Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Ultralong Hydroxyapatite Nanowire-Based Layered Catalytic Paper for Highly Efficient Continuous Flow Reactions

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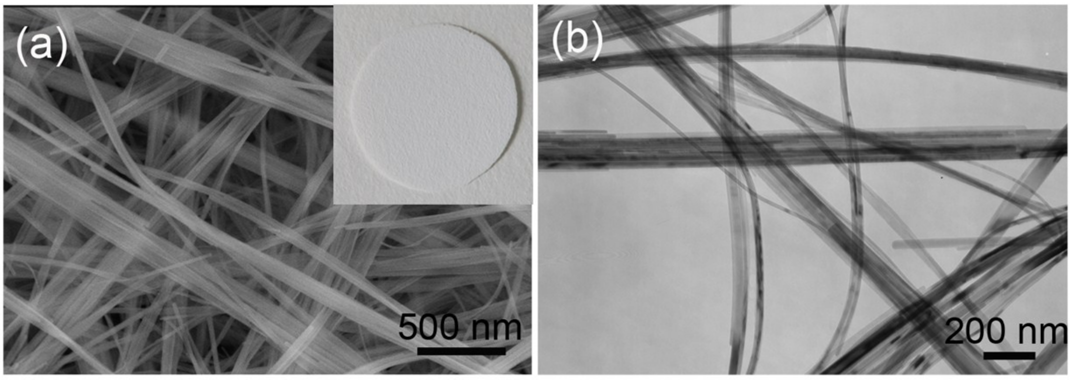

Fig. S1 (a) SEM micrograph and (b) TEM micrograph of ultralong hydroxyapatite nanowires (HAPNWs). Inset is a digital image of the highly flexible fire-resistant HAPNW paper with a diameter of 4 cm.

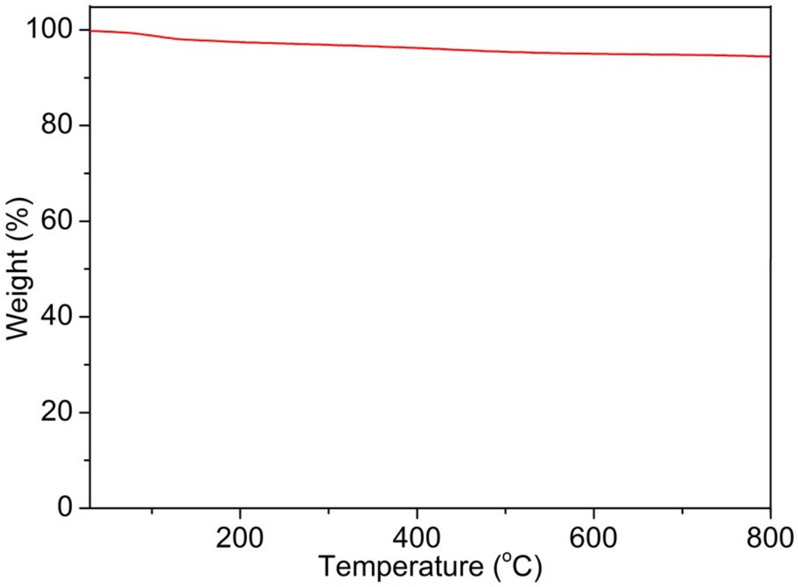

Fig. S2 TG curve of the as-prepared HAPNW/AuNP layered catalytic paper.

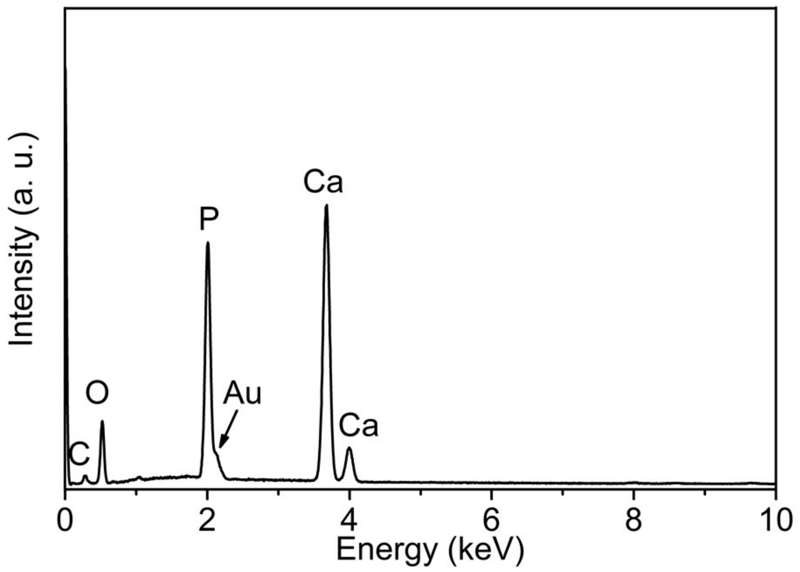

Fig. S3 EDS pattern of the as-prepared HAPNW/AuNP layered catalytic paper.

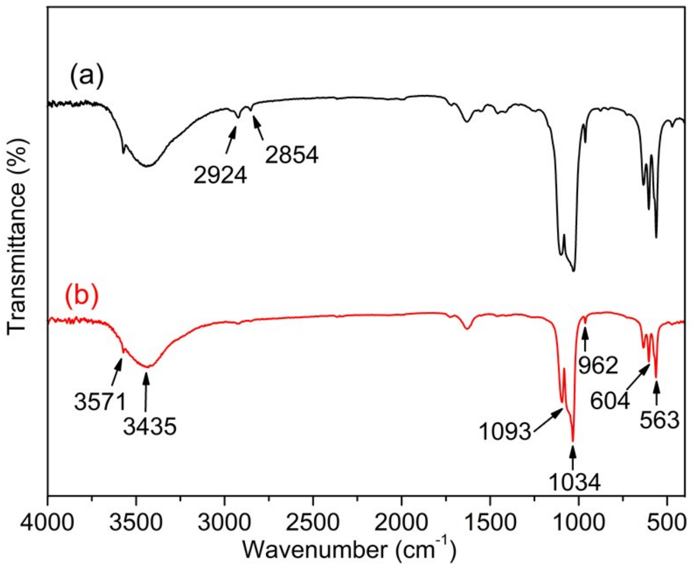

Fig. S4 FTIR spectra: (a) HAPNWs with adsorbed oleic acid molecules, and (b) the heat-treated HAPNWs at 600 ^{o}C for 4 h.

