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Novel membrane emulsification method of producing highly uniform silica particles using inexpensive silica sources

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Abstract

A membrane emulsification method for production of monodispersed silica-based ion exchange particles through water-in-oil emulsion route is developed. A hydrophobic microsieve membrane with 15 µm pore size and 200 µm pore spacing was used to produce droplets, with a mean size between 65 and 240 µm containing acidified sodium silicate solution (with 4 and 6% wt. SiO₂) in kerosene. After drying, the final silica particles had a mean size in the range between 30 and 70 µm. Coefficient of variation for both the droplets and particles did not exceed 35%. The most uniform particles had a mean diameter of 40 µm and coefficient of variation of 17%. The particles were functionalised with 3-aminopropyltrimethoxysilane and used for chemisorption of Cu(II) from an aqueous solution of CuSO₄ in a continuous flow stirred cell with slotted pore microfiltration membrane. Functionalised silica particles showed a higher binding affinity toward Cu(II) than non-treated silica particles.

Key words Membrane emulsification · Silica particles · Ion-exchange · Microfiltration · monodisperse particles · Functionalised silica gel

1 Introduction

There has been an increasing interest in the production of functionalised porous silica microspheres for use in analytical, preparative, and ion exchange columns, requiring particle diameters greater than 1 µm. A control of particle size and internal microstructure of silica particles is critically important in ion exchange, biochemical sensing [1], drug delivery [2], catalysis [3], and chromatography. Silica particles can be fabricated from organic silicon precursors, e.g. siliciumalkoxide [4] or inorganic materials, such as silicate solutions [5]. In the latter case, acidified sodium silicate solution is dispersed in an organic phase to form water-in-oil (W/O) emulsion [5] or atomized in air [6]. Silicic acid formed by acidification of sodium silicate immediately undergoes spontaneous

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condensation polymerisation which progresses within the dispersed droplets, eventually leading to the formation of branched polymer with –Si–O–Si– bonds. Upon drying the formed silica hydrogel shrinks to xerogel. A surfactant can be dissolved in the silica solution to additionally tailor the internal gel structure (surfactant templating) [7]. This paper reports a novel W/O emulsion route based on using microsieve-type membrane to prepare porous silica microspheres with a controllable size between 30 and 70 μm . To the best of our knowledge, membrane emulsification has only been used for fabrication of silica particles up to 3 μm in size and only inorganic membranes were used in this application [8-11].

After functionalisation, the produced silica particles have been used as ion-exchange particles for removal of copper from an aqueous solution. Copper(II) is often used as a model cation for investigation of performance of ion exchangers. In addition, copper is widely present in industrial wastewaters and its disposal represents a big environmental threat, since it can induce severe health problems. Classical techniques for removal of copper from waste waters are flotation, chemical precipitation, and ion exchange with organic resins, such as sulfonated poly(styrene-co-divinylbenzene) resins [12]. In this work, new inorganic ion-exchange particles have been fabricated and tested for copper removal.

2 Experimental

Preparation of W/O emulsion. The dispersed phase was prepared by dripping sodium silicate solution, containing 10 or 15 wt % SiO_2 , into 1M H_2SO_4 under vigorous stirring until pH of 3.5 was achieved. The continuous phase was 5 wt% Span 80 in low odour kerosene (both supplied by Sigma Aldrich, UK). Emulsification was performed using a Micropore Technologies Ltd. Dispersion Cell (Figure 1a) equipped with a hydrophobic nickel membrane with 15 μm pore size, 200 μm spacing between the pores and 8.5 cm^2 effective membrane area. The cell was filled with 100 ml of continuous phase and 10 ml of dispersed phase was injected at constant controllable rate using a Harvard Apparatus model 11 Plus syringe pump.

Production of silica particles. The resultant W/O emulsion was transferred to a beaker, diluted with kerosene and continuously stirred until the hydrogel was formed. Beside the spherical silica particles, needle shapes of silica were also created. To filter them out, a microfiltration cell with slotted pore membrane was used. The membrane with an effective membrane area of 8.5 cm^2 was provided by Micropore Technologies Ltd. Slots were 4 μm wide and 250 μm long enabling that even the smallest silica particles were maintained above the membrane. No spherical particles were observed in the filtrate and

the amount of needle-like silica was less than 2% of the total particle mass being filtered. After removal of non-spherical silica, the particles were washed with at least 250 ml of acetone followed by water washing to remove Span 80 and kerosene. After that, the particles were dried at room temperature and calcined at 550°C with a ramp step of 20°C min⁻¹ for 6 hours. Specific surface area of calcined silica particles was determined by the adsorption of nitrogen gas using Micromeritics ASAP 2020 [13].

