CHAPTER III

LITERATURE REVIEW

3.1 Introduction

The ability to synthesize fixed diameter colloidal spheres has opened the door to a variety of applications involving drug delivery or manipulation of light (photonic band gap crystals) [38]. In particular, colloidal carbon spheres are of great interest because the diffusion of guest species through the micropores can be significantly manipulated by changing their particle sizes and shapes [39]. Surface modification is a key to realizing many of these applications as the prepared surface is often inert [40]. There have been only a few reports regarding to colloidal carbon spheres. The main concern is the aggregation of carbon nanospheres [22]. Nanosized polymer particles exhibit a strong tendency toward aggregation during carbonization, which makes it difficult to prepare well-dispersed carbon nanospheres [27]. The remarkable transformation of carbohydrate molecules including sugars to form homogeneous carbon spheres readily occurs by a dehydration mechanism and subsequent nanoscale sequestering in aqueous solutions when heated at 160-180°C in a pressurized vessel [3]. Under such conditions, these molecules actually dehydrate even though they are dissolved in water [41]. The synthetic "green" approach involves none of the toxic organic solvents, initiators, or surfactants that are commonly used for the preparation of polymer micro- or nanospheres [42]. The surface of colloidal sphere products is hydrophilic and a distribution of -OH and –C=O groups, which makes surface modification unnecessary. Size-tunable metal and metal oxides with uniform shell thickness have also been prepared by using the carbon spheres as templates [43].

3.2 Mechanisms of carbon microspheres formation

3.2.1 Hydrothermal of glucose for preparing CMSs [30]

The transformation of carbohydrate molecules to form homogeneous carbon spheres occurs by a dehydration mechanism and subsequent nanoscale sequestering in aqueous solutions when heated at 160-180°C. For reactions involving glucose, it was difficult to detect 5-hydroxymethyl-2-furaldehyde (HMF) formation during initial hydrothermal treatment at <180°C, suggesting that carbon spheres were more likely formed via an intermolecular dehydration route followed by carbonization. Glucose loses water first through an intermolecular condensation reaction as a result of its stable pyranose structure when heated under pressure. Thus carbon spheres prepared from glucose exhibit smooth surfaces (see Figure 3.1).

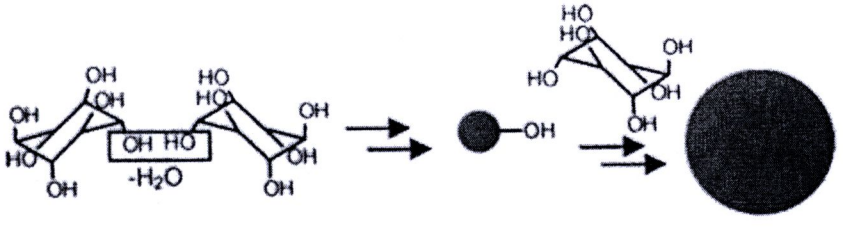

Figure 3.1 Schematic of the dehydration and hydrothermal process of glucose [30]

3.2.2 Hydrothermal of fructose for preparing CMSs [30]

For reactions involving fructose, an aqueous fructose solution was heated in a closed vessel to 120-140°C during the initial dehydration reaction, 5-hydroxymethylfurfuraldehyde (5-HMF) was formed by intramolecular dehydration. Upon subsequent dehydration (polymerization), microscopic nonpolar carbon-containing spheres were found to spontaneously assemble in a manner analogous to the mechanism by which a detergent emulsifier a mixture of oil and water. Subsequent loss of water by these assemblies leads to further coalescence of microscopic spheres to larger spheres, thereby generating a grain-like surface morphology with interconnected porosity as shown in Figure 3.2.