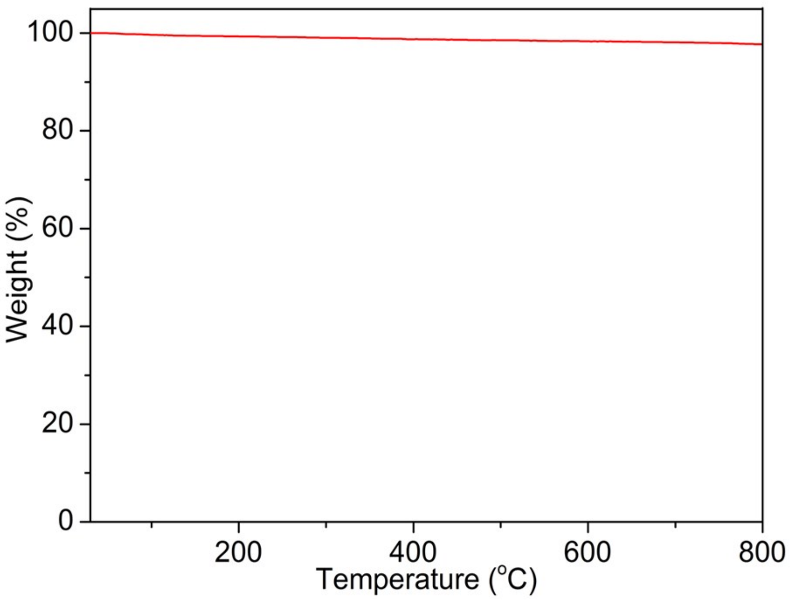

Fig. S5 TG curve of the heat-treated HAPNWs at 600 °C for 4 h.

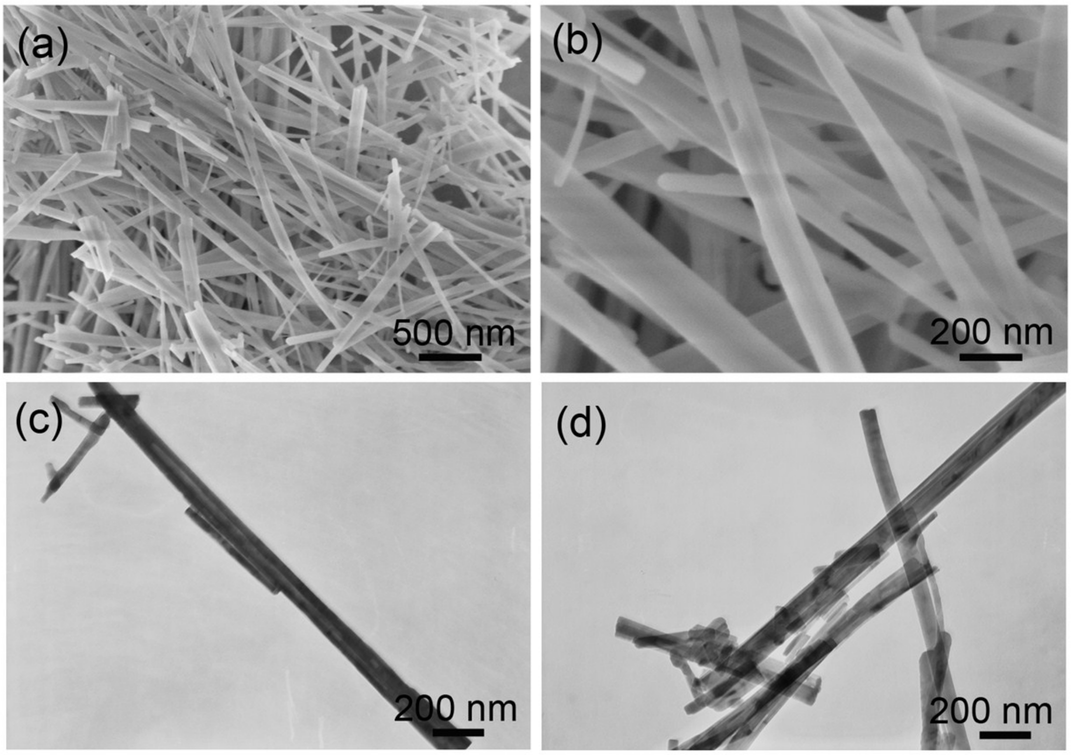

Fig. S6 (a, b) SEM micrographs and (c, d) TEM micrographs of the product prepared using the heat-treated HAPNWs and tetrachloroauric (III) acid aqueous solution at room temperature without additional reducing reagent. The experiments show no formation of AuNPs on the surface of HAPNWs.

