Supplementary Information

Silver-doped hydroxyapatite for formaldehyde determination by digital-image colorimetry

Uma Pongkitdachoti, Fuangfa Unob

Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, 10330

Experimental

Synthesis of hydroxyapatite and characterization

Hydroxyapatite was synthesized *via* the co-precipitation between $Ca(NO_3)_2$ and H_3PO_4 solution at a Ca/P ratio of 1.67.[22] The pH of this mixture was adjusted to 11 using an ammonia solution (25% v/v). After stirring for 2 hours, the obtained white precipitate was filtered, washed with deionized water to remove the residual base, and dried overnight in an oven at 120 °C. The material was characterized by PXRD and TEM.

Analytical performance of HPLC method

Under the optimized experimental conditions, an external standard calibration curve was constructed using the peak area of the formaldehyde derivative and formaldehyde concentration. The linear working range of 30 – 200 μg L^{-1} was obtained. The limit of detection (LOD) and limit of quantification (LOQ) were determined using 3 and 10 times the standard deviation (σ) of the blank values, respectively (σ is the standard deviation of blank values (n= 10)) and the standard calibration curve in Fig. S1. The LOD and LOQ for formaldehyde determination were determined to be 10 and 24 μg L^{-1}, respectively.

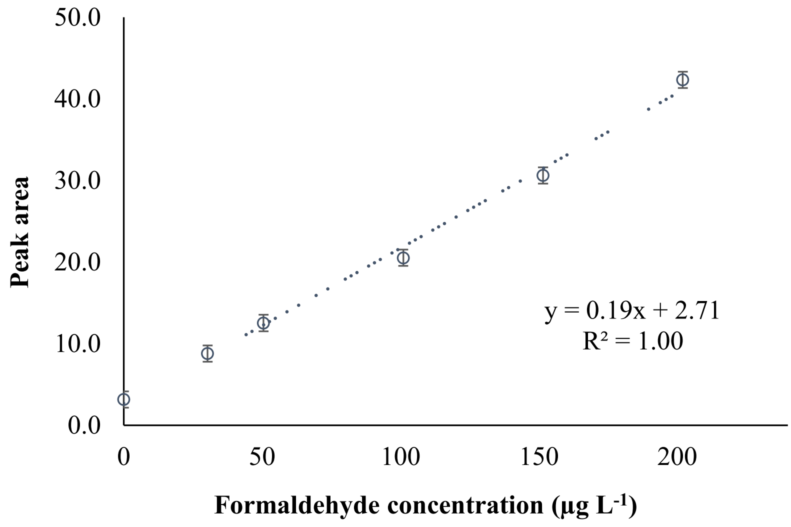

Fig. S1. The calibration curve for formaldehyde determination by the HPLC method.

Characterization of materials

X-Ray diffraction spectroscopy (XRD)

The PXRD pattern of the synthesized material showed a set of strong peaks at 2θ 10–60° corresponding to a hexagonal structure (JCPDS card 9-0432).

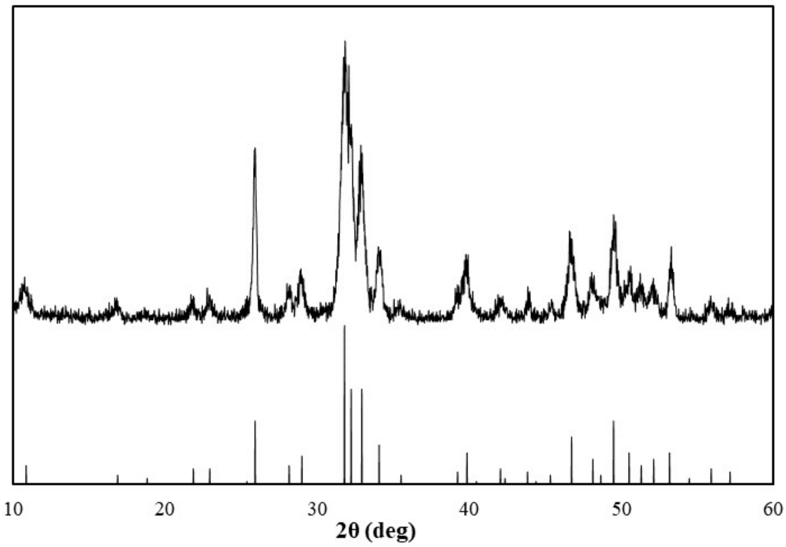

Fig. S2. XRD pattern of the synthesized hydroxyapatite compared to JCPDS card 9-0432 (below).

