

## Simple Synthesis of Clay–Gold Nanocomposites with Tunable Color

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Clay-based nanocomposites have been studied for several decades, mainly focusing on clay–polymer nanocomposites. Here, we report on a simple wet chemical method to synthesize clay-APTES-Au (CAAu) nanocomposites, where 3-aminopropyltriethoxysilane (APTES) acts as the linkage. The silane terminal of APTES formed bonds with the clay surface, while the other -NH<sub>2</sub> terminal bonds to gold nanoparticles. The color of clay changed when these CAAu nanocomposites were formed. By changing the size of the gold nanoparticles, the color of CAAu could be adjusted, simply by changing process parameters. TEM characterization of the synthesized nanocomposites showed an even distribution of gold nanoparticles on the clay surfaces. The nanocomposites were stable in strong acid and high concentration of salt conditions, while strong basic solution like NaOH could slightly influence the status of the gold nanoparticles due to the rupture of the Si–O–Si bonds between APTES and clay. To demonstrate the potential for label free sensing application of CAAu nanocomposites, we made hybrids of clay-APTES-Au-HD-Au (CAAuHAu), where hexamethylene diamine (HD) served as links between CAAu nanocomposites and the gold nanoparticles. The color of the composites changed from red to blue, when the hybrids were formed. Moreover, hemoglobin was loaded on the CAAu nanocomposites, which can potentially be used as a biosensor. These synthesized nanocomposites may combine the catalytic properties of clay and the well-known excellent properties of gold nanoparticles, such as the ability to anchor biological and chemical molecules. Furthermore, the color change of CAAu, when the CAAuHAu hybrids were observed, suggests the applications of these nanocomposites in biochemical and chemical sensing.

### Introduction

As a low cost inorganic material, clays are used in industrial, engineering, and scientific fields. In industrial and engineering fields, clays have been used in ceramics, oil drilling, and the paper industry.<sup>1</sup> In science, they are commonly used as catalysts, decoloration agents, and adsorbents.<sup>1,2</sup> For example, the catalytic effects of clays are of great interests due to several attractive properties such as cation exchangers with appreciable surface area, ordered structure, intercalation properties, high stability, and high exchange capacity.<sup>3–5</sup> Hu and co-workers reported the catalytic and cation exchange properties of clays and demonstrated the applications of clays in biocatalysts.<sup>3,5–7</sup> Moreover, clays can also be used as adsorbents, since they offer an environmental remediation platform for investigations.<sup>8,9</sup>

With the aim to extend the applications, clay-based nanocomposites have recently attracted widespread attention.<sup>10–18</sup> Among those nanocomposites, polymer–clay nanocomposites are the most well investigated ones, and they show high dimensional stability, high heat deflection temperature, reduced gas permeability, and enhanced mechanical properties.<sup>19,20</sup> Large amounts of polymer–clay nanocomposites were synthesized after the development of nylon–clay nanocomposites in the 1990s.<sup>17,21</sup> Generally, three kinds of methods<sup>22</sup> are commonly used to fabricate polymer–clay nanocomposites: in situ polymerization,<sup>23</sup> solvent intercalation,<sup>24</sup> and polymer melt intercalation.<sup>25</sup> Polyurethane,<sup>17,19</sup> polypropylene,<sup>26,27</sup> and polyolefin<sup>18</sup> are commonly used polymers for preparing polymer–clay nanocomposites.