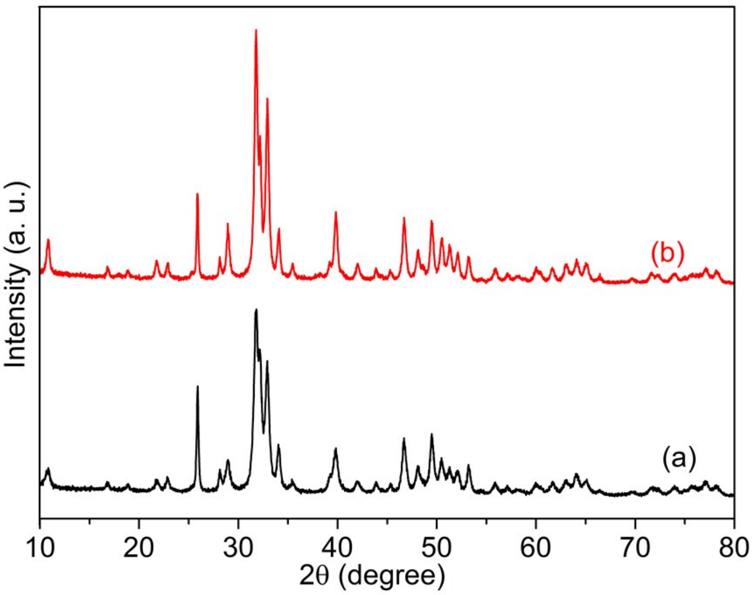

Fig. S7 XRD patterns: (a) HAPNWs; (b) the product prepared using the heat-treated HAPNWs and tetrachloroauric (III) acid aqueous solution at room temperature without additional reducing reagent, indicating that no Au peaks are obviously observed.

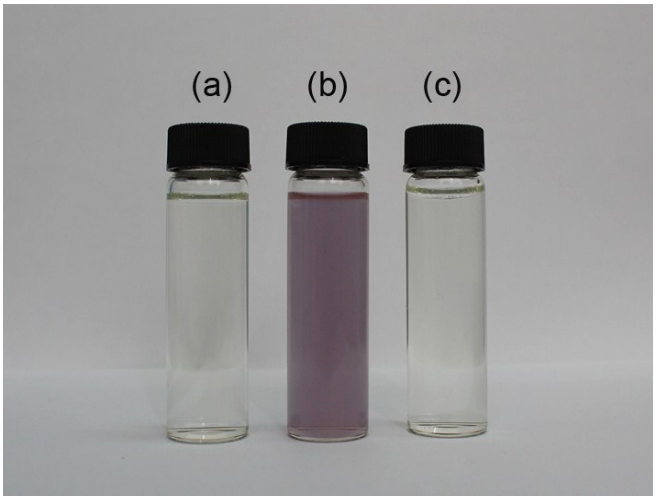

Fig. S8 Digital images. (a) The initial tetrachloroauric (III) acid aqueous solution; (b) the mixed aqueous solution containing sodium oleate and tetrachloroauric (III) acid after stirring for 12 h at room temperature; (c) the mixed aqueous solution containing sodium stearate and tetrachloroauric (III) acid after stirring for 12 h at room temperature. The experiments show that sodium oleate can reduce Au (III) to AuNPs in aqueous solution at room temperature.

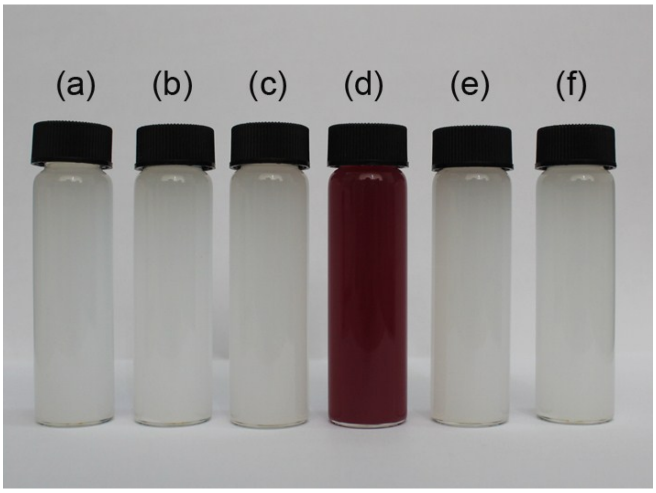

Fig. S9 Digital images. (a) The aqueous suspension containing the heat-treated HAPNWs; (b) the aqueous suspension containing the heat-treated HAPNWs and tetrachloroauric (Ⅲ) acid after stirring for 12 h at room temperature; (c) the aqueous suspension containing sodium oleate modified heat-treated HAPNWs; (d) the aqueous suspension containing sodium oleate modified heat-treated HAPNWs and tetrachloroauric (Ⅲ) acid after stirring for 12 h at room temperature; (e) the aqueous suspension containing sodium stearate modified heat-treated HAPNWs; (f) the aqueous suspension containing sodium stearate modified heat-treated HAPNWs and tetrachloroauric (Ⅲ) acid after stirring for 12 h at room temperature.

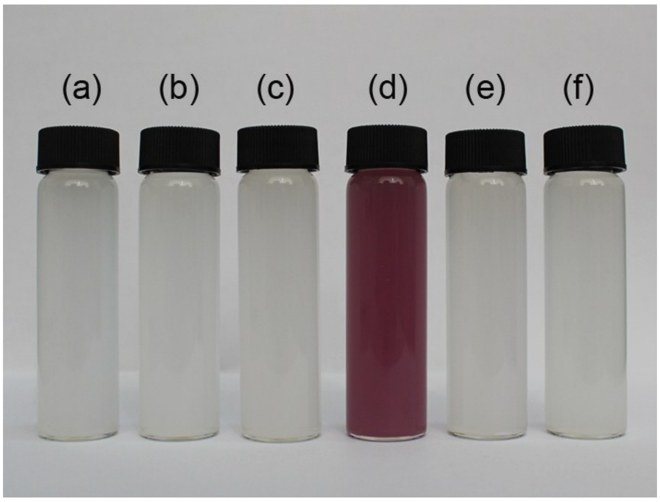

Fig. S10 Digital images. (a) The aqueous suspension containing the commercial HAP particles; (b) the aqueous suspension containing commercial HAP particles and tetrachloroauric (Ⅲ) acid after stirring for 12 h at room temperature; (c) the aqueous suspension containing sodium oleate modified commercial HAP particles; (d) the aqueous suspension containing sodium oleate modified commercial HAP particles and tetrachloroauric (Ⅲ) acid after stirring for 12 h at room temperature; (e) the aqueous suspension containing sodium stearate modified commercial HAP particles; (f) the aqueous suspension containing sodium stearate modified commercial HAP particles and tetrachloroauric (Ⅲ) acid after stirring for 12 h at room temperature.