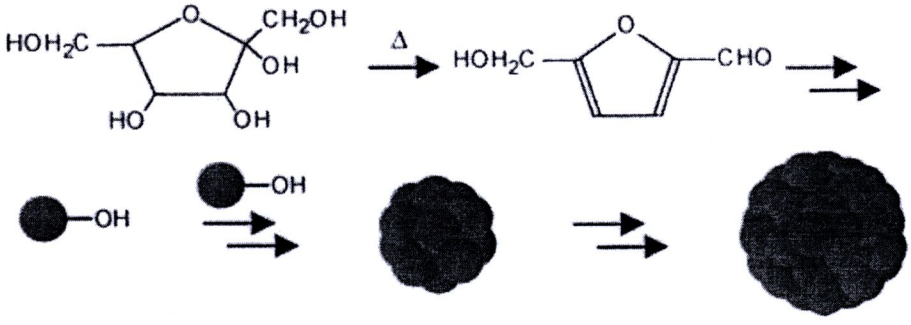

Figure 3.2 Schematic of the dehydration and hydrothermal process of fructose [30]

The fructose dehydrates in water under 3-4 atm at somewhat lower temperature (120°C) due to the presence of a more reactive furanose unit in contrast to glucose, where a pyranose group is present. However, fructose initially forms HMF through an intramolecular dehydration process followed by subsequent water loss to form carbon.

3.2.3 Hydrothermal of polysaccharide for preparing CMSs [29]

The schematic shows in Figure 3.3 which explains the mechanism of the formation of hydrothermal products from polysaccharide (starch, cellulose, etc). In a first step, when a polysaccharide aqueous dispersion is hydrothermally treated at set point temperatures (160-220°C). At this step, the hydronium ions which generate by water autoionization accelerate the hydrolysis of polysaccharide. The hydrolysis gives the different oligomers (cellobiose, cellohexaose, cellopentaose, cellotetraose and cellotriose) and glucose, which subsequently isomerizes to form fructose. Furthermore, the decomposition of the monomers produces organic acids (acetic, lactic, propenoic, levulinic and formic acids), the hydronium ions formed from these acids being the catalysts of the degradation in subsequent reaction stages. The oligomers also are hydrolyzed into their monomers, which undergo dehydration and fragmentation reactions (i.e. ring opening and C-C bond breaking) leading to the formation of different soluble products, such as 1,6-anhydroglucose, erythrose, furfural- like compounds (i.e. 5-hydroxymethylfurfural, furfural, 5-methylfurfural),

the hydroxymethylfurfural-related, 1,2,4-benzenetriol, acids and aldehydes (acetaldehyde, acetonylacetone, glyceraldehyde, glycolaldehyde, pyruvaldehyde).

The decomposition of the furfural-like compounds also generates acids, aldehydes and phenols. The subsequent reaction stages consist of polymerization or condensation reactions, which lead to the formation of soluble polymers. These reactions may be induced by intermolecular dehydration or aldol condensation. At the same time, the aromatization of polymers takes place. C=O groups appear due to the dehydration of water from the equatorial hydroxyl groups in the monomers. Alternatively, the C=C bonds may result from the keto–enol tautomerism of dehydrated species or from intramolecular dehydration. Aromatic clusters may be produced by the condensation (by intermolecular dehydration) of the aromatized molecules generated in the decomposition/dehydration of the oligosaccharides or monosaccharides. When the concentration of aromatic clusters in the aqueous solution reaches the critical supersaturation point, a burst nucleation takes place. The nuclei so formed grow outwards by diffusion towards the surface of the chemical species present in the solution. These species are linked to the surface of the microspheres via the reactive oxygen functionalities (hydroxyl, carbonyl, carboxylic, etc.) present in both the outer surface of the particles and in the reactive species. As a result of this linkage, stable oxygen groups such as ether or quinone are formed. Under these circumstances, once the growth process stops, the outer surface of the carbon microspheres particles will contain a high concentration of reactive oxygen groups, whereas the oxygen in the core forms less reactive groups.