In addition, there are a few reports on composites of metal/metal-oxide nanoparticles and clays, which are systems with widespread potential applications due to the unique properties of the nanoparticles.<sup>28</sup> For example, Fe<sub>2</sub>O<sub>3</sub> deposited on clay has

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good catalytic properties and could be used for growing carbon nanotubes.<sup>29</sup>

Another approach to fabricate clay-based nanocomposites is to functionalize the clay particles with molecules containing silane groups, where the silane group could form bonds to SiO<sub>2</sub> and/or Al<sub>2</sub>O<sub>3</sub> of the clay surfaces.<sup>15,30</sup> Chen and co-workers reported on a method to modify clay particles with (glycidoxypentyl) trimethoxysilane.<sup>30</sup> Other molecules like tetraethoxysilane and ethyltriethoxysilane are also used to modify clay surfaces.<sup>15</sup>

Some attempts to make gold nanoparticle–clay nanocomposites have been made recently. Zhu et al. used a solution-based method to deposit small Au nanoparticles on clay using a cationic gold coordination compound as precursor.<sup>31</sup> Zhao et al. developed a method for a clay-chitosan-gold nanoparticle composite,<sup>32,33</sup> following a recipe developed for depositing Au nanoparticles on glass.<sup>34</sup> The chitosan–gold composites are first synthesized and then hybridized with clay by electrostatic interaction. Nakamura and Mori report the preparation of gold nanoparticles in clay gel, obtaining polydispersed gold nanoparticles on clay particles.<sup>35</sup>

Although several methods have been attempted, a simple and efficient method to synthesize clay–gold nanocomposites with monodispersed gold distribution and controllable gold nanoparticles size is desired. Monodispersed nanoparticles are important in sensor applications to get a stable signal. The control of size is of importance because it is directly related to the effective surface area; small nanoparticles lead to higher surface area for the same weight amount. Gold nanoparticles are an attractive material in many fields. An important aspects of gold nanoparticles is the surface properties, which allow modification by many molecules or groups. A gold nanoparticles-decorated clay particle could increase the surface activity of the clay particle, while the chemical and physical stability of clay could support the gold nanoparticles under some extreme environments. The synergistic effect of gold and clay may increase the applications of these two materials.

Here, we reported on a simple method to decorate clay particles with gold nanoparticles using 3-aminopropyltriethoxysilane (APTES) as the linkage, where the silane group of APTES formed Si–O–Si bonds with clay and the –NH<sub>2</sub> group bound to the gold nanoparticle. Well-ordered distributions of gold nanoparticles on clay particles were achieved with different gold nanoparticle sizes. These clay-APTES-Au (CAAu) nanocomposites had different colors depending on the gold nanoparticle sizes. The stability of the CAAu nanocomposites was characterized under strong acidic, basic, and high salt concentration conditions. To make a simple demonstration of a potential application of the CAAu composites, we made clay-APTES-Au-hexamethylene diamine-Au (CAAuHAu) hybrids, which changed the color of CAAu from red to blue. Moreover, hemoglobin was loaded on CAAu composites to show the potential application of sensors. The optical properties and the potential synergistic effect of clay and gold nanoparticles of these novel CAAu nanocomposites suggest wide-ranging applications, including biological and chemical sensing.

## Materials and Methods

**Materials.** 3-Aminopropyltriethoxysilane (APTES) and hexamethylene diamine were purchased from Sigma. HAuCl<sub>4</sub> and sodium citrate were purchased from Sigma and prepared using doubly distilled water at the concentration of 1.0 wt %. Clay (Capim DG) particles were kindly afforded by SCA R&D.

**Synthesis of Clay-APTES-Au (CAA) Nanocomposites.** Clay particles (5 g) were dispersed in 100 mL doubly distilled water and treated with ultrasonication for 30 min. The suspension was then kept for 2 h, and the precipitate was removed. The remaining clay particles were between 5 and 40 nm thick, the length and width were in the range 100–1000 nm. Subsequently, 4 mL clay suspension was mixed with 1.0 mL APTES for 12 h, and the modified clay particles were sedimented by centrifuge at 2500 rpm for 5 min. The particles were collected and rinsed with doubly distilled water 3 times, and were then mixed with 0.5 mL HAuCl<sub>4</sub> solution (1.0 wt %) for 5 min while sonicating. The mixture was diluted to 100 mL and heated to boil, and then 0.2, 0.5, 1.0, and 1.5 mL of sodium citrate (1.0 wt % in doubly distilled water) were injected, separately. This procedure is similar to one developed for coating gold nanoparticles on carbon nanotubes.<sup>36</sup> For a control, another clay sample was prepared using the same procedure as above, but without APTES modification. The obtained nanocomposites were rinsed three times and sedimented by centrifuge at 2500 rpm. Finally, the nanocomposites were diluted with 1.0 mL doubly distilled water.