Functionalisation of calcined silica particles and combined microfiltration and ion exchange. 10 g of calcined silica particles, with a specific surface area of 360 m² g⁻¹ was first washed with a mixture of nitric and hydrochloric acid in a ratio of 1:3 for 2 h in order to remove possible metal impurities. The particles were then filtered, dried in a vacuum at 200 °C, and refluxed in a mixture of 80 ml of toluene and 10 ml of 3-aminopropyltrimethoxysilane for 24 h. After that, the particles were collected by filtration, washed with ethanol and then transferred to a Soxhlet extractor and washed with toluene for 24 h, to eliminate possible traces of 3-aminopropyltrimethoxysilane. According to Lam et al. [14] silica functionalised with 3-aminopropyltrimethoxysilane is capable of adsorbing copper ions from solutions. Combined microfiltration and ion exchange was carried out at room temperature in a continuous flow stirred cell (Figure 1b) provided by Micropore Technologies Ltd. A metal membrane with 8×400 μm slots was fitted to the bottom of the cell. This slot width was fine enough to keep all particles in the cell. An aqueous solution of CuSO₄ containing 10 g cm⁻³ Cu(II) was continuously delivered to the cell at a constant flow rate of 8 ml min⁻¹. 10 ml samples of the effluent stream were taken at regular time intervals to determine Cu(II) concentration using an Atomic Absorbance Spectrophotometer (Spectra AA-200 Varian).

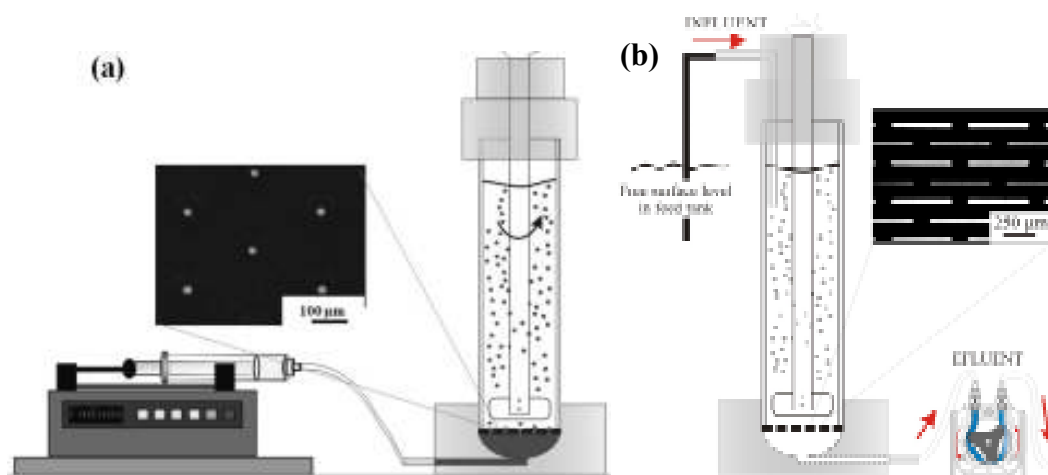


Figure 1 Schematic illustration of: (a) Dispersion Cell containing a paddle stirrer above a disk membrane with cylindrical 15 μm pores used for membrane emulsification and (b) microfiltration system with slotted pore membrane used for combined microfiltration and ion exchange [12].