X-Ray photoelectron spectroscopy (XPS)

The XPS spectrum in Fig. S3 showed signals for Ag 3d 5/2 and Ag 3d 3/2 at 368 eV and 373.5 eV, respectively.[28] The deconvoluted spectrum of Ag 3d revealed two peaks at 368.971 eV and 374.298 eV with a peak splitting of approximately 6 eV, corresponding to elemental silver. The peaks at 367.490 eV and 373.019 eV with slightly lower binding energy show the association of silver with oxygen in Ag_2O. These results confirmed the existence of AgNPs and Ag_2O on the material surface after chemical reduction with formaldehyde under basic conditions.

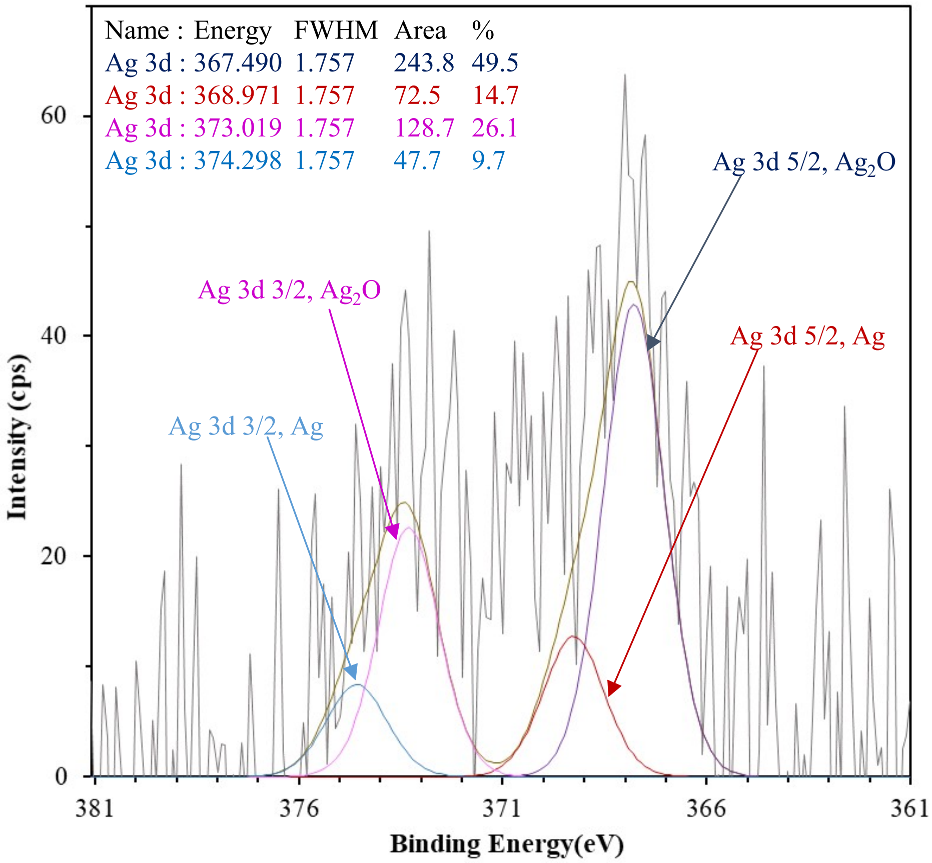

Fig S3 XPS spectrum of AgNPs-HAP obtained by using 70 mg L^{-1} formaldehyde and corresponding deconvoluted peaks of Ag (3d).