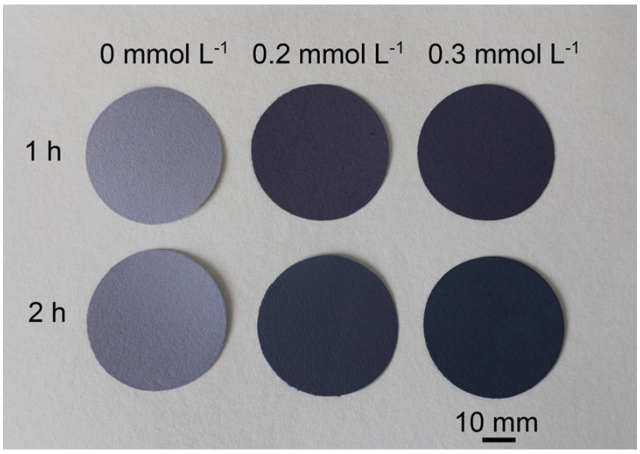

Fig. S11 Digital images of the HAPNW/AuNP layered catalytic paper sheets prepared using the aqueous suspension containing HAPNWs and tetrachloroauric (Ⅲ) acid in the presence of ferrous sulfate with different molar concentrations for different reaction times.

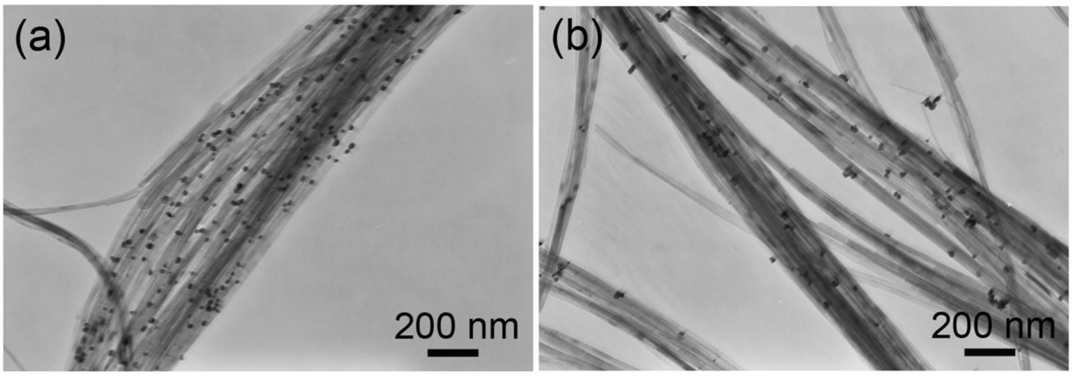

Fig. S12 TEM images of the as-prepared AuNPs-loaded HAPNWs after immersion in ethanol (a) and deionized water (b) for three months, respectively.

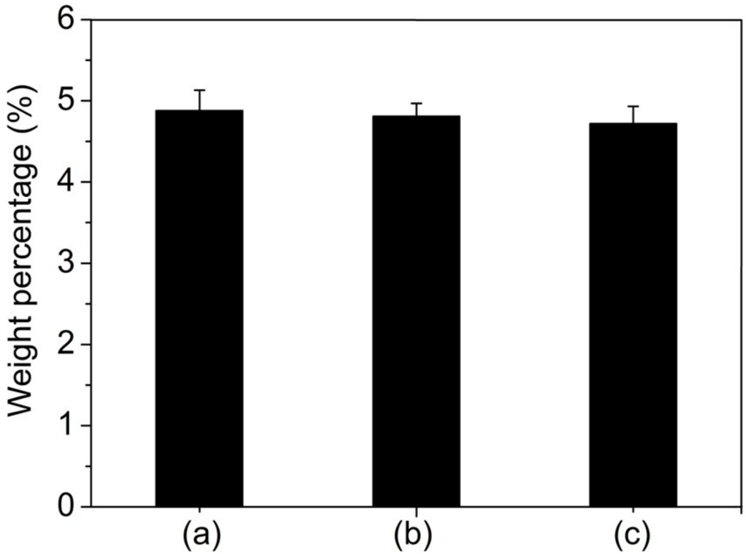

Fig. S13 The AuNP weight percentage obtained by the ICP analysis of the as-prepared AuNPs-loaded HAPNWs before (a) and after immersion in ethanol (b) and deionized water (c) for three months, respectively.