**Stability of CAAu Nanocomposites in Extreme Conditions.** 0.2 mL of synthesized CAAu nanocomposites was mixed with 0.2 mL H<sub>2</sub>SO<sub>4</sub> (98%), 0.2 mL HNO<sub>3</sub> (65%), 0.2 mL 3 M NaOH, or 0.2 mL 2 M MgSO<sub>4</sub>, separately. The mixtures were kept for 10 min, followed by 2500 rpm centrifuge for 5 min to sediment the composites and then rinsed with doubly distilled water 3 times and collected by centrifuge. The collected samples were redispersed in 1.0 mL doubly distilled water.

**Fabrication of Clay-APTES-Au-HD-Au (CAAuHAu) Hybrids.** 0.4 mL of obtained CAAu nanocomposites (sodium citrate amount of 1.0 mL) with average gold nanoparticle size of 15 nm was mixed with 0.02 mg hexamethylene diamine (HD) and kept for 20 min. Then, 0.4 mL of gold nanoparticles was added to the mixture and kept for another 20 min. After that, the sample was rinsed three times and collected by centrifuge at 2500 rpm. Here, gold nanoparticles were synthesized by the reaction of 0.5 mL HAuCl<sub>4</sub> and 1.0 mL sodium citrate, which was the same amount as for the CAAu nanocomposite, and as observed in TEM, the average size of gold nanoparticles was also about 15 nm. For a control experiment, 0.4 mL of CAA nanocomposite was mixed with 0.02 mg HD and then added to 0.4 mL doubly distilled water.

**Load of Hemoglobin on CAAu Nanocomposites.** 0.2 mL of CAAu nanocomposites (sodium citrate amount of 1.0 mL) with average gold nanoparticle size of 15 nm was mixed with 0.5 mL 2 mg/mL hemoglobin (purchased from Sigma) in pH 8.0 phosphate buffer and kept for 24 h at 4 °C.<sup>37</sup> After that, hemoglobin-loaded CAAu composite was collected by 2500 rpm centrifuge and rinsed three times with doubly distilled water. This hemoglobin-loaded composite was then characterized by FTIR.

**Characterizations.** The synthesized CAAu nanocomposites and CAAuHAu hybrids were imaged by transmission electron microscope (TEM) using a JEOL 2000FX operating at 160 kV. The electron diffraction of gold nanoparticles was done on a nanoparticle (size of 80 nm) at the edge of a clay particle; the CAAu sample used here was the one synthesized by adding 0.2 mL sodium citrate, since some of the gold nanoparticles here were large enough to cause diffraction on a single nanoparticle. UV–vis spectroscopy experiments were done on a UV-160A spectrometer (Shimadzu) to measure the adsorption of the

