

## Electronic Supplementary Information

### Histidine-directed formation of Ag octopods *via* pseudomorphic transformation of Ag<sub>2</sub>O

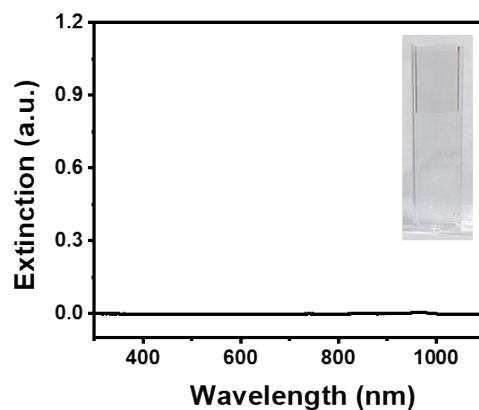
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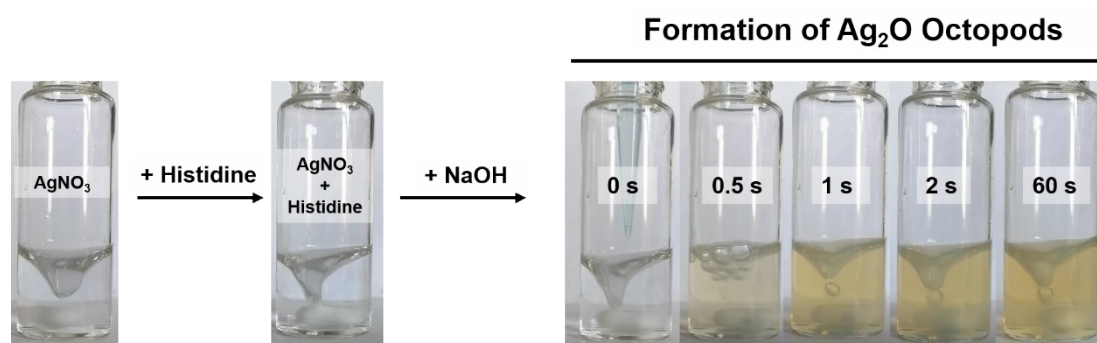
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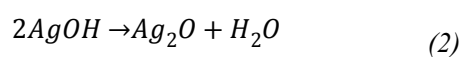
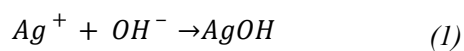
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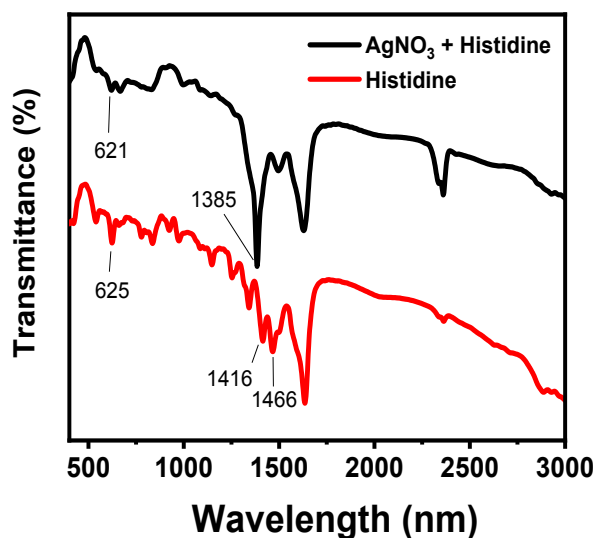


**Fig. S1** UV-Vis-NIR spectrum and photograph (inset) of the mixture of histidine and AgNO<sub>3</sub> recorded after 6 h stirring in the dark. The concentrations of histidine and AgNO<sub>3</sub> were 20.0 μM and 0.25 mM respectively. After 6 h stirring, the mixture (pH 4.7) was still colorless and no LSPR peak of Ag particles was observed in the spectrum, meaning histidine was not effective to reduce Ag<sup>+</sup> into Ag<sup>0</sup> at this time. This was reasonable since the imidazole group of histidine is primarily protonated and presents very poor reducing ability at this acidic pH (pH 4.7, see Ref. 12 in the text).

