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ARTICLE *in* BIOMACROMOLECULES · OCTOBER 2008

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# Carboxymethyl Chitosan as a Matrix Material for Platinum, Gold, and Silver Nanoparticles

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Received July 24, 2008; Revised Manuscript Received August 25, 2008

Carboxymethyl chitosan (CMC) was evaluated for its use in the synthesis and stabilization of catalytic nanoparticles for the first time. Many studies have reported on the ability of chitosan to bind with metal ions and support metal nanoparticles. CMC has a higher reported chelation capacity than chitosan, which has potential implications for improved catalyst formation and immobilization. Platinum, gold, and silver nanoparticles were synthesized in both chitosan and CMC. Particle size, morphology, and aggregation were examined using transmission electron microscopy (TEM). Complexation of nanoparticles was studied through Fourier transform infrared spectroscopy (FTIR). Similar nanoparticle size distributions were observed in the two polymers; however, CMC was observed to have higher rates of aggregation. This indicates that the carboxymethyl groups did not change nanoparticle formation; however, poor cross-linking and a limited anchoring ability of CMC led to the inability to immobilize the catalyst materials effectively.

## Introduction

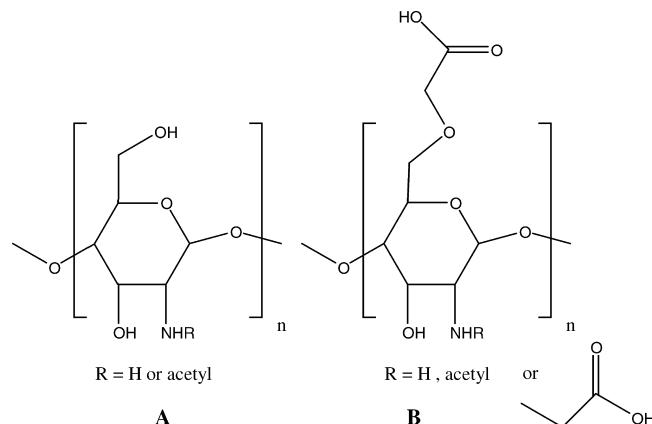
Heterogeneous catalysts are often precious metals such as platinum, gold, and silver. By immobilizing nanoparticles on matrix materials, the exposed surface area is greatly increased. The matrix material prevents aggregation of the nanoparticles and allows separation of the products from the catalyst particles. Typical matrix materials include: activated carbon, silica, and alumina; however, polymers are gaining increasing interest as matrix materials due to their ability to control particle growth as well as stabilize the resulting particles.<sup>1</sup>

Polyelectrolytes, such as chitosan, are particularly interesting in metal nanoparticle synthesis due to their interactions with metal ions and metal nanoparticles. Chelation evenly disperses metal ions throughout the polymer. Subsequently, the dispersed metal ions can be reduced to a zerovalent state forming dispersed nanoparticles.<sup>2–5</sup> The polymer then binds with the nanoparticles preventing catalyst leaching.<sup>6</sup> These characteristics make polyelectrolytes ideal catalyst supports.

Chitosan, a polyelectrolyte derivative of chitin, is a polysaccharide composed of  $\beta(1\rightarrow4)$  linked 2-amino-2-deoxy- $\beta$ -D-glucopyranose (*N*-acetylglucosamine).<sup>7</sup> Chitin predominantly comes from crab and shrimp shells, but is also found in a myriad of other sources making it the most abundant natural polymer after cellulose.<sup>8</sup> However, chitin has limited solubility and is commonly deacetylated to varying degrees to improve solubility and form chitosan, Figure 1a.<sup>9</sup> The primary amines on chitosan are involved in metal ion chelation and nanoparticle immobilization.<sup>1</sup>

Solubility in neutral and basic solutions can be achieved by further modification to the structure of chitosan, such as in carboxymethyl chitosan (CMC). This chitosan modification is synthesized by carboxylation of the hydroxyl and amine groups.<sup>10</sup> The degree of carboxymethylation, which is controlled by reaction temperature and duration, strongly affects the solubility of CMC.<sup>11</sup> Figure 1b shows possible addition sites of the carboxymethyl groups.