3 Production of silica gel using membrane emulsification

Figure 2 illustrates the effect of paddle rotation speed and flow rate of the dispersed phase on the droplet size of the W/O emulsions produced. An increase of the rotation speed increases the shear stress on the membrane surface and the droplet formation time shortens, therefore, the smaller droplets are produced. The force balance model based on average shear stress [15] provided a good prediction of the droplet size for a very low flux of $1 \text{ L m}^{-2} \text{ h}^{-1}$. The parameters used for modeling are provided elsewhere [15]. Droplets produced using the higher injection rate are larger than the ones produced at lower injection rate and do not fit the model curve. Two explanations of this phenomenon are possible. First, the model does not take into consideration a dispersed phase inflow during the necking time. The detachment of the droplet is not instantaneous but requires a finite time, the necking time [16], during which an additional amount of dispersed phase flows into the droplet. Secondly, the model calculations are made using the equilibrium interfacial tension (2.7 mN m^{-1}) which is lower than the actual interfacial tension during drop formation. It should be noted that the interfacial tension if no surfactant is present is 16 mN m^{-1} and during drop generation the liquid/liquid interface is not fully saturated with surfactant molecules. The produced droplets were stirred in a beaker in order to allow gelling and formation of a hydrogel. Once gelled, the hydrogel particles were dried to form a xerogel. Figure 3 illustrates the shrinkage of the dispersed phase droplets during their transformation into silica gel particles. During condensation polymerization the droplets will shrink due to water loss as the hydrogel is formed. The hydrogel particles were left to dry for several days at room temperature. During this drying stage liquid present in the pores is removed, the structure compresses and the porosity is reduced by the surface tension forces as the liquid is removed leaving dried silica particles (xerogel). Drying at room temperature was followed by calcination, but further shrinkage of the dried silica particles was not observed. The size of final silica particles was found to be 2.3 times smaller than the initial droplet size. However, the particles are still significantly bigger than would be predicted by a mass balance of the silica used in their formation. It can be explained by a significant amount of internal porosity, which is 88% and 64% for the hydrogel and xerogel particles, respectively. The coefficient of variation (CV) for xerogel particles was below 31% and was minimal (17%) for the particle diameter of $40 \mu\text{m}$.

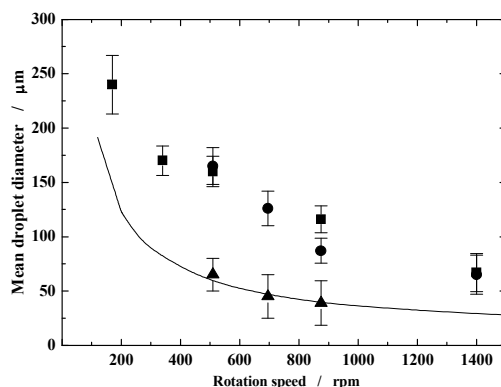


Figure 2 Droplet diameters of produced W/O emulsions as a function of rotation speed. Line represents the model prediction valid at low injection rates [15]. Dispersed phase: (■) Sodium silicate with 6 wt% SiO₂ in 1 M H₂SO₄ injected at 350 L m⁻² h⁻¹. (●) Sodium silicate with 4 wt % SiO₂ in 1 M H₂SO₄ injected at 350 L m⁻² h⁻¹. (▲) Sodium silicate with 6 wt% SiO₂ in distilled water injected at 1 L m⁻² h⁻¹. Error bars in the figure represent one standard deviation ($\sigma=CV \times d/100$) from the mean value.

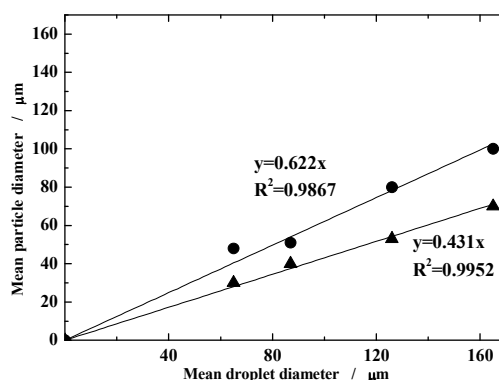


Figure 3 Relationship between the particle diameter in the resultant gels and the droplet diameter. Dispersed phase: Sodium silicate with 6 wt % SiO₂ in 1 M H₂SO₄. (●) Hydrogel. (▲) Xerogel.

The surface structure of the silica particles after calcination was imaged by SEM (operated at 2.6 kV) and FEG SEM (operated at 10 kV) and microphotographs are presented in Figure 4. The silica particles are almost perfectly round as can be seen from Figs. 4a and 4b, while the close-up of the particle surface shows a cloudy and corrugated external and internal surface morphology (Figs. 4c and 4d). The presence of pores is visible on the surface.

