due to the infiltrated water. When density of HGB is bigger than that of water, they will precipitate onto the bottom under gravity when left to stand. During the separation process with the aid of reduced pressure, the bigger the through-hole size, the faster the infiltration of water and thereafter the deposition process for the same reduced pressure at 25 mbar or 250 mbar.

Figure 7(a) shows the obtained etched HGBs with very small through-hole. In order to check how large the hole size and how many holes in the shell, one HGB chosen from Figure 7(a) was observed from different views, as schematically shown in Figure 7(b). Figure 7(c–i) gives images of different views and enlargements. It is observed that only one very small through-hole at sub-micron level can be found on almost all the HGBs after the process at reduced pressure of 25 mbar. It is not sure whether there are any holes at the point adhered to the bottom tape. Nevertheless, the fact that HGBs with very few through-holes (one or two) at sub-micron level can be confirmed. Figure 8(a,b) separately shows general view and enlarged view of the etched HGBs precipitating at

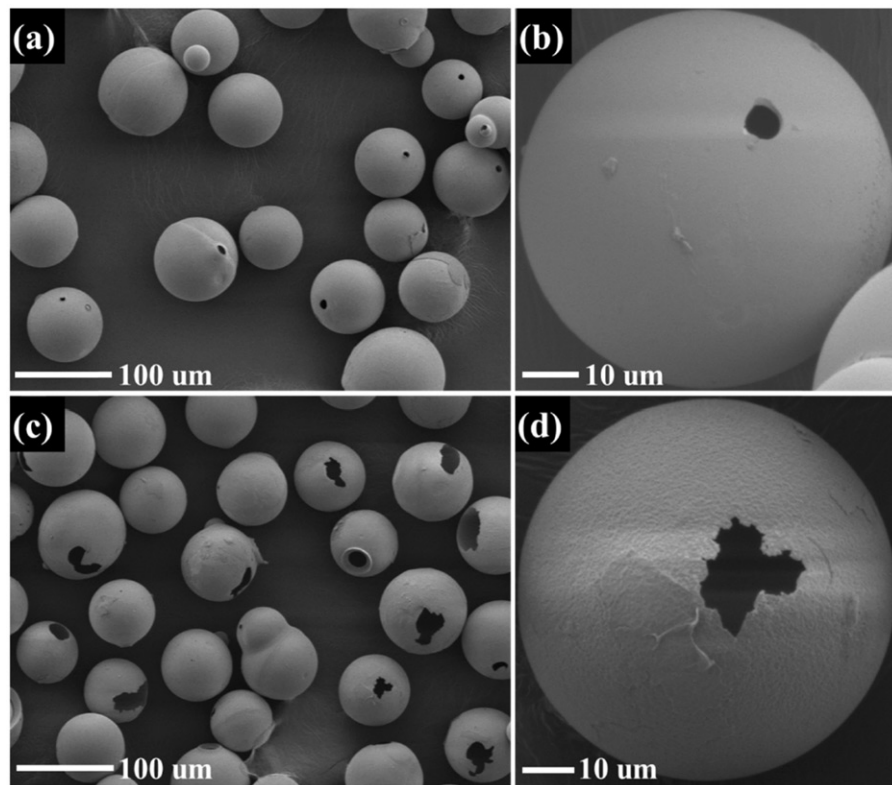


Figure 8. (a,b) Etched HGBs with through-holes less than 10 μm . The imaged HGBs float under reduced pressure of 250 mbar but precipitate under reduced pressure of 25 mbar; (c,d) Etched HGBs with through-holes bigger than 10 μm . The imaged HGBs float during water-deposition to remove debris but precipitate under reduced pressure of 250 mbar.

bottom under 25 mbar but floating on water top under 250 mbar. It is observed that the size range of through-holes is roughly less than 10 μm . Figure 8(c,d) shows general view and enlarged view of the etched HGBs precipitating under 250 mbar. It can be seen from the images that most of the hole is bigger than 10 μm . In summary, after the separation process, etched HGBs with different hole sizes can be separated roughly for different purposes.

4. Conclusions

The etching quality of HGBs was determined by not only configuration of the specially designed device, but also process control. The components, i.e. separator, separation meshes and cross barriers, and feeder for HF solution, of the etching system are all of great significance to guarantee the controllable etching process of HGBs with high quality and yield. Parametric study revealed that the optimised etching condition for 2.0 g HGBs is 160 ml HF solution with feeding rate of 35–40 drops/min when they are stirred at 45 rpm for about 12 h. The gross yield and effective yield arrive 85% and 50%, respectively, under this condition. And finally, the etched HGBs with different hole sizes, i.e. sub-micron, less than 10 μm , bigger than 10 μm , were roughly separated with the aid of reduced pressure.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

Yang greatly acknowledges the partial financial support from HKUST Start-up Fund (R9365). Zhang is grateful to the support from the Key Program of National Natural Science Foundation of China [Grant No. 51435005], the National Instrumentation Program [Grant No. 2012YQ230043], the Science and Technology Program of Guangzhou, China [Grant No. 201607010240], and the Science and Technology Planning Project of Guangdong Province, China [Grant No. 2015B090904004].

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