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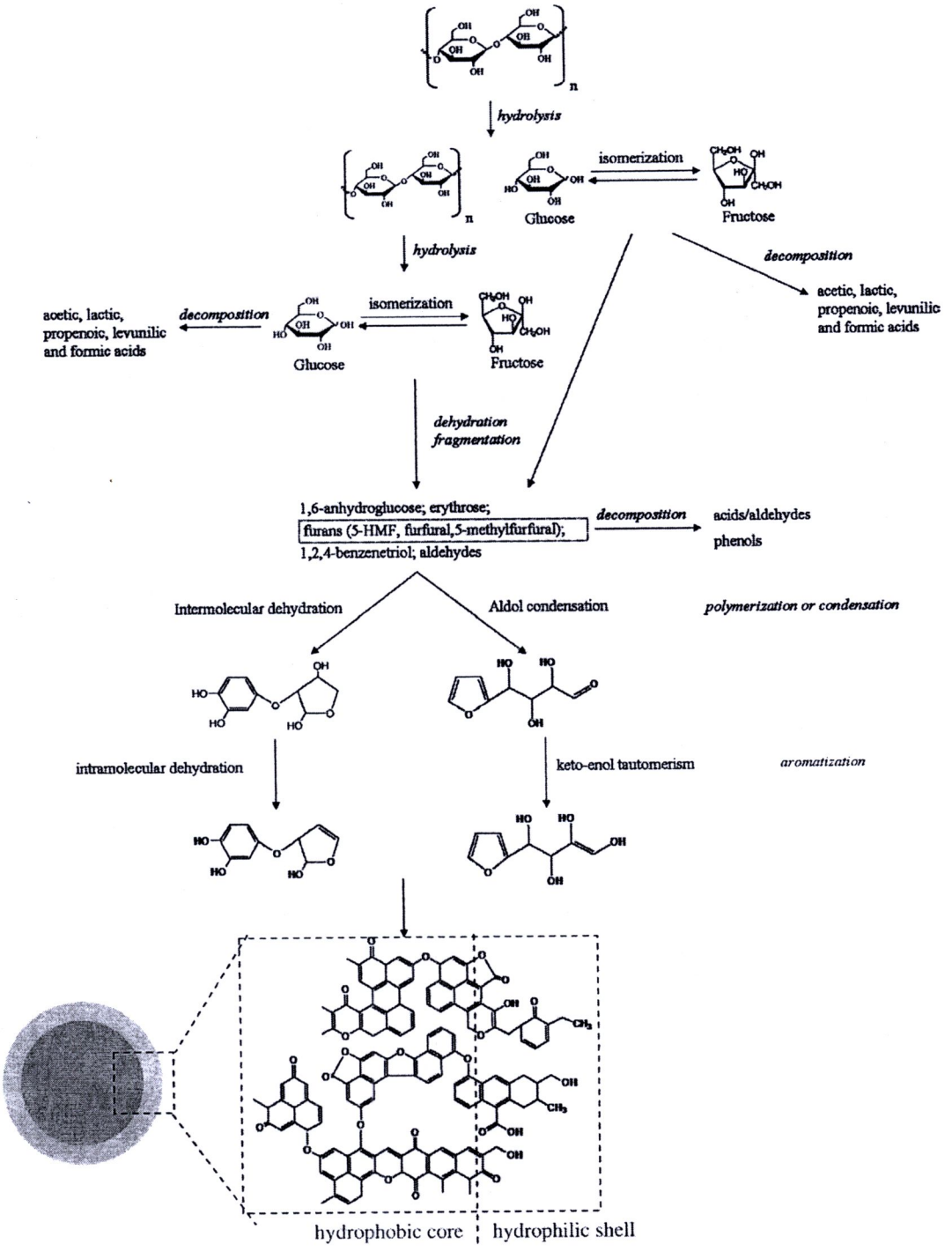

Figure 3.3 Formation mechanisms of carbon microspheres from cellulose [29]

3.3 Synthesis of carbon microspheres

3.2.1 Starting materials for preparing carbon microspheres

Wang et al. [20]: In this paper hard carbon with perfect spherical morphology was prepared for the first time by a hydrothermal method using sugar as carbon precursor. It has controllable monodispersed particle size and a smooth surface. The particle size of the spherules can be controlled through regulating the concentration of the sugar solution and the dwell time. Apparently, the diameter of the obtained carbon spherules decreases with diluting of the solution or shortening of dwell time whereas the size of the carbon spherules does not always increase with the concentration of sugar solution. As the solution turns dense enough, the size of the carbon spherules tends to be constant. The formation of dewatering sugar spherules is presumably more similar to the conventional emulsion polymerization mechanism of colloidal spheres.

Sun and Li [3]: In this paper the carbon spheres were prepared from glucose under hydrothermal conditions. The hydrothermal conditions were maintained at 160–180°C for 4–20 h which is higher than the normal glycosidation temperature and leads to aromatization and carbonization.