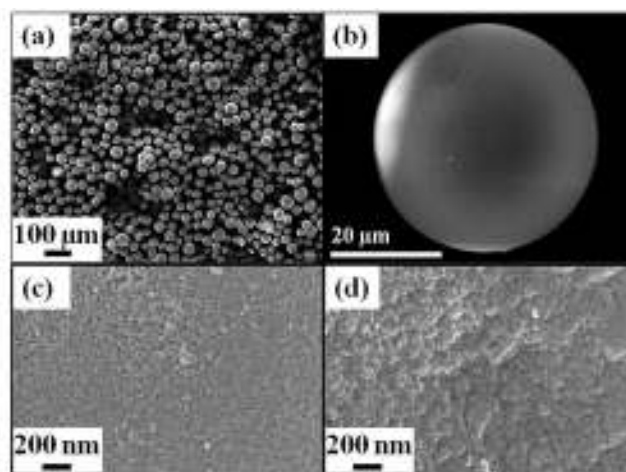


Figure 4 (a) Scanning electron micrograph (SEM) of the silica particles with an average size of 40 μm . (b) SEM of a single silica sphere. (c) Field emission gun (FEG) SEM of a silica sphere external surface structure. (d) FEG SEM of a broken silica sphere.

4 Functionalisation of silica gel and combined microfiltration/ion exchange

The ability of functionalised particles to adsorb Cu(II) was demonstrated in a continuous flow stirred cell. The volume of the liquid phase in the cell was 140 ml and the stirrer speed was 270 rpm. As can be seen from response curves in Figure 5, the functionalised silica particles had a higher binding affinity toward Cu(II). After about 80 min, both non-treated and functionalized particles were fully saturated with Cu(II) and from that time the Cu(II) concentration in the effluent matched the Cu(II) content in the feed stream.

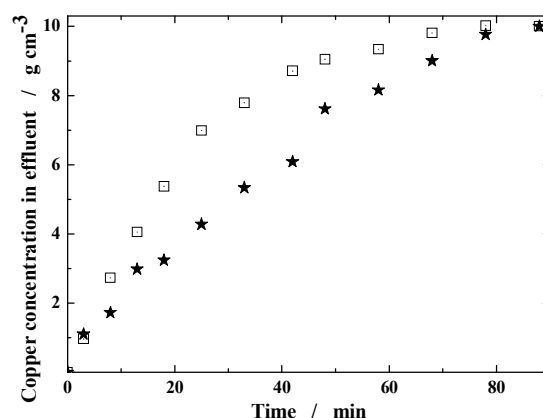


Figure 5 Chemisorption of CuSO_4 on silica gel in a continuous flow stirred cell with slotted pore membrane. The copper concentration in feed stream was 10 g cm^{-3} , the flow rate of feed stream was 8 ml min^{-1} , and the particle loading in the cell was 3.5 g. (□) Non-treated silica gel. (★) Silica gel functionalised with 3-aminopropyltrimethoxysilane.

Conclusions

Spherical silica particles with mean particle sizes controllable within a range between 30 and 70 μm have been produced from inexpensive sodium silicate solution using

membrane emulsification. The initial droplet size was precisely controlled by controlling the stirrer speed and the injection rate of the dispersed phase through the membrane and the final particle size was 2.7 times smaller than the initial droplet size. The internal porosity of the particles aged in water was 88% and 64% for the hydrogel and xerogel, respectively. Xerogel particles were functionalised with 3-aminopropyltrimethoxysilane and successfully used as ion-exchange media for chemisorption of Cu(II) from aqueous solutions of CuSO₄.

Acknowledgement

This research was supported by Engineering and Physical Sciences Research Council, UK (DIAMOND project into Decommissioning, Immobilisation And Management Of Nuclear wastes for Disposal).