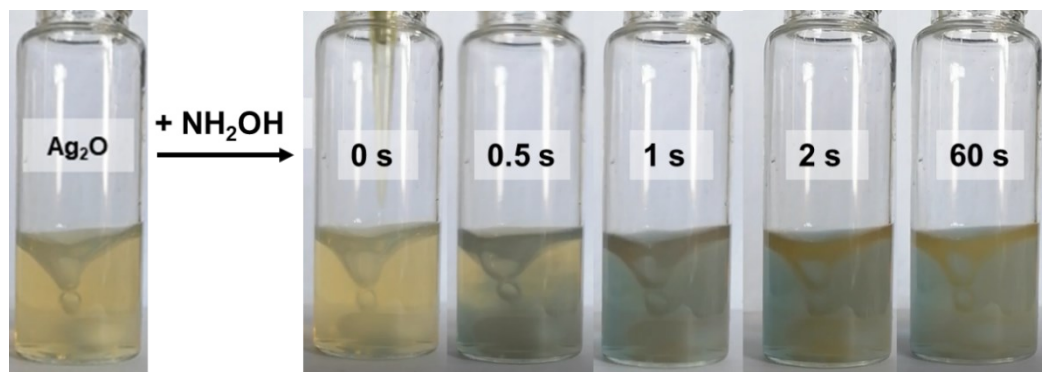


**Fig. S2** Photographs of the AgNO<sub>3</sub> solution, the mixture of AgNO<sub>3</sub> and histidine (pH ca. 4.7), and the mixture of AgNO<sub>3</sub> and histidine upon the addition of NaOH at different times. Final concentrations of AgNO<sub>3</sub>, histidine and NaOH in the mixtures were set to be 0.25 mM, 0.5 μM and 20.0 mM respectively. After the addition of NaOH into the mixture of AgNO<sub>3</sub> and histidine, color of the mixture evolved from colorless to light yellow and then yellow within 1 s, attributed to the formation of Ag<sub>2</sub>O precipitations (see Fig. 1b in the text). The proposed reaction equations of the formation of Ag<sub>2</sub>O were as follows according to Ref. 14 and Ref. 15 in the text:



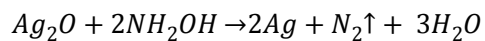


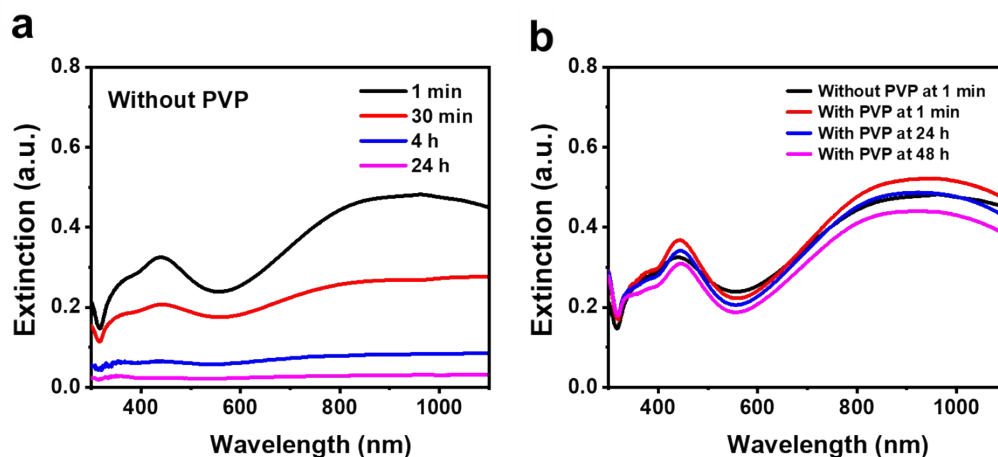
**Fig. S3** FTIR spectra of histidine and the mixture of  $\text{AgNO}_3$  and histidine. Pristine histidine presented symmetric bending of amino group at  $1466\text{ cm}^{-1}$ , stretching vibration of carboxyl group at  $1416\text{ cm}^{-1}$  and that of imidazole ring at  $625\text{ cm}^{-1}$  (see Ref. 16 and Ref. 17 in the text). After being mixed with  $\text{AgNO}_3$ , the symmetric bending of the amino group at  $1466\text{ cm}^{-1}$  almost disappeared, stretching vibration of the carboxyl group shifted from  $1416$  to  $1385\text{ cm}^{-1}$ , and that of the imidazole ring shifted from  $625$  to  $621\text{ cm}^{-1}$ , attributed to the formation of  $\text{Ag}^+$ -histidine complex. It was expected that the  $\text{Ag}^+$ -histidine complex should remain in the supernatant after the addition of  $\text{NaOH}$  due to the stronger affinity of histidine to  $\text{Ag}^+$  (stability constant  $K_c = 10^{5.4}$ ) than that of the hydroxyl group ( $K_c = 10^{2.3}$ ) (see Ref. 18 in the text).