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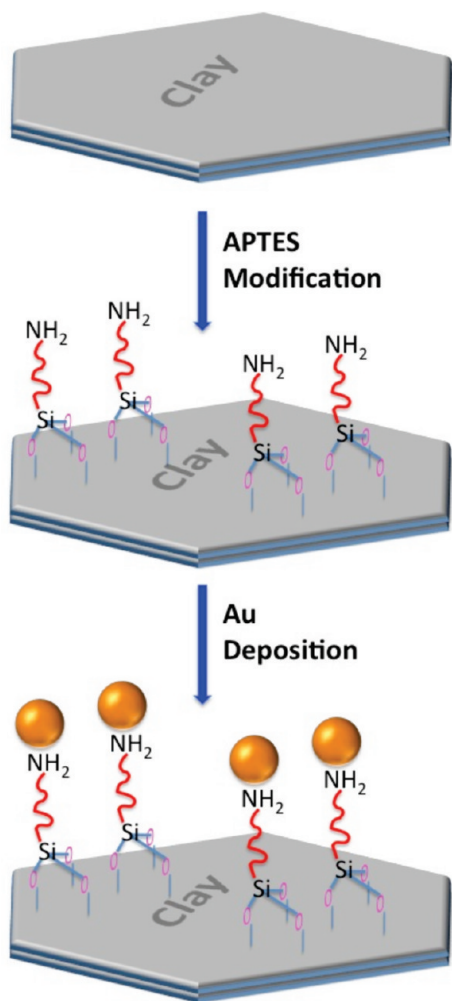
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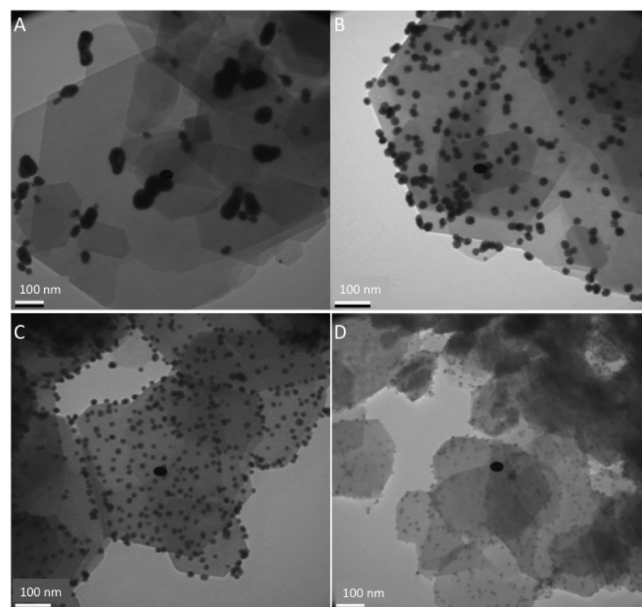
**Figure 1.** Synthetic procedures of clay-APTES-Au (CAAu) nanocomposites. The clay was modified by APTES and then gold nanoparticles were loaded to the clay-APTES surface.

nanocomposites. FTIR characterizations were performed on a Nicolet 6700 (Thermo) spectrometer using the suspension of all samples. Photographs of the colorful nanocomposites were recorded by digital camera.

## Results and Discussion

Figure 1 shows a diagram of the synthetic procedure. To break up larger aggregations of clay particles into smaller ones, we used ultrasonication treatment. After allowing the clay suspension to rest for a period of 2 h, larger particles were deposited on the bottom of the beaker, while smaller particles remained in the suspension. This procedure selected small particles, which made further characterizations, like TEM, easier. Subsequently, the selected clay particles were treated and thus modified with APTES. These clay-APTES particles contain an  $\text{-NH}_2$  group at one terminal, allowing gold nanoparticles to bind to the clay particles since gold are easily conjugated with molecules via the  $\text{-NH}_2$  functional group.<sup>38</sup> Once APTES was modified on clay particles, gold nanoparticles could be deposited during the synthetic process using a single-step procedure.<sup>36</sup>

Figure S1 (Supporting Information) shows the TEM images of clay particles, clay-Au nanocomposites synthesized without