Xu et al. [23]: Carbon microspheres were prepared from sucrose by a hydrothermal method. The temperature of the hydrothermal reaction was increased to 600°C from ambient temperature at a rate of 10°C/ min and maintained at 600°C for 10 h. After hydrothermal process, it can be observed that the diameter of carbon microspheres is about 1500–2000 nm. The carbon microspheres which were prepared from sucrose dissolved in water under hydrothermal conditions have abundant hydroxyl group remaining on the outer surface of those carbon microspheres. The hydroxyl groups on the surface of CMSs can be acted as ''glue'' to immobilize noble metal nanoparticles on the surface of carbon microspheres.

Sevilla et al. [29]: Highly functionalized carbonaceous materials were produced by means of the hydrothermal carbonization of cellulose at temperatures in the 220–250°C range. The formation of this material follows essentially the path of a dehydration process, similar to that previously observed for the hydrothermal transformation of saccharides such as glucose, sucrose or starch. The materials so formed are composed of agglomerates of carbonaceous microspheres (size 2–5 μm).

The temperature for the onset of hydrothermal carbonization of cellulose is considerably higher than for glucose, sucrose or starch (160–170°C). The strong resistance of the cellulose to decompose is a consequence of the fact that the hydroxyl groups of the glucose residues present in the structure of the cellulose form hydrogen bonds that hold the polymeric chains firmly together and side-by-side.

Shin et al. [44]: Colloidal carbon spheres have been prepared from aqueous α-, β-, and γ-cyclodextrin (CD) solutions in closed systems under hydrothermal conditions at 160°C. They could obtain the homogeneous carbon spheres with a very narrow size distribution (100-200 nm in diameter). Specially, carbon spheres prepared from γ-CD solution showed a monodisperse size distribution with an average dimension of 100 nm. The isolated carbon spheres exhibit a narrow size distribution (70-150 nm in diameter) and the carbon spheres prepared from β- and γ-CD showed a core-shell structure comprised of a relatively dense hydrophobic core and a hydrophilic shell. The carbon surface appears smooth, and results from continuous intermolecular dehydration of glucose followed by carbonization.

Zheng et al. [25]: In this paper, they reported an easy catalyst-free method to prepare carbon microspheres via a hydrothermal carbonization process using starch solution as starting materials. SEM and TEM images show that the products consist of a large scale of monodisperse carbon microspheres with a size of about 2 μm. The size of the carbon microspheres can be easily controlled by regulating the concentration of the starch solution and the reaction temperature. Furthermore, the surface of the spheres is functionalized with hydroxyl and carboxyl groups, which make further surface modification unnecessary and facilitate immobilization of noble metal nanoparticles and fabrication of core-shell materials or hollow structures. Through SEM observation, the mechanism of the formation of carbon microspheres under hydrothermal conditions was suggested to be a direct dehydration polymerization and self-assemble fusion process. The present work provides a convenient yet effective method for large-scale synthesis of monodisperse carbon microspheres with high purity.

3.3.2 Carbon microspheres with uniform nanopore

Wang et al. [20]: In this paper hard carbon with perfect spherical morphology was prepared by a hydrothermal method using sugar as carbon precursor. Transmission electron microscopy shows that there is a large quantity of uniform nanopores of about 0.4 nm in diameter. This hard carbon material has a specific BET surface area of 400 m^2/g for N_2 as adsorbate. In addition, there are only very few parallel grapheme sheets with a d_{002} spacing of about 0.39 nm (XRD result) in the bulk. After carbonization process, the extraction of H, O and C gives rise to large quantities of micropores throughout the bulk of the samples. However at such a high pressure and temperature in this experiment, the escape of water through the flexible dewatering sugar may play a more important role in construction of microporous structures.

Yi et al. [14]: In this work, disordered carbon spheres were successfully synthesized by a hydrothermal method under a relatively mild condition and carbonization at 500°C for 4 h under argon atmosphere. X-ray diffraction studies showed that the pyrolytic product was highly disordered. This sample had a perfect spherical morphology, 100 nm in diameter, uniform particle size, large surface area and large amount of microspores.

