

Can Carbon Spheres Be Created through the Stöber Method?*

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Monodisperse colloidal nanospheres, including those composed of silica, polymers, and carbon, have received considerable attention during the past decade because they promise wide applications in drug delivery,^[1] active material encapsulation,^[2] colloidal catalysts,^[3] and particle templates.^[4a,b] The success of all these applications strongly depends on the availability of colloidal spheres with tightly controlled sizes and surface properties, and on their ability to self-assemble into ordered superstructures.^[5] The classical Stöber method, which usually relies on sol–gel chemistry involving the hydrolysis of tetraalkyl silicates in an alcohol/water solution using ammonia as the catalyst, is a general approach for the synthesis of silica spheres having a size mostly in the range of 150–500 nm.^[6a] Monodisperse polymer spheres, such as polystyrene,^[4c] poly(methyl methacrylate),^[4d] and poly(hydroxyethyl methacrylate)^[4e] can be prepared by the emulsion polymerization approach. However, these colloidal spheres have failed to be converted into their carbonaceous analogues because of thermal decomposition. Differing from most polymers and silica materials, carbon materials in general show a series of excellent characteristics such as high surface area, high thermal stability (in an inert atmosphere), and acid/base resistance, and can be applied in harsh reaction conditions. Hence, to integrate the advantages of carbon materials and colloids into one type of material, remains a grand challenge, which could be exploited by the new synthesis of monodisperse colloidal carbon spheres.

Phenolic resins derived from the polymerization of phenols (e.g. phenol, resorcinol) and aldehydes (e.g. formaldehyde, furfuraldehyde), are commonly employed as excellent precursors for the production of carbon materials. Although there are several reports regarding the synthesis of carbon microspheres and nanospheres from phenolic resins,^[7,1b] it is rather rare to find a report about truly monodisperse phenolic resin nanospheres that can form colloidal crystals by self-assembly.

Recently, Liu et al. smartly associated the synthesis of carbon spheres with silica spheres.^[6b] They considered that the synthesis of silica spheres based on the Stöber method involves the condensation of silicon alkoxides (e.g. tetraethyl orthosilicate (TEOS)) in ethanol/water mixtures under alkaline conditions (e.g. ammonia solution) at room temperature. Coincidentally, the resorcinol-formaldehyde precursors exhibit structural similarities to silanes, i.e. similar coordination sites and tetrahedral geometry, so their condensation behavior should be analogous to the hydrolysis and subsequent condensation of silicon alkoxides. Hence, a curious question arises: can carbon spheres really be created by the Stöber method?

The answer is “yes”. Liu et al. have developed methods that are inspired by and exploit the Stöber method for the synthesis of monodisperse resorcinol-formaldehyde (RF) resin polymer colloidal spheres and their carbonaceous analogues (Figure 1). The particle size of the obtained colloidal products can be easily tuned by changing the ratio of alcohol to water, changing the amounts of NH₄OH and of the RF precursor, using alcohols with short alkyl chains, and introducing a triblock copolymer surfactant. Critical to the successful synthesis of such polymer spheres is the use of ammonia in the reaction system; its role, they consider, lies in not only accelerating the polymerization of RF, but also supplying the positive charges that adhere to the outer surface of the spheres and thus, prevent the aggregation. Firstly, ammonia molecules catalyze the polymerization of RF inside the emulsion droplets, thus initiating their condensation process. Resorcinol reacts quickly with formaldehyde, forming numerous hydroxymethyl-substituted species. These hydroxymethyl-substituted species are positioned at the surface of the emulsion droplets owing to the electrostatic interaction with the ammonia molecules, and further cross-linking of these species during the hydrothermal treatment results in uniform colloidal spheres.

The ammonia, indeed, plays a key role in such a copolymerization system. However, it may serve other functions than that mentioned above, and this ability may lead to a rather different reaction sequence. Early in 1948, Richmond et al. investigated the reaction between formaldehyde and ammonia, and found that a fast reaction occurs after their mixing, thus resulting in cyclotrimethylenetriamine as the intermediate in the eventual formation of hexamine.^[8a] This was further confirmed by a recent report which shows