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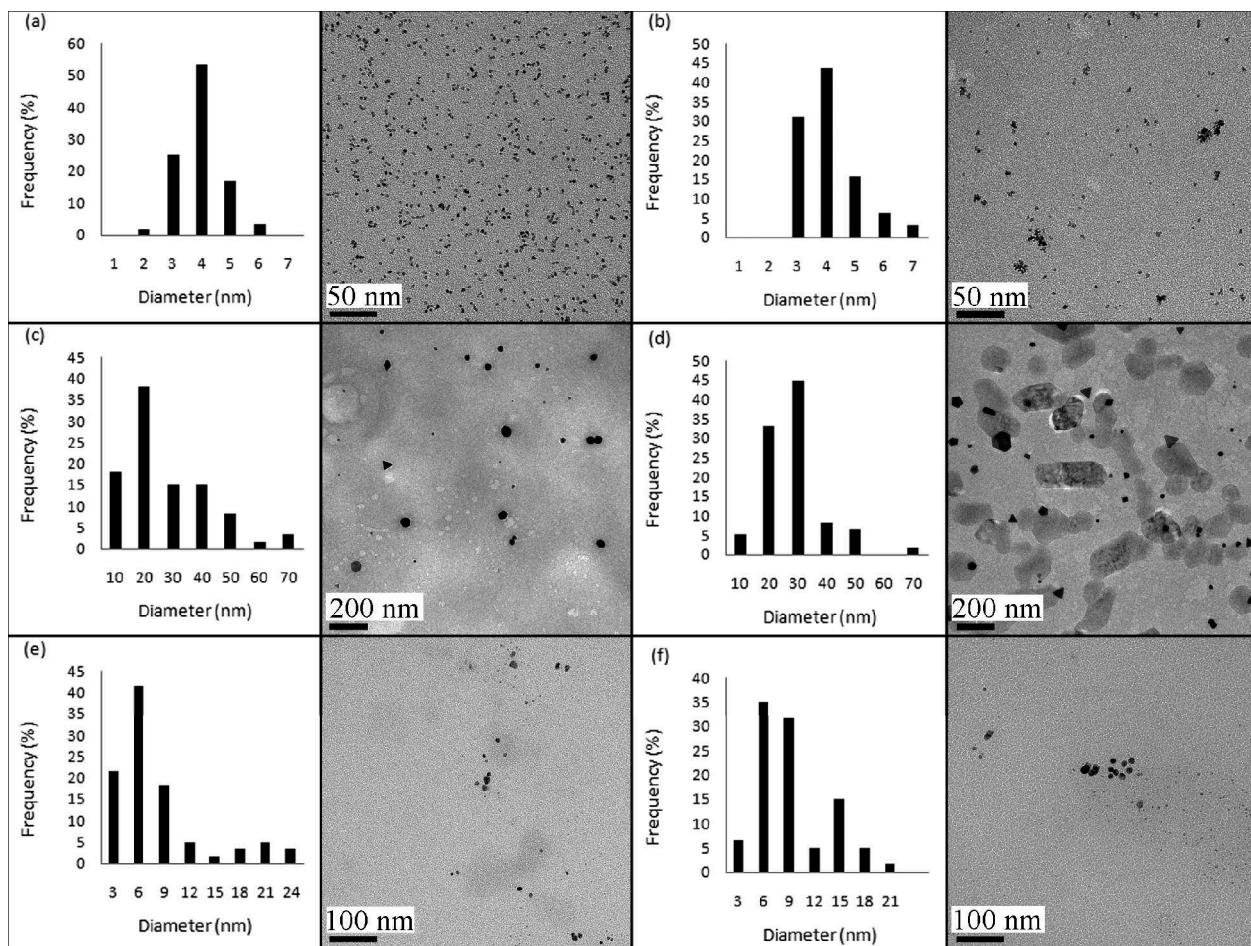


**Figure 1.** (A) Chemical structure of chitosan. The degree of deacetylation is determined by the ratio of H to acetyl groups on the amine. (B) Chemical structure of possible carboxymethyl addition sites in N,O-CMC.

CMC is reported to have a higher sorption of metal ions than chitosan.<sup>12</sup> It has been proposed that the higher sorption capacity is due to increased chain flexibility<sup>13</sup> and higher concentrations of chelating groups.<sup>14</sup> Therefore, it is of interest to compare the formation and complexation of nanoparticles in the two polymer systems. This paper is the first to compare the size, morphology, and binding mechanisms of nanoparticles in chitosan and CMC.

## Experimental Section

**Materials.** All compounds were used as received. Acetic acid (99.7% ACS reagent), chloroplatinic acid (8 wt % in water), monochloroacetic acid (99% ACS reagent), sodium borohydride (98%), sodium hydroxide (97%), and 4-nitrophenol (99%) were obtained from Sigma Aldrich (St. Louis, MO). Gold(III) chloride hydrate (50% Au) and silver nitrate (99.5%) were obtained from Fluka (Switzerland). Pharmaceutical grade chitosan (90% deacetylated) was obtained from the Naval Research Laboratory, Washington, DC. Ultrapure water was obtained from a Millipore Milli-Q Plus filtration system.



**Figure 2.** Distributions of 60 random nanoparticles and TEM images: platinum nanoparticles in (a) chitosan and (b) CMC; gold nanoparticles in (c) chitosan and (d) CMC; silver nanoparticles in (e) chitosan and (f) CMC.