References

1. T. Buranda, J. Huang, G.V. Ramarao, K. Linnea, R.S. Larson, T.L. Ward, L.A. Sklar, G.P. Lopez, *Langmuir* **19**, 1654 (2003).
2. C. Barbé, J. Bartlett, L. Kong, K. Finnie, H.Q. Lin, M. Larkin, S. Calleja, A. Bush, G. Calleja, *Adv. Mat.* **16**, 1959 (2004).
3. T.M. Suzuki, M. Yamamoto, K. Fukumoto, Y. Akimoto, K. Yano, *J. Catal.* **251**, 249 (2007).
4. N.J. Carroll, S.B. Rathod, E. Derbins, S. Mendez, D.A. Weitz, D.N. Petsev, *Langmuir* **24**, 658 (2008).
5. M.K. Titulaer, M.J. den Exter, H. Talsma, J.B.H. Jansen, J.W. Geus, *J. Non-Cryst. Solids* **170**, 113 (1994).
6. R.K. Iler, *The chemistry of silica: solubility, polymerization, colloid and surface properties, and biochemistry*, 1st ed. 1979. Wiley.
7. H.P. Lin, C.Y. Mou, *Accounts Chem. Res.* **35**, 927 (2002).
8. T. Yanagishita, Y. Tomabechi, K. Nishio, H. Masuda, *Langmuir* **20**, 554 (2004).
9. K. Hosoya, M. Bendo, N. Tanaka, Y. Watabe, T. Ikegami, H. Minakuchi, K. Nakanishi, *Macromol. Mater. Eng.* **290**, 753 (2005).
10. K. Kandori, K. Kishi & T. Ishikawa, *Colloid. Surface.* **62**, 259 (1992).
11. T. Fuchigami, M. Toki, K. Nakanishi, *J Sol-Gel Sci. Techn.* **19**, 337 (2000).
12. M.M. Dragosavac, R.G. Holdich, G.T. Vladisavljević, *Ind. Eng. Chem. Res.* **50**, 2408 (2011).
13. S. Brunauer, P.H. Emmett, E. Teller, *AIChE* **60**, 309 (1938).
14. K.F. Lam, K.L. Yeung, G. McKay, *Langmuir* **22**, 9632 (2006).

15. M.M. Dragosavac, M.N. Sovilj, S.R. Kosvintsev, R.G. Holdich, G.T. Vladisavljević, *J. Membr. Sci.* **322**, 178 (2008).
16. S. van der Graaf, M.L.J. Steegmans, R.G.M. van der Sman, C.G.P.H. Schroën, R.M. Boom, *Colloid. Surface. A* **266**, 106 (2005).

Figure legends

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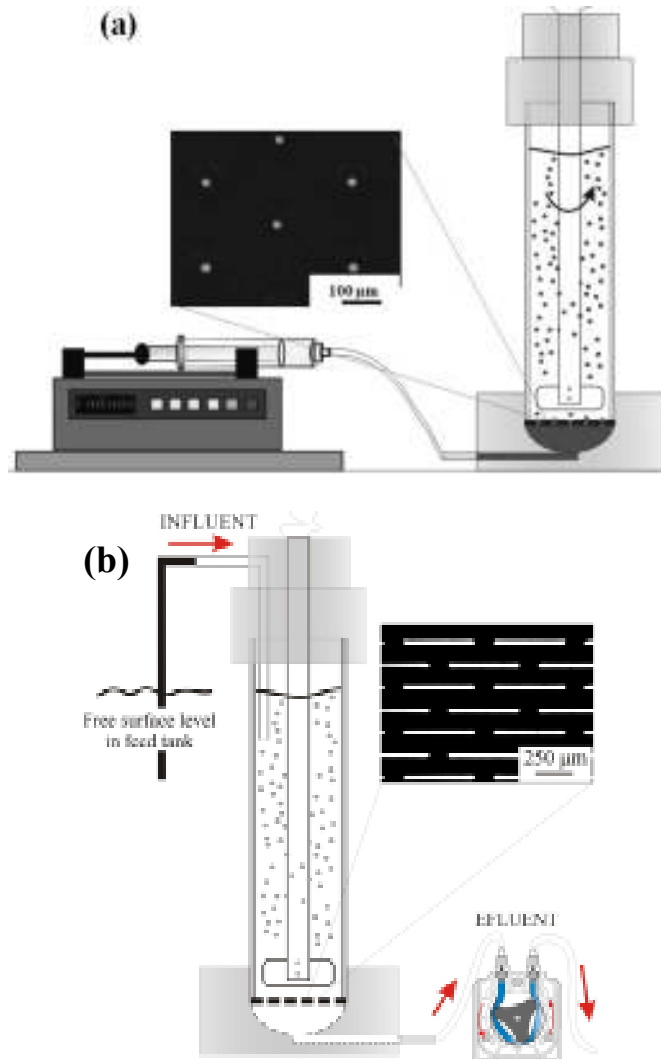