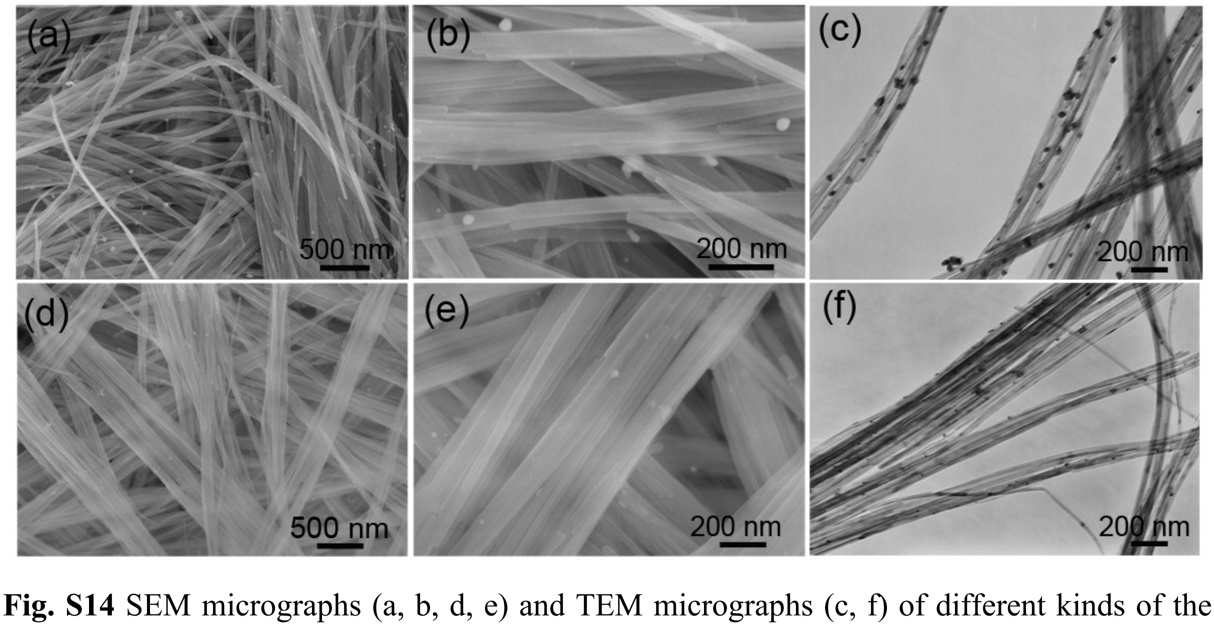

Fig. S14 SEM micrographs (a, b, d, e) and TEM micrographs (c, f) of different kinds of the HAPNW/AuNP samples. (a–c) The H-HAPNW/AuNP sample, (d–f) the L-HAPNW/AuNP sample. The SEM and TEM micrographs of the M-HAPNW/AuNP sample are shown in Fig. 1b–1d.

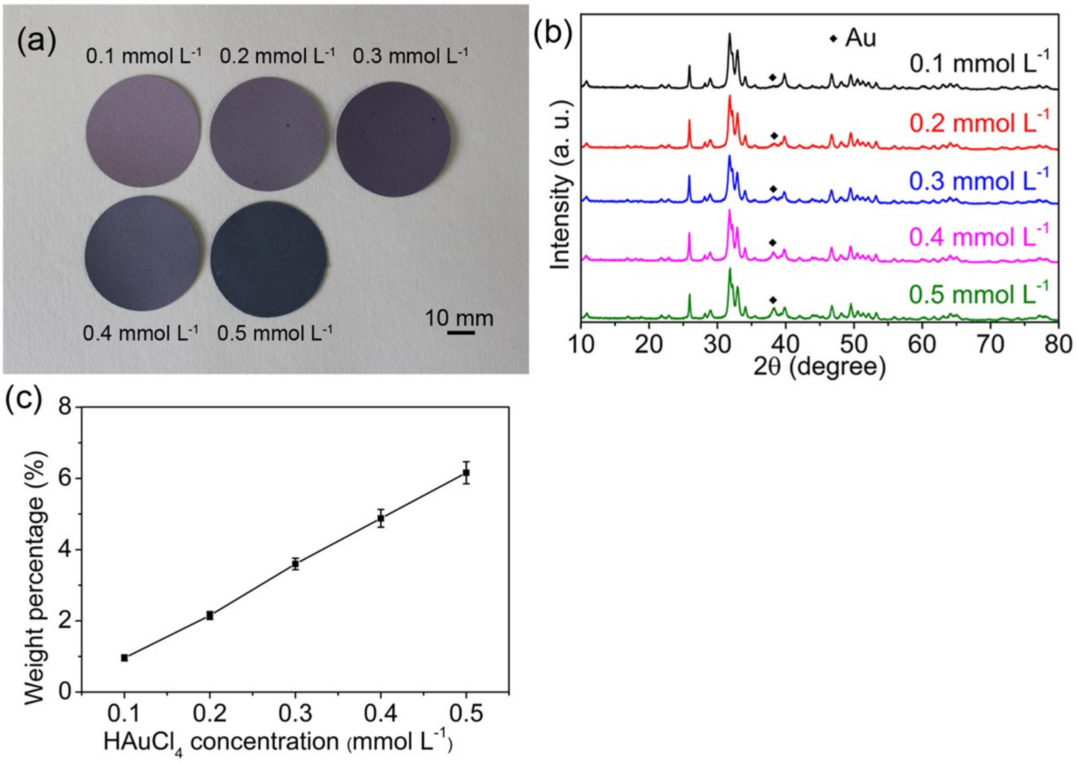

Fig. S15 (a) Digital images, (b) XRD patterns, and (c) ICP analysis results of the AuNP weight percentage of the HAPNW/AuNP layered catalytic paper sheets prepared at different molar concentrations of tetrachloroauric (III) acid in the reaction system ranging from 0.1 to 0.5 mmol L^{-1} for 12 h at room temperature.