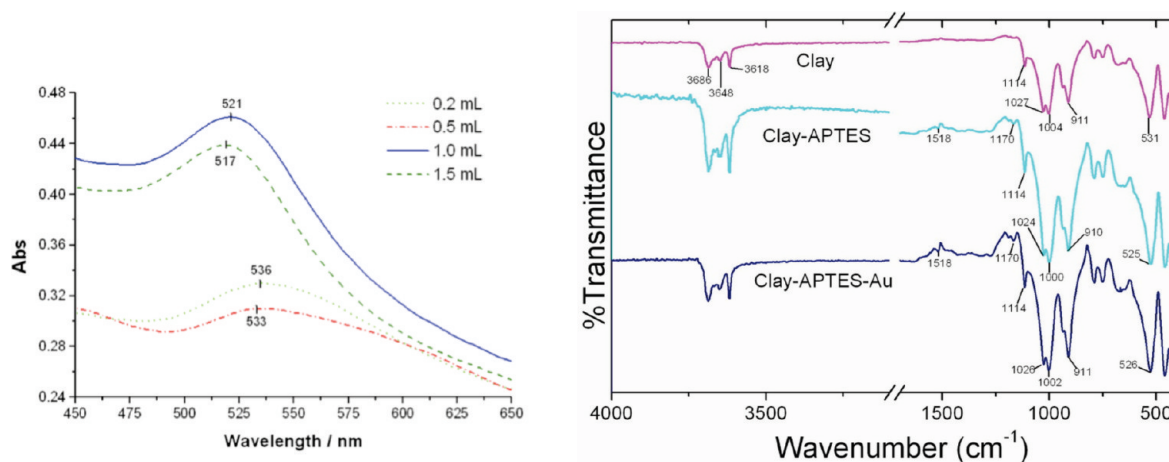
**Figure 2.** TEM images of synthesized clay-APTES-Au (CAAu) nanocomposites at the added sodium citrate amounts of 0.2 (A), 0.5 (B), 1.0 (C), and 1.5 mL (D). (The black dot in the center of the images is an imaging artifact).

APTES modification, and CAAu nanocomposites. Small clay particles were selected, using the above-mentioned sonication treatment, making the samples suitable for TEM imaging (Supporting Information Figure S1 A). As shown in Supporting Information Figure S1 B, gold nanoparticles were barely deposited on clay without APTES modification of clay, while with APTES modification, gold nanoparticles were evenly deposited on clay particles with a high density (Supporting Information Figure S1 C).

As previously reported, the sizes of gold nanoparticles can be adjusted by changing the injected amount of sodium citrate.<sup>36</sup> Here, we also investigated the adjustment of gold nanoparticle sizes. In Figure 2, TEM images are shown of CAAu nanocomposites with different gold nanoparticle sizes. When 0.2 mL sodium citrate was injected into the reaction solution, gold nanoparticles were larger but the distribution of gold nanoparticles was not evenly distributed on the clay surfaces (Figure 2A). When 0.5 mL sodium citrate was added, gold nanoparticles had a more uniform shape and size ( $20 \pm 2$  nm), as well as an even distribution on surface of the clay particles (Figure 2B). As sodium citrate increased to 1.0 mL, the size of gold nanoparticles decreased to  $15 \pm 2$  nm, while the even distribution remained (Figure 2C). Gold nanoparticles with an average diameter of  $10 \pm 1$  nm were obtained when 1.5 mL sodium citrate was used, and the even distribution remained (Figure 2D). The diameter distribution of gold nanoparticles on clay particles and the numbers of gold nanoparticles per square micrometer on the clay particles are shown in Supporting Information Figure S2. To observe the crystalline structure of the gold nanoparticles on clay, TEM electron diffraction was performed. The obtained electron diffraction showed that the gold nanoparticles on clay have the same crystalline structure as pure gold nanoparticles (as shown in Supporting Information Figure S3).

Clay particles are white, and this color remained after the APTES modification. However, after gold nanoparticles deposition, the color of the clay particles changed. In our experiments, four different colors were obtained by adjusting the sizes of gold nanoparticles. Figure S4 (Supporting Information) shows

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**Figure 3.** (Left) UV-vis of synthesized clay-APTES-Au (CAAu) nanocomposite suspensions. (Right) FTIR of clay, clay-APTES (CA), and clay-APTES-Au (CAAu). The CAAu sample used for FTIR measurement was that synthesized at a sodium amount of 1.0 mL.

photographs of the CAAu nanocomposites in suspension. The colors of these suspensions tuned from purple, to plum, and to red in the order of injected sodium citrate amount of 0.2, 0.5, 1.0, and 1.5 mL. When the suspensions were resting for 30 min, the synthesized CAAu nanocomposites sedimented on the bottom of the tube, with the same colors as the suspensions.