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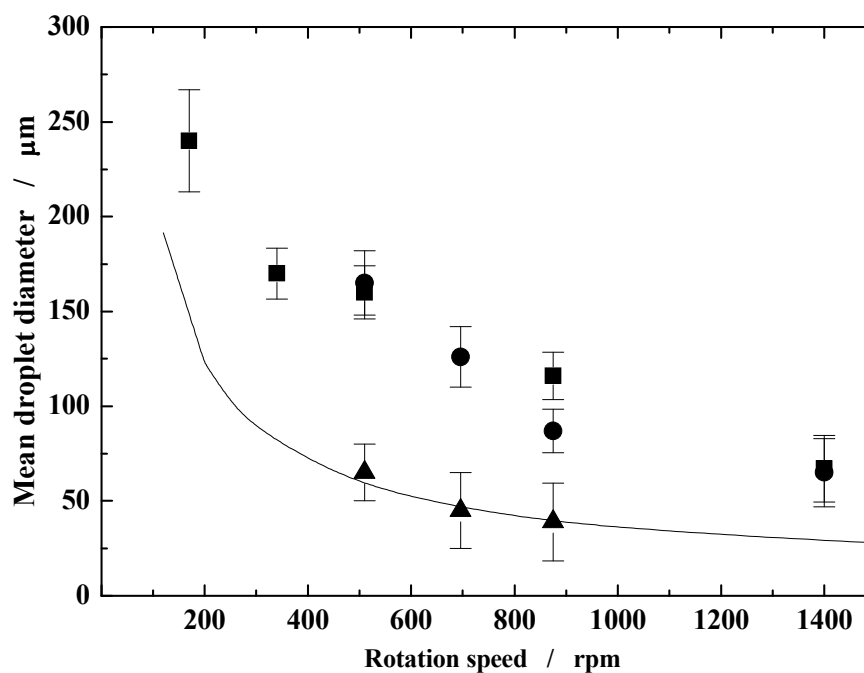


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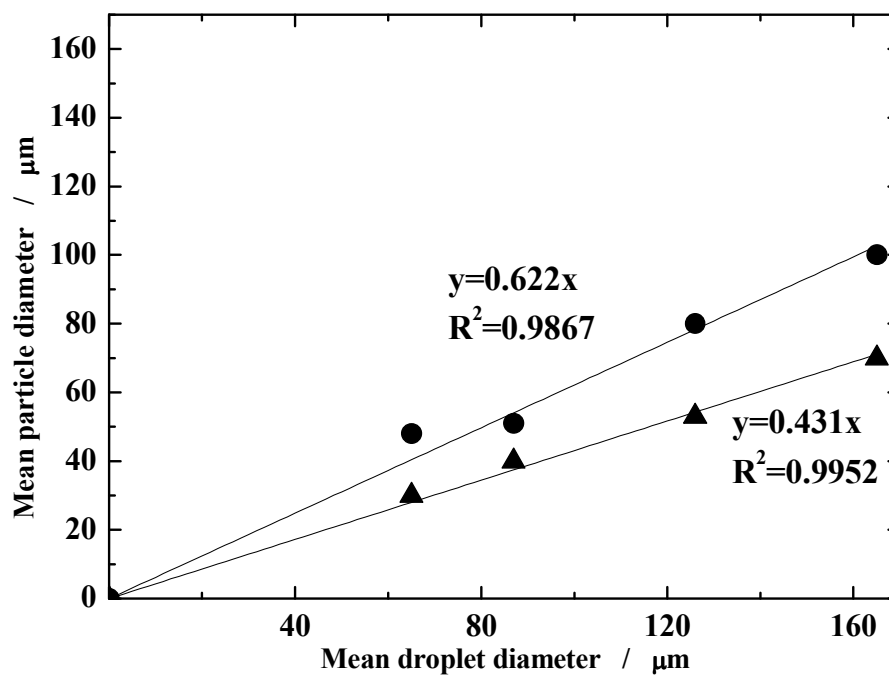