3.3.3 Carbon microspheres with functional group on surface

Hu et al. [45]: Well-dispersed nanosized hard carbon spherules (nano-HCS) with different hydrogen contents were prepared by a modified hydrothermal method by adding polyacrylamide (PAM). Their electrochemical behaviors were investigated. The results from Raman spectra and the HRTEM images at different lithiation states show that the microstructure of the nano-HCS with high hydrogen content becomes slightly ordered after several discharging/charging cycles. This "disorder-to-order" transition phenomenon was not observed in the nano-HCS with low hydrogen content. A mechanism is proposed to interpret this phenomenon. Furthermore, the formation of a thick solid electrolyte interphase (SEI) film on the surface of the nano-HCS is demonstrated and it could be decomposed after charging.

Zheng et al. [25]: In this paper, they reported an easy catalyst-free method to prepare carbon microspheres via a hydrothermal carbonization process using starch solution as starting materials. The CMSs derived from soluble starch under hydrothermal conditions have abundant functional groups remaining on the surface of the spheres. These results indicate that there are a large number of residues including hydroxyl and carboxyl groups on the surface of the as-prepared CMSs due to an incomplete carbonization process, and they play important roles in the formation process of the spherical structures. Furthermore, the functional groups provide a potential avenue to load other functional groups, molecules, ions, and nanoparticles or fabricate other core-shell or hollow structures.

Sun and Li [3]: In this paper the carbon spheres were prepared from glucose under hydrothermal conditions. The hydrothermal conditions were maintained at 160–180°C for 4–20 h. Dehydration and aromatization are usually regarded as a process of decreasing the number of functional groups. Partially dehydrated residues in which reductive OH or CHO groups are covalently bonded to the carbon frameworks improve the hydrophilicity and stability of the microspheres in aqueous systems, and greatly widen their range of applications in biochemistry, diagnostics, and drug delivery, and as templates for hybrid core/shell structures or hollow/porous materials. For instance, they could be covalently bonded to biomacromolecules and used as a hydrophilic drug-delivery system, or react with metal ions to form metal nanoparticles, which could be used as probes for detection of molecules by surface-enhanced Raman scattering (SERS). To demonstrate the reactivity of as-prepared carbon microspheres, silver and palladium nanoparticles were loaded onto their surfaces by room-temperature surface reduction or by the reflux method.

3.3.4 Controlling size of carbon microspheres

Mi et al. [13]: In summary, they synthesized carbon micro-spheres with the aqueous glucose solution as starting materials in a stainless steel autoclave at 500°C for 12 h. The carbon micro-spheres have a regular and perfect shape, high yields and narrow-range distributions, and diameters ranging from 1 to 2 μm. Compared with other methods, this approach was simple and feasible. Our work was to simplify the search for an extremely facile and reliable recipe for carbon micro-spheres. The

carbon microspheres are of a narrow range of diameters, which show a potential for controlling the size for commercial application.

Sun and Li [3]: In this paper the carbon spheres were prepared from glucose under hydrothermal conditions. The diameters of the carbon spheres were influenced by reaction time, temperature, and concentration of starting material, of which the first-named was dominant. At constant concentration and temperature (e.g., 0.5M, 160°C), as the time increased from 2 to 4, 6, 8, and 10 h, the diameter grew from 200 to 500, 800, 1100, and 1500 nm. No carbon spheres formed when a 0.5M glucose solution was hydrothermally treated below 140°C or for less than 1 h. However, the orange or red color and increased viscosity of the resulting solutions indicate that some aromatic compounds and oligosaccharides are formed, in what has been denoted the "polymerization" step. When the solution reached a critical supersaturation (e.g., 0.5M, 160°C, 3 h), a short single burst of nucleation resulted. This carbonization step may arise from cross-linking induced by intermolecular dehydration of linear or branchlike oligosaccharides, or other macromolecules formed in prior step. The resulting nuclei then grew uniformly and isotropically by diffusion of solutes toward the particle surfaces until the final size was attained.