After an additional 2 h (not shown in Supporting Information Figure S4), CAAu in all tubes sedimented; however, the two with the largest amount of sodium citrate (1.0 and 1.5 mL) remained red. This red color is due to the free gold nanoparticles remaining in the solution. The mole amounts of gold nanoparticles were obviously higher for smaller particles than for larger particles when the mole amount of gold was the same. In the first two cases, the synthesized gold nanoparticles were almost all deposited on the clay. Moreover, the larger gold particles on the clay surface increased the specific weight; thus, the CAAu composites were more easily sedimented and resulted in a more clear solution. For the last two cases (1.0 and 1.5 mL citrate), the amounts of gold nanoparticles were higher, but the specific weights were less than in the first two cases; thus, the sediment time were longer (more than 2 h). Another reason is that the greater amount of free gold nanoparticles over the quantity needed to cover the clay particles resulted in a solution that remained red after sedimentation.

The UV-vis spectra (Figure 3) of the synthesized CAAu nanocomposites show that, depending on the sizes of gold nanoparticles, the absorption peaks of CAAu nanocomposite suspensions shifted toward shorter wavelengths when the added sodium citrate increased from 0.2 to 1.5 mL. Figure 3 also shows the FTIR spectra of clay, APTES modified clay, and CAAu nanocomposites. After the modification of APTES, new peaks at 1170 and 1518  $\text{cm}^{-1}$  appeared, which we interpreted as due to the  $-\text{CH}$  and  $-\text{NH}$  bonds of the APTES.<sup>39</sup> In addition, slight shifts of the peaks at 1027, 1004, and 531  $\text{cm}^{-1}$ ,<sup>40</sup> corresponding to  $\text{SiO}$  and  $\text{AlO}$  stretching, were found. After the deposition of gold nanoparticles on the clay particles, the shifted peaks moved slightly back, and the  $-\text{CH}$  and  $-\text{NH}$  stretching was slightly enhanced.

To test the stability of the nanocomposites in strong acids and bases, we studied the color of the nanocomposites in such solutions and did TEM characterization of the composites.

0.2 mL CAAu nanocomposite suspensions were mixed with 0.2 mL  $\text{H}_2\text{SO}_4$  (98%), 0.2 mL  $\text{HNO}_3$  (65%), 0.2 mL 3 M NaOH, or 0.2 mL 2 M  $\text{MgSO}_4$  solutions. No obvious color changes were found on the CAAu nanocomposites upon the addition of these reagents. However, in TEM images (Figure S5 and Figure S6 in Supporting Information), we found that some of the gold nanoparticles aggregated into larger clusters when NaOH was added, in contrast to the even distribution of the starting samples. That may due to the fact that a strong basic solution like 3 M NaOH could slightly influence the status of the gold nanoparticles because of the rupture of the  $\text{Si}-\text{O}-\text{Si}$  bond between APTES and clay,<sup>41</sup> and then, released gold particles could aggregate again to another gold particle. This aggregation could also be due to NaOH, as is known for colloidal gold solutions. Except for the NaOH case, no obvious changes were found for the other three reagents as observed from the TEM images (Supporting Information Figures S5 and S6). Compared with colloidal gold nanoparticles, the gold nanoparticles on clay showed a much higher stability under these extreme conditions (see the photographs in Figure S7 in Supporting Information). While the colloidal gold exhibited an obvious change in color, the CAAu nanocomposites did not show any visible change in color. These results showed that the CAAu composites were stable in strong acid and high salt concentration, while it was slightly influenced by a high concentration of NaOH.