Optimization of parameters

Effect of silver ion concentration on formaldehyde detection

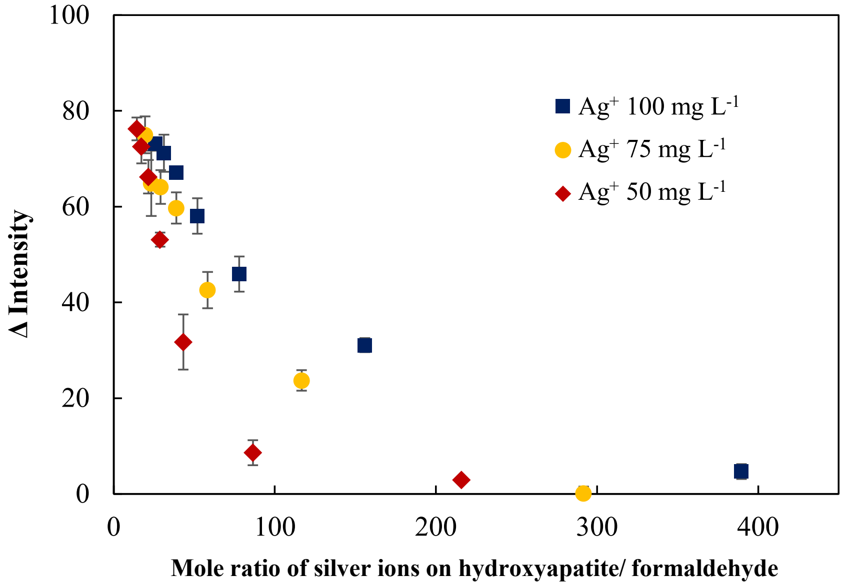

Fig. S4 ΔIntensity of the detection of formaldehyde with variation of mole ratio of silver ions on hydroxyapatite to formaldehyde. (40 mg Ag-HAP were used in the detection of 5.00 mL solution containing 10 – 150 µg L^{-1} formaldehyde. The amount of silver ions on hydroxyapatite (Ag^{+}_{HAP}) were 0.97, 1.31, and 1.75 mg g^{-1} when 50, 75, and 100 mg L^{-1} silver ion solutions were used in the modification, respectively).

At low formaldehyde concentrations, the concentration gradient between the bulk solution and the solid surface was low and hence, resulted in low driving force for formaldehyde diffusion. However, once formaldehyde diffused to the solid surface, the larger the content of silver on the Ag-HAP surface resulted in a higher ΔI observed due to the higher probability of nanoparticle formation on the surface. On the other hand, the effect of Ag^{+}_{HAP} to formaldehyde mole ratio was less prominent at high formaldehyde concentrations (50 – 150 μg L^{-1}) due to a high concentration gradient and higher driving force for formaldehyde diffusion from bulk solution to the Ag-HAP surface. Hence, with sufficient silver on the Ag-HAP materials, the chemical reduction occurred essentially to the same extent. It should be noted that when high amounts of AgNPs were produced on the hydroxyapatite surface, the materials turned brown and dark-brown, and only a slight change in color intensity was observed. Consequently, the sensitivity in the detection of high formaldehyde levels was lower.

Selectivity test

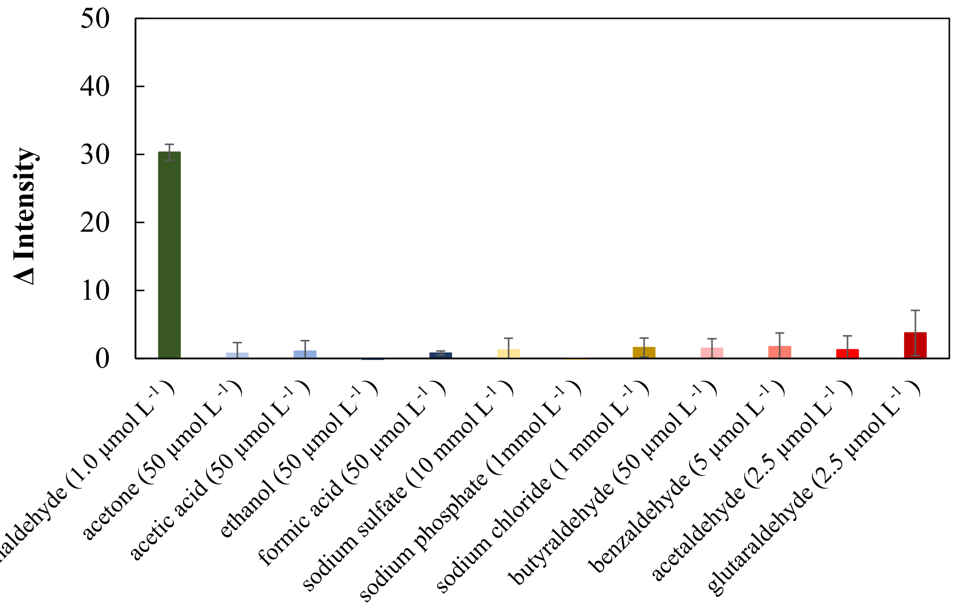

Fig. S5 Comparison of the Δintensity of AgNPs-HAP in the single solution of various compounds compared to a single formaldehyde solution (1.0 μmol L^{-1}).