**Synthesis of Carboxymethyl Chitosan.** CMC was synthesized using procedures similar to the method described by Chen and Park.<sup>11</sup> The degree of substitution and the yield are strongly dependent on the reaction time, temperature, and ratio of isopropyl alcohol to water; therefore, the reaction is very sensitive to the method of preparation. The synthesis of carboxymethyl chitosan is summarized as follows. Chitosan (2 g) was alkalinized in NaOH (8 g) for 12 h in a 50:50 mixture of deionized water and isopropanol (20 mL). After heating the mixture to 60 °C, monochloroacetic acid (8 g) was dissolved in isopropanol (2 mL) and slowly added to the solution over 30 min. After 6 h, the reaction was quenched by adding ethanol (50 mL) to the solution.

The resulting CMC was repeatedly rinsed in ethanol and vacuum-dried until the pH of the filtered solution was neutral. The products were dissolved in water and centrifuged to separate the unreacted chitosan; the water soluble portion of the sample was removed, precipitated in ethanol, and vacuum-dried. The sample was then placed in an oven at 50 °C to dry.

**Synthesis of Platinum, Silver, and Gold Nanoparticles.** Stock solutions of chitosan and CMC (1 g) were prepared in 2% aqueous acetic acid (100 mL). From the two polymer solutions, metal ion solutions of platinum, gold, and silver were prepared in 1 mM concentrations.

Chloroplatinic acid was added to chitosan and CMC and reduced to form platinum nanoparticles with an excess of sodium borohydride (20 µL of a 1 M solution of NaBH<sub>4</sub> per 1 mL chitosan solution).

Gold sols were prepared using the reducing ability of chitosan.<sup>2</sup> Solutions of chitosan and CMC, with the addition of gold chloride (1 mM), were heated to 60 °C for 2 h. After removing from heat, the solutions were stirred for 1 h.

Silver sols were formed by the reduction of silver nitrate (AgNO<sub>3</sub>).<sup>4,15</sup> First, AgNO<sub>3</sub> (1 mM) was dissolved in chitosan and CMC solutions

and then placed in an ice bath for 10 min to chill. Next, the solutions were stirred, and an excess of sodium borohydride (15 µL of a 1 M solution of NaBH<sub>4</sub> per 1 mL chitosan solution) was added. After a clear yellow sol formed, the container was removed from stirring.

All metal nanoparticle-biopolymer samples were made immediately before characterization.

**Characterization.** Infrared spectra were obtained from an Excalibur ETS-3000 Fourier transform spectrometer in transmission mode by accumulation of 64 scans with a resolution of 4 cm<sup>-1</sup>. Thin film samples were prepared for FTIR by drying solutions at 60 °C on glass slides. After the water evaporated, films were removed using a razor blade and placed in a Secador autodesiccator (Bel-Art Products, Pequannock, NJ) overnight prior to recording the spectra. Spectra are found in the supplemental section.

Transmission electron microscopy (TEM) experiments were conducted on a JEOL 2000FX TEM with an accelerating voltage of 120 kV. Platinum samples were diluted with five parts water to one part sol while other samples were diluted with two parts water to one part sol prior to depositing on a TEM grid to increase nanoparticle visibility. Nanoparticle diameters were measured from four different regions of each sample. The average diameters are reported from measurements of 60 random nanoparticles for each sample.

## Results and Discussion

**Characterization of Synthesized Nanoparticles.** The morphology and distribution of nanoparticles in chitosan and CMC were determined through TEM analysis, Figure 2. Chitosan and CMC produced sols of varying stabilities and uniformity of particle sizes. Platinum, gold, and silver have distinctive color changes upon formation: black, wine red, and yellow, respec-

**Table 1.** Mean Particle Size and Standard Deviation of Synthesized Nanoparticles

polymer	catalyst	mean (nm)	$\sigma$ (nm)
CMC	platinum	3.4	0.8
	gold	22.9	15.4
	silver	6.8	5.3
	platinum	3.5	1.0
	gold	23.0	11.0
	silver	7.7	4.2

tively. Sols tend to darken within minutes as aggregation increases, and it was observed the CMC sols darkened more quickly than chitosan sols. The darkening of the sols was monitored over days.

Platinum nanoparticles have a narrow size distribution for both chitosan and CMC. The size of the platinum nanoparticles agreed well with literature values for two different synthetic procedures.<sup>16</sup> However, CMC did not disperse the platinum particles as well as chitosan, and aggregation of the platinum particles is apparent in Figure 2b. Within 48 h, platinum sols formed gels due to a cross-linking effect. Solutions of chloroplatinic acid in chitosan did not show evidence of cross-linking over several weeks; the solutions, both chitosan and CMC, only gelled in the presence of nanoparticles.