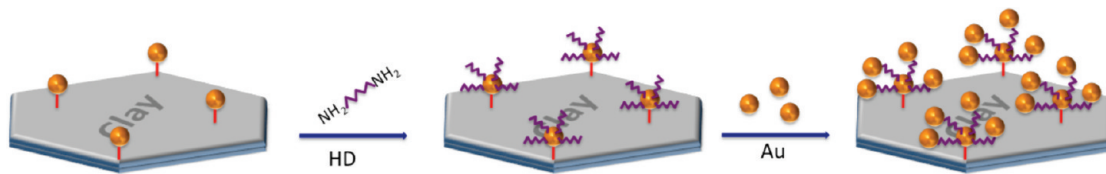
The color of the CAAu nanocomposites may be used a visible signal for some interactions based on the gold nanoparticles. Hybridization of oligonucleotide-labeled gold nanoparticles is used to detect the single base mismatch in short sequences of DNA, by detecting the change in color.<sup>42</sup> To study whether the aggregation of the gold nanoparticles on clay surfaces can change the color of the CAAu nanocomposites, we further fabricated CAAuHAu hybrids, by assembling free gold nanoparticles onto the CAAu nanocomposites. As shown in Figure 4, CAAu nanocomposites were first incubated with hexamethylene diamine (HD), which formed clay-APTES-Au-HD (CAAuH) by the interaction between the  $-\text{NH}_2$  group of the HD and the gold nanoparticles on clay surface. Then, when free gold nanoparticles were added, bonds were formed between HD molecules and the free gold nanoparticles, causing the gold nanoparticles to

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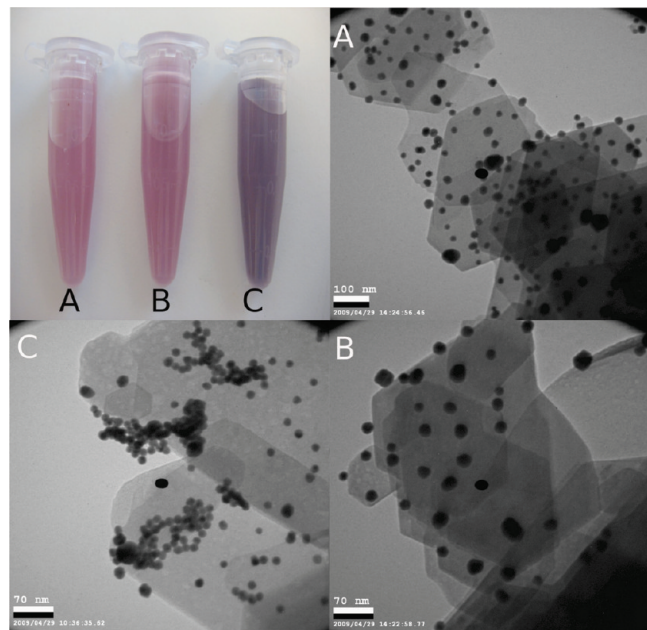
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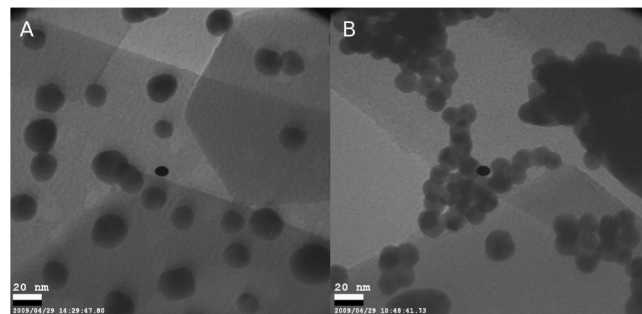
**Figure 4.** Scheme of the fabrication of clay-APTES-Au-HD-Au (CAAuHAu) hybrids.