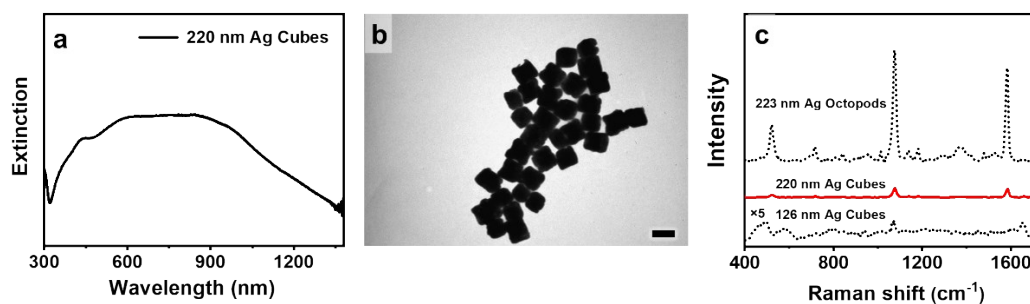
### Formation of Ag Octopods via Pseudomorphic Transformation of Ag<sub>2</sub>O

**Fig. S4** Photographs of the Ag<sub>2</sub>O octopod dispersion formed at 0.5 μM histidine, the dispersion upon the addition of NH<sub>2</sub>OH (100 μL, 50.0 mM) at different times. Color of the dispersion evolved from yellow to cyan within 2 s after the addition of NH<sub>2</sub>OH and no further change in color was observed within 1 min, meaning the rapid reduction of Ag<sub>2</sub>O into Ag, profitable for the pseudomorphic transformation of Ag<sub>2</sub>O particles into Ag ones via NH<sub>2</sub>OH reduction as follows (see Ref. 32 and Ref. 33 in the text):





**Fig. S5** UV-Vis-NIR spectrum of the Ag octopods prepared from the Ag<sub>2</sub>O ones formed at 2.0  $\mu$ M histidine recorded after 1 min, 30 min, 4 h and 24 h of the reaction in (a) absence of PVP and (b) presence of PVP (1 mL, 5 wt.%, added after 1 min of the reaction) recorded after 1 min, 24 h and 48 h of the reaction. The extinction decreased rapidly in absence of PVP, indicating the extensive aggregation of the Ag octopods, attributed to the poor stabilizing ability of histidine ligand (see Ref. 34 in the text). In presence of PVP, the extinction only decreased slightly after 48 h, meaning greatly improved stability of the Ag octopods in presence of PVP.



**Fig. S6** (a) UV–Vis–NIR spectrum and (b) TEM image of the ca. 220 nm Ag cubes (see Experimental section in the text). The scale bars are 200 nm. (c) SERS spectrum of p-MBA ( $10^{-5}$  M) recorded after being mixed with the ca. 220 nm Ag cubes. The spectra of Ag octopods with the similar size (223 nm, see Fig. 4d in the text) and smaller Ag cubes (126 nm, see Fig. 4a in the text) were given as dotted curves for comparison. The intensity of the  $1076\text{ cm}^{-1}$  band in presence of the 223 nm Ag octopods was ca. 11.6 times of that in presence of the 220 nm Ag cubes and ca. 45.8 times of that in presence of 126 nm Ag cubes, meaning the difference in SERS performance of the Ag particles is primarily related to their difference in shape rather than in size.