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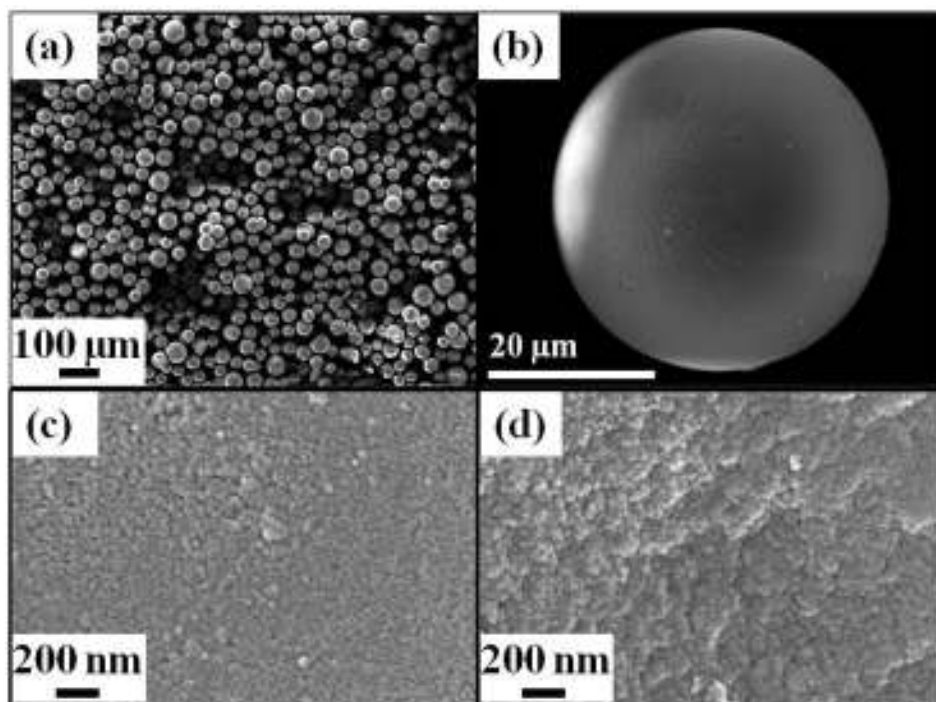


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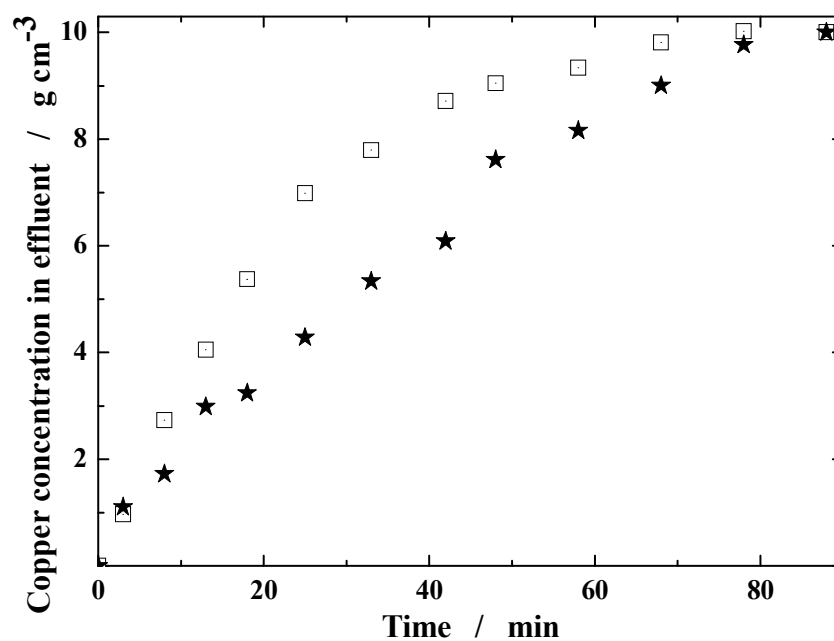


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