**Figure 5.** Solutions and TEM images of (A) clay-APTES-Au (CAAu), (B) clay-APTES-Au-HD (CAAuH), and (C) clay-APTES-Au-HD-Au (CAAuHAu).

assemble. When these CAAuHAu hybrids were formed on the clay surfaces, the color changed from red to blue.

Figure 5 shows photographs of CAAu, CAAuH, and CAAuHAu hybrids, as well as the TEM images of these three samples. The incubation of CAAu with HD caused an almost negligible change to the original color of CAAu nanocomposites, while the color turned from red to blue when CAAuHAu hybrids were formed. After the CAAuHAu hybrids were rinsed and collected by centrifuge, the influence of free gold nanoparticles on the color change was removed, demonstrating that the color change occurred on the clay surface. As shown in the TEM images, almost no change could be found after the modification of CAAu nanocomposites with HD, while aggregations were found after CAAuHAu hybrids were fabricated. Figure 6 shows TEM images at higher magnification of the CAAuH and CAAuHAu hybrids, showing aggregations of the gold nanoparticles on the clay surface. The red to blue color change was considered similar to those DNA hybridization caused color change, where two kinds of gold nanoparticles, labeled with two matched DNA sequences, aggregated upon the hybridization of DNA sequence.<sup>42</sup> These results demonstrate the feasibility of using CAAu nanocomposites in sensing applications. For example, one can design a similar process as reported by Mirkin et al.<sup>43</sup> and use pure gold particles modified with a sample oligonucleotide and a modified CAA with a completely matching oligonucleotide. Then, through DNA



**Figure 6.** Higher-magnification TEM images of (A) clay-APTES-Au-HD (CAAuH) and (B) clay-APTES-Au-HD-Au (CAAuHAu).

hybridization, CAAu-(DNA)-Au hybrids will be formed resulting in a color change.<sup>44</sup>

Moreover, these CAAu composites could serve as substrates for loading biomolecules, which can be used for other kinds of sensors. To make a first step toward such a sensor, we loaded hemoglobin onto the nanocomposites. As shown in the FTIR measurement in Supporting Information Figure S8, hemoglobin was deposited on CAAu composites after the loading process, as is evident from the presence of new bands at 1653 and 1540  $\text{cm}^{-1}$ .<sup>45</sup> These two bands were attributed to the amide I and amide II infrared absorbance bands of hemoglobin. The successful loading of hemoglobin suggests a potential application of CAAu composites as a sensor for hydrogen peroxide.<sup>46</sup>

Furthermore, these CAAu nanocomposites may also increase the use of clay particles in other applications. For example, it has recently been demonstrated that clay nanoparticles can support single-molecule fluorescence spectroelectrochemistry,<sup>47</sup> showing that fluorescent redox molecules can absorb on clay layers. If there are gold nanoparticles on the clay, like the nanocomposites described in this paper, one may covalently modify molecules on the nanocomposites, and that may increase the stability of the fluorescence. As another example, these CAAu nanocomposites could be used in electrochemical studies by modifying the electrodes with or without functionalizing the nanocomposites. Furthermore, the decoration of gold nanoparticles may enhance the charge transfer of clay on the electrode and improve the electrochemical signal.<sup>6</sup>

## Conclusions

We report here a simple method to synthesize colored CAAu nanocomposites and CAAuHAu hybrids. TEM characterizations showed uniformly shaped gold nanoparticles on clay with an even distribution. The size of the gold nanoparticles, and thus the corresponding color of the composite, was determined by adjusting process parameters. These CAAu nanocomposites had a high stability in extreme acid and basic environments. To demonstrate the use of these composites in sensor application, we used linkage

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molecules (HD) to aggregate free gold nanoparticles onto the composites, causing a shift in color. Moreover, the loading of hemoglobin on CAAu composites suggests potential applications such as in sensing hydrogen peroxide. In summary, these nanocomposites might provide a simple route to several applications, including label-free biological or chemical sensing.

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**Supporting Information Available:** Additional figures as described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.