3.4 Applications of carbon microspheres

3.4.1 Carbon microspheres for catalyst supports

Yang et al. [12]: In this paper hard carbon spherules (HCS) were used as support of Pt nanoparticles as electrocatalyst for direct methanol fuel cells (DMFCs). Scanning electron microscopy (SEM) images show that the size of the Pt particles on HCS by reduction of K_2PtCl_6 with ethylene glycol is 4–5 nm. High-resolution transmission electron microscopy (HRTEM) study reveals that the Pt particles on the HCS surface have faceted crystalline structures. The size and aggregation of the Pt particles depend on the surface properties of the carbon support and the medium of the reduction reaction. Cyclic voltammetry and galvanostatic polarization experiments show that the Pt/HCS catalyst exhibits a higher catalytic activity in the electrooxidation of methanol than either the Pt/MCMB or the commercial Pt/Vulcan XC-72 catalyst does.

Xu et al [23]: Noble metal (Pt, Pd) electrocatalysts supported on carbon microspheres (CMS) are used for methanol and ethanol oxidation in alkaline media. The results show that noble metal electrocatalysts supported on carbon microspheres give better performance than that supported on carbon black. It is well known that palladium is not a good electrocatalyst for methanol oxidation, but it shows excellently higher activity and better steady-state electrolysis than Pt for ethanol electrooxidation in alkaline media. The results show a synergistic effect by the interaction between Pd and carbon microspheres. The Pd supported on carbon microspheres in this paper possesses excellent electrocatalytic properties and may be of great potential in direct ethanol fuel cells.

Tusi et al. [46]: PtRu/C electrocatalysts were prepared by hydrothermal carbonization process using starch as carbon sources and reducing agents and platinum and ruthenium salts as catalysts of carbonization process and metal source. The pH of the reaction medium was adjusted using KOH or TPAOH (tetrapropylammonium hydroxide). The obtained PtRu/C electrocatalysts were characterized by SEM/EDX, TGA, XRD and cyclic voltammetry. The electro-oxidation of methanol was studied by cyclic voltammetry and chronoamperometry. The PtRu/C electrocatalyst prepared using TPAOH was more active for methanol electro-oxidation than the material prepared with KOH.

3.4.2 Carbon microspheres for lithium ion batteries

Li et al. [21]: In this paper, nanosized SnSb alloy particles were pinned on the surface of micrometer-sized hard carbon spherules by a co-precipitation method in glycol solution at low temperature. Thanks to the small alloy particle size, good dispersion, and tight pinning of the alloy particles on the surface of carbon, in addition to the fact that both the alloy and the carbon are active for Li storage, the composite materials as prepared show much improved electrochemical performances as anode materials for lithium ion batteries compared with alloy and carbon alone.

Wang et al. [22]: In this paper, the Coulombic efficiency of HCS has been improved by surface modifications such as CVD of acetylene and coating of tetraethoxysilane (TEOS) on the surface of HCS. Furthermore, pinning of the nanosized SnSb alloy particles on the surface of HCS hinders the electrochemical

aggregation of alloy particles effectively during charge/discharge cycles. Consequently, the cyclic performance and reversible capacity are much enhanced.

3.4.3 Carbon microspheres for templates

Sun and Li [3]: In this paper, the carbon spheres were prepared from glucose under hydrothermal conditions. To investigate the chemical reactivity of as-prepared carbon spheres, noble-metal (Ag, Au, Pd, Pt) nanoparticles were loaded onto or encapsulated in carbon spheres to form hybrid structures. A layered structure integrating differently sized noble-metal nanoparticles was obtained when a combination of both synthetic strategies was utilized.

Sun and Li [18]: Silver nanoparticles with tunable sizes were encapsulated in a carbonaceous shell through a green wet chemical routes which is the catalyzed dehydration of glucose under hydrothermal condition. In this one-pot synthesis, glucose was used as the reducing agent to react with Ag^{+} or $Ag(NH_3)^{2+}$, and it also served as the source of carbonaceous shells. The presence of competitive molecules poly(vinyl pyrolidone) was found to be able to relieve the carbonization process, to incorporate themselves into carbonaceous shell, and to make the carbonaceous shell colorless. All these approaches provided diverse means to tailor the Ag@C nanostructures. By evaporation of the solvents gradually in a moist atmosphere, the monodispersed nanoparticles could self-assemble into arrays.