The size and shape of gold nanoparticles varied more than the other two catalysts. Gold nanoparticles are found to vary in size depending on chitosan concentration.<sup>17</sup> The size distribution of gold is similar in chitosan and CMC. Gold particles varied in cross-sectional area appearing as triangles, hexagons, and circles.<sup>2</sup> In CMC, the gold chloride did not fully react resulting in the gold chelates in Figure 2d; however, the nanoparticles were well dispersed in both solutions. Furthermore, UV-vis absorbance spectra of gold nanoparticles did not change considerably over three weeks, indicating that gold forms particularly stable sols.

The reduction of silver nitrate formed spherical nanoparticles with a broad size distribution. The silver nanoparticles ranged in size from 3–24 nm and were not as evenly dispersed as platinum and gold sols. Others have used a different procedure to create smaller (2–6 nm) silver nanoparticles.<sup>18</sup> Chitosan and CMC formed yellow sols that darkened to brown over several days, which is evidence of particle aggregation.<sup>4</sup> CMC sols aggregated more quickly than chitosan sols.

A summary of the particle sizes is shown in Table 1. Chitosan and CMC produced nanoparticles of similar shape and size for platinum and gold, while silver nanoparticles formed in CMC were slightly larger. Platinum nanoparticles exhibited a very narrow size distribution with a standard deviation close to 1 nm for both polymers, while gold formed the largest range of nanoparticles.

**FTIR Analysis.** Key peaks in the FTIR spectra of chitosan and CMC are shown in Table 2. The peak at 1550 cm<sup>-1</sup> is affected by the degree of deacetylation.<sup>10,19</sup> The characteristic peaks of CMC are the carboxy group at 1714 cm<sup>-1</sup>, indicating the addition of a carboxylic acid and a decrease in the primary hydroxyl peak at 1029 cm<sup>-1</sup>. The decreased peak at 1029 cm<sup>-1</sup> indicates that the addition occurred predominantly on the hydroxyl groups, but it also occurs to some extent on the amines.<sup>10,11</sup>

FTIR spectra shift in the presence of nanoparticles. For the chitosan samples, key peaks, which were monitored, include the primary and secondary alcohols, amines and amides. The major changes for the chitosan peaks were not in the alcohols but in the amine and amide region as seen in Table 2. For the

**Table 2.** Characteristic FTIR Peaks Monitored for Spectral Shifts (cm<sup>-1</sup>)

polymer	nanoparticles				
	none	Pt	Au	Ag	region
chitosan	1029	1012	1029	1013	alcohol
	1076	1074	1082	1080	alcohol
	1155	1155	1155	1155	alcohol
	1209		1211	1211	C—O stretch
	1260		1261	1249	C—O—C stretch
	1560	1570	1558	1560	amine and amide
	1626	1649	1632	1694	amine and amide
	939	943	937	926	O—H bend
				1024	alcohol
	1082	1088	1086	1072	alcohol
CMC	1155	1153	1155	1140	alcohol
	1215	1231	1207		C—O stretch
	1252	1256	1254	1244	amine and amide
	1597	1605	1599	1572	amine and amide
	1719	1717	1717		carboxylic acid

CMC samples, key peaks which were monitored were the primary and secondary alcohols, carboxylic acids, amines, and amides. The alcohols undergo the most significant spectral change with the amines and carboxylic acids undergoing minor changes as seen in Table 2.

## Conclusions

Both chitosan and the chemically modified chitosan, CMC, can be used to synthesize and stabilize nanoparticles of platinum, gold, and silver. The average nanoparticle sizes were around 3.5, 23, and 7.5 nm for platinum, gold, and silver nanoparticles, respectively. Despite a higher metal ion chelation capacity in CMC, similar size distributions were observed when nanoparticles were formed in both polymer systems; however, the ability of the two polymers to stabilize the solutions varied. In CMC, a noticeable amount of particle aggregation occurred in the platinum solutions while chitosan attained a more uniform distribution.

FTIR data suggest different binding mechanisms in the two polymers. In chitosan, it was observed that the amine and amide region has the strongest interaction, while in CMC, the alcohol region has the strongest interactions. However, CMC did not effectively immobilize the nanoparticles. The reduced anchoring ability of CMC is most likely caused by the lower availability of amines due to partial substitution of carboxymethyl groups, as well as the reduced cross-linking ability of CMC. The lack of free amines limits the extent of cross-linking in the polymer, which makes CMC a poor choice for a catalyst support material.

**Acknowledgment.** The authors thank Bing Li for his assistance with TEM experiments. J.D.S. would like to thank the NSF-Integrative Graduate Education and Research Traineeship (NSF IGERT) (DGE-0221664) and Graduate Assistance in Areas of National Need-Drexel Research and Education in Advanced Materials (GAANN-DREAM; P200A060117), which is funded by the Department of Education's Office of Postsecondary Education for funding.

**Supporting Information Available.** FTIR spectra of chitosan and CMC films with and without nanoparticles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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BM800835E