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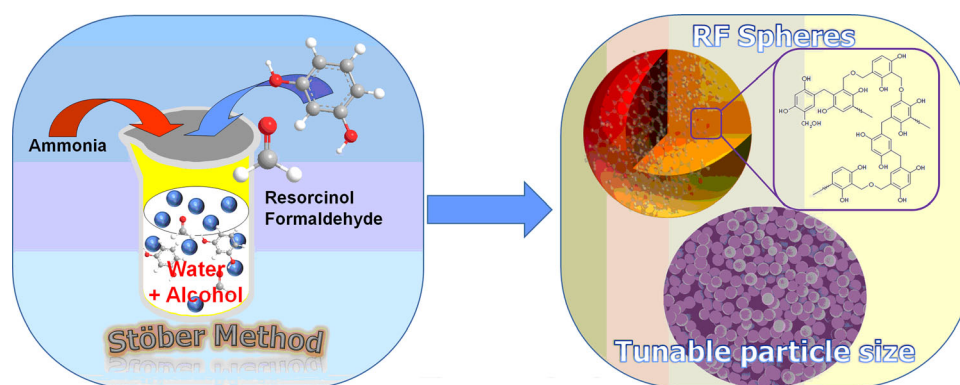


Figure 1. Schematic of the formation of RF resins spheres using the extended Stöber method. Adapted from Ref. [6b].

that formaldehyde reacts with ammonium hydroxide to form a polymer in a rapid manner.^[8b] On the other hand, the condensation of resorcinol and formaldehyde is much slower requiring at least a couple of hours, even in the presence of catalysts such as the sodium carbonate and magnesium acetate.^[8c] Given the two possible reactions, what will happen if resorcinol and formaldehyde are treated with ammonia? Another possibility arises: the reaction of resorcinol, which has two active hydrogens, with formaldehyde and ammonia may be initiated to give an aminomethylated product (Mannich base).^[8d–f] Even more interesting, the mechanism of this copolymerization starts with the quick formation of an iminium ion generated from an amine and formaldehyde. This essentially agrees with the investigations into the reaction between formaldehyde and ammonia, and gives insights into the role of ammonia during the quick copolymerization of phenols and aldehydes.

As well as the work by Liu et al., there are several other reports of the successful preparation of polymer and carbon products based on a similar principle.^[7b,c,9a] For example, polymer and carbon spheres with sizes ranging from 30 nm to 1.2 μm could be prepared through the copolymerization of resorcinol^[7b] (or 2,4-dihydroxybenzoic acid)^[7c] and formaldehyde with lysine (organic base). However, in most cases, the amine (or ammonia) is believed to initiate the polymerization of the precursors instead of directly participating in the reaction. The difference between the multicomponent reactions of phenols and aldehydes in the presence of amines (or ammonia), and the condensation of TEOS (single component) may be overlooked, thus leading to a direct analogy between these two systems. Even now, the factors and the mechanisms involved in controlling the copolymerization of phenols, aldehydes, and amines (or ammonia) have not yet been fully clarified. The previously unnoticed function of the amines (or ammonia) in the current and other analogous polymerizations merits further investigation because their participation may substantially change the reaction pathway.

Such colloidal carbon nanospheres have outstanding physical and chemical properties and hence, are of strong practical interest, for example, as supports for catalysts.^[3b] In the study by Liu et al., platinum nanoparticles (≈ 6 nm) were loaded onto the carbon sphere surface by a microwave-assisted reduction process.^[6b] The obtained catalyst showed

substantial electrocatalytic oxygen reduction performance under an O₂ atmosphere. In fact, carbon materials with a series of advantages have attracted great interest for potential applications not only as supports for catalysts, but also as adsorbents, electrodes, drug delivery carriers, biomedical applications, etc.^[1b,9] Guo et al. have used hollow mesoporous carbon spheres as bilirubin adsorbents, which showed high bilirubin adsorption selectivity and negligible hemolytic activity.^[9b] In addition, colloidal polymer nano- and microspheres usually have a complex mixture of organic functional groups on the surface, which ensure easy surface modification before the desired application.^[7c,10a] In this regard, the colloidal polymer and carbon materials can offer new opportunities in the fields of catalysis, drug delivery, and water treatment. When the biocompatibility and the chemical stability in acid and base environments are specifically emphasized in an application, carbon spheres would be the most suitable candidates. Undoubtedly, Liu et al. have provided an efficient method to achieve such monodisperse carbon spheres. With regards to their applications, a more precise control in size and distribution of carbon nanospheres is highly desired in future and ongoing research. Particularly in the fields of biomedicine and nanodevices, a strict control on the monodispersity, and particle sizes smaller than 200 nm is of necessity.^[10b] If the structural similarities between the RF polymer and silica materials are indeed true, one can possibly extend the existing synthetic methods for silica materials to prepare various analogues of nanostructured RF architectures with different morphologies and pore structures.

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