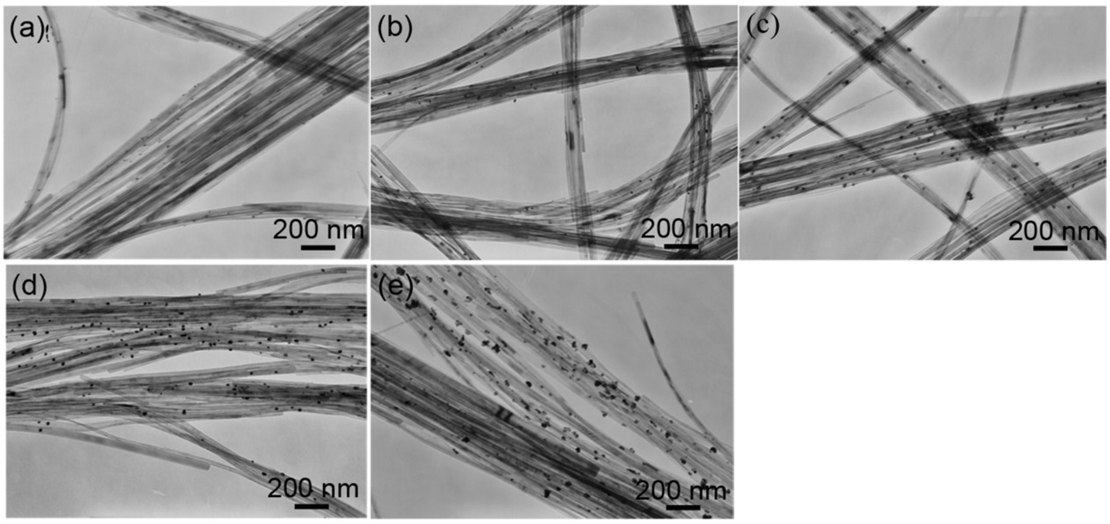

Fig. S16 TEM micrographs of the AuNPs-loaded HAPNWs prepared at different molar concentrations of tetrachloroauric (III) acid in the reaction system for 12 h at room temperature: (a) 0.1 mmol L^{-1}, (b) 0.2 mmol L^{-1}, (c) 0.3 mmol L^{-1}, (d) 0.4 mmol L^{-1}, and (e) 0.5 mmol L^{-1}.

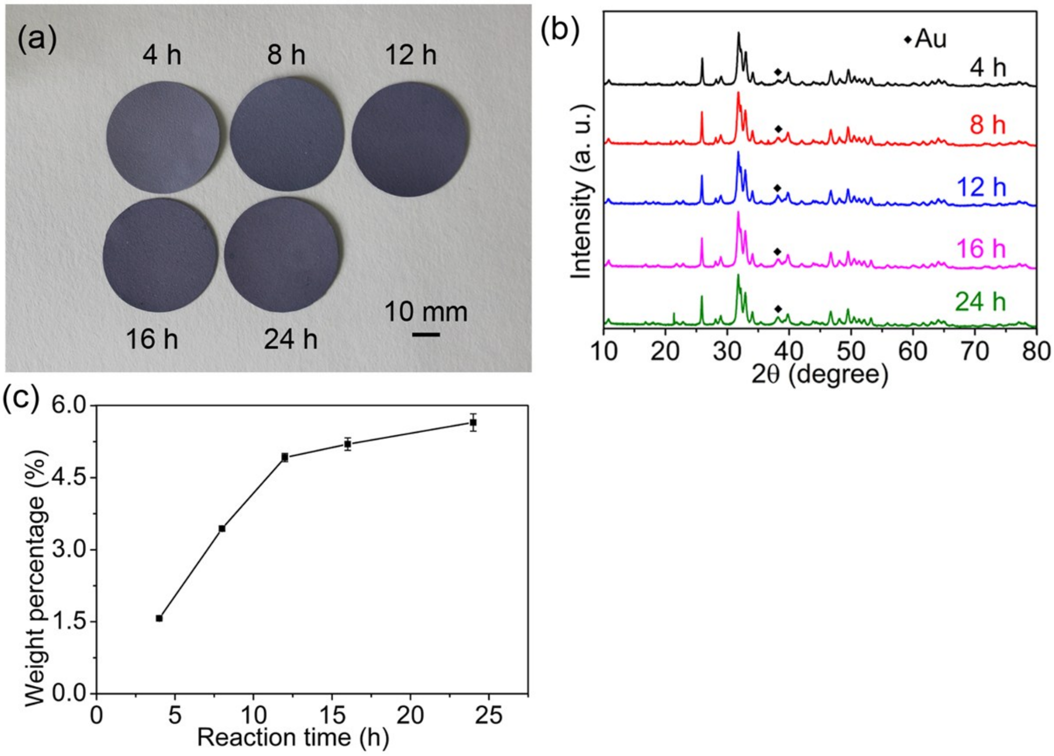

Fig. S17 The HAPNW/AuNP layered catalytic paper sheets prepared using tetrachloroauric (Ⅲ) acid (3296 μL, 5 mg mL^{-1}) for different reaction times ranging from 4 to 24 h at room temperature: (a) digital images, (b) XRD patterns, and (c) ICP analysis results of the AuNP weight percentage.

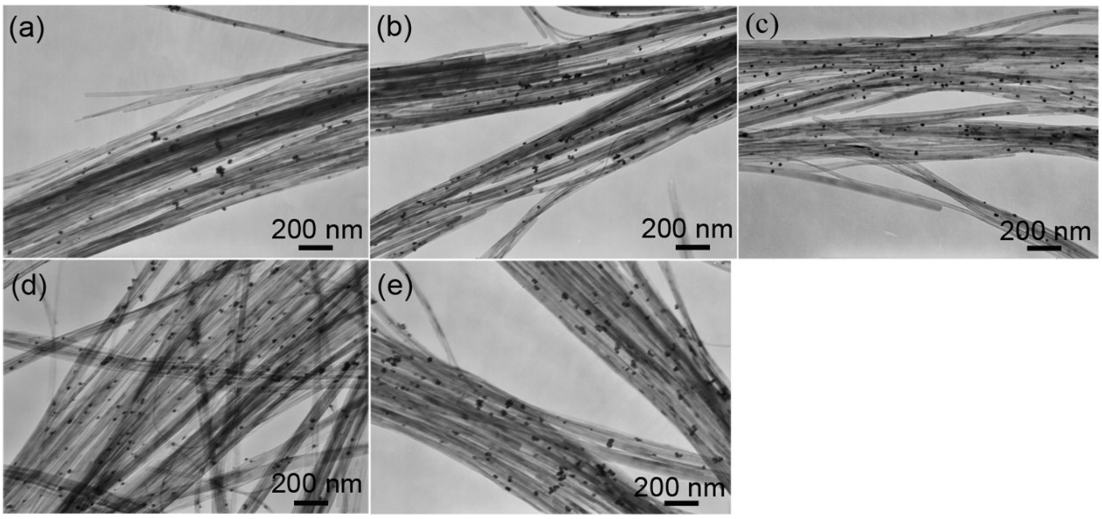

Fig. S18 TEM micrographs of the AuNPs-loaded HAPNWs prepared using tetrachloroauric (Ⅲ) acid (3296 μL, 5 mg mL^{-1}) for different reaction times at room temperature: (a) 4 h, (b) 8 h, (c) 12 h, (d) 16 h and (e) 24 h.

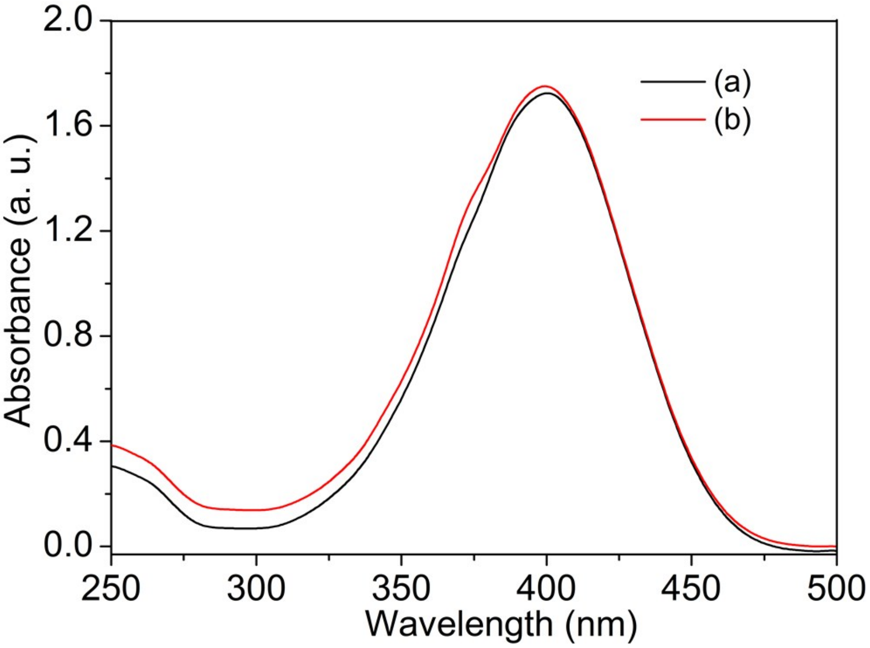

Fig. S19 UV-vis absorption spectra of an aqueous solution containing 4-NP and $NaBH_4$ before (a) and after (b) flowing through the HAPNW paper without loading AuNPs.

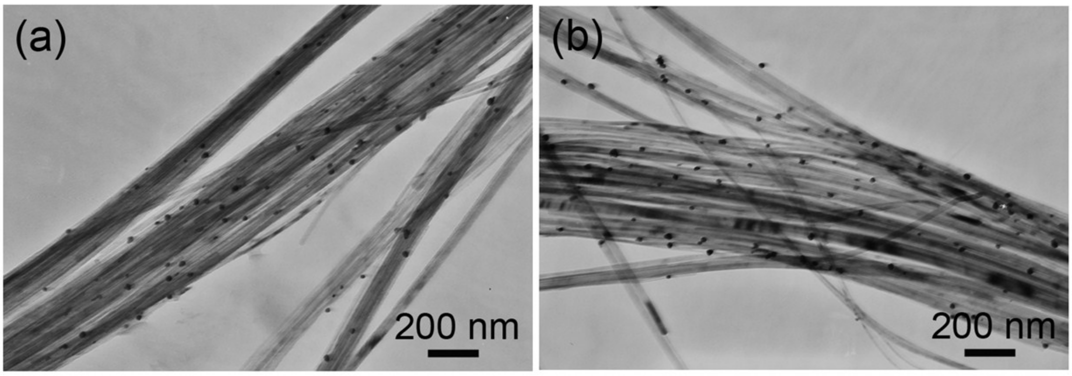

Fig. S20 (a, b) TEM micrographs of the AuNPs-loaded HAPNWs from the HAPNW/AuNP layered catalytic paper after the continuous flow catalytic reaction for about 200 h.

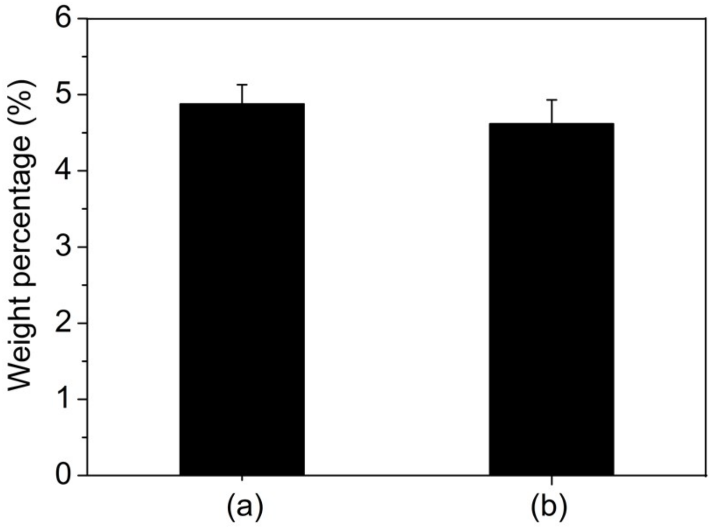

Fig. S21 ICP analysis results of the AuNP weight percentage of the HAPNW/AuNP layered catalytic paper before (a) and after (b) the continuous flow catalytic reaction for about 200 h.

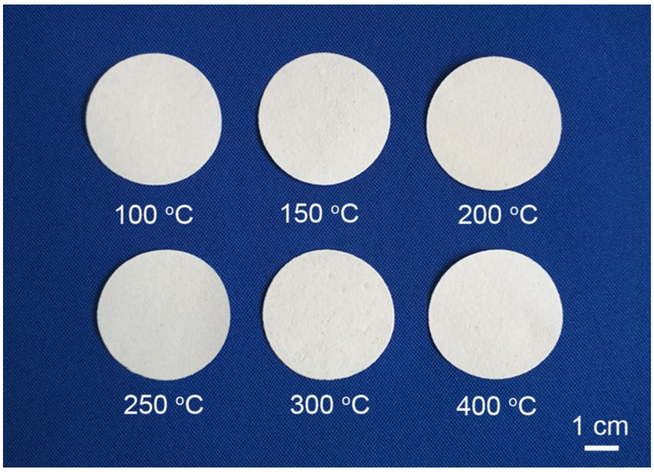

Fig. S22 Digital images of the HAPNW paper sheets after heat treatment at different temperatures for 1 h.

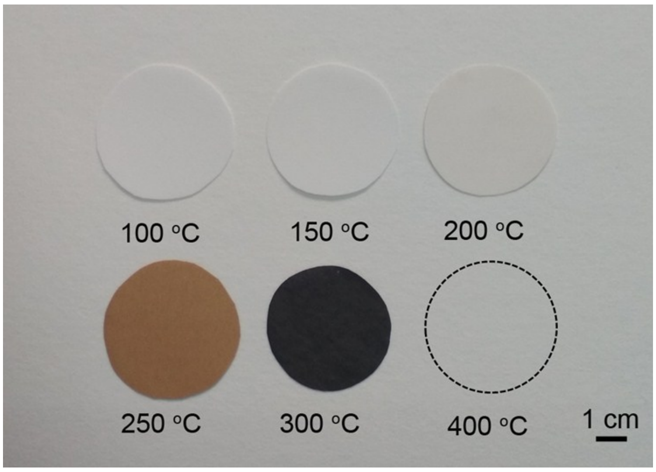

Fig. S23 Digital images of the commercial filter paper sheets after heat treatment at different temperatures for 1 h. The filter paper is completely burned off at 400 °C for 1 h.

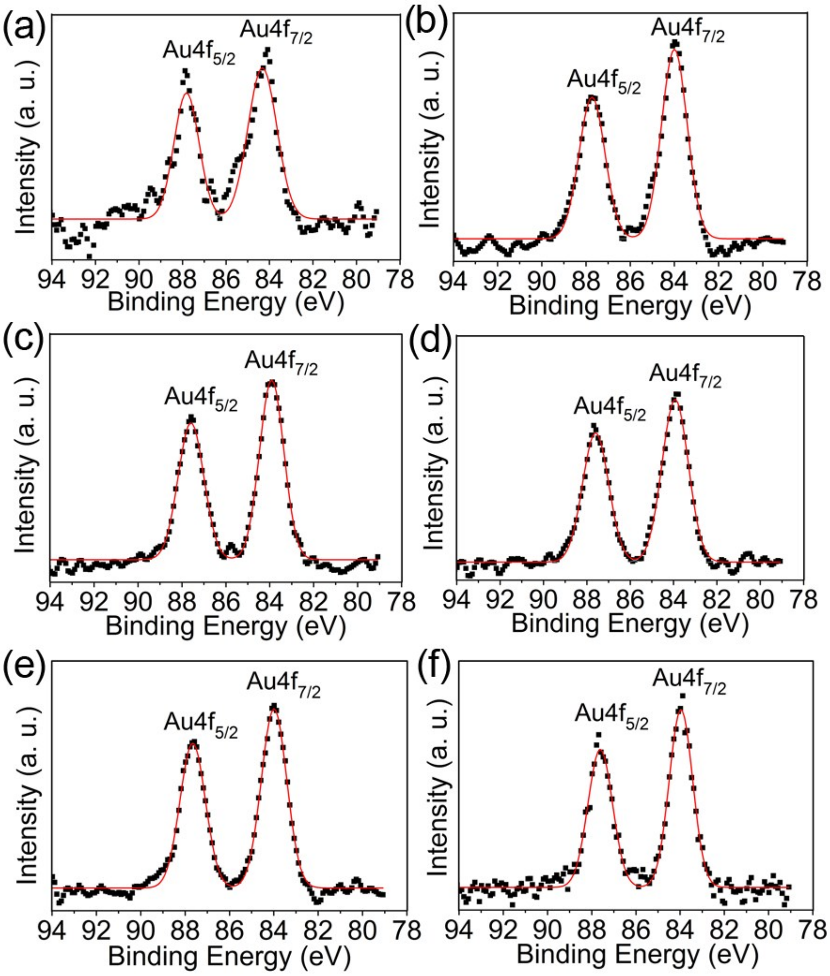

Fig. S24 XPS patterns of the HAPNW/AuNP layered catalytic paper sheets after heat treatment at different temperatures for 1 h: (a) 100 °C, (b) 150 °C, (c) 200 °C, (d) 250 °C, (e) 300 °C, and (f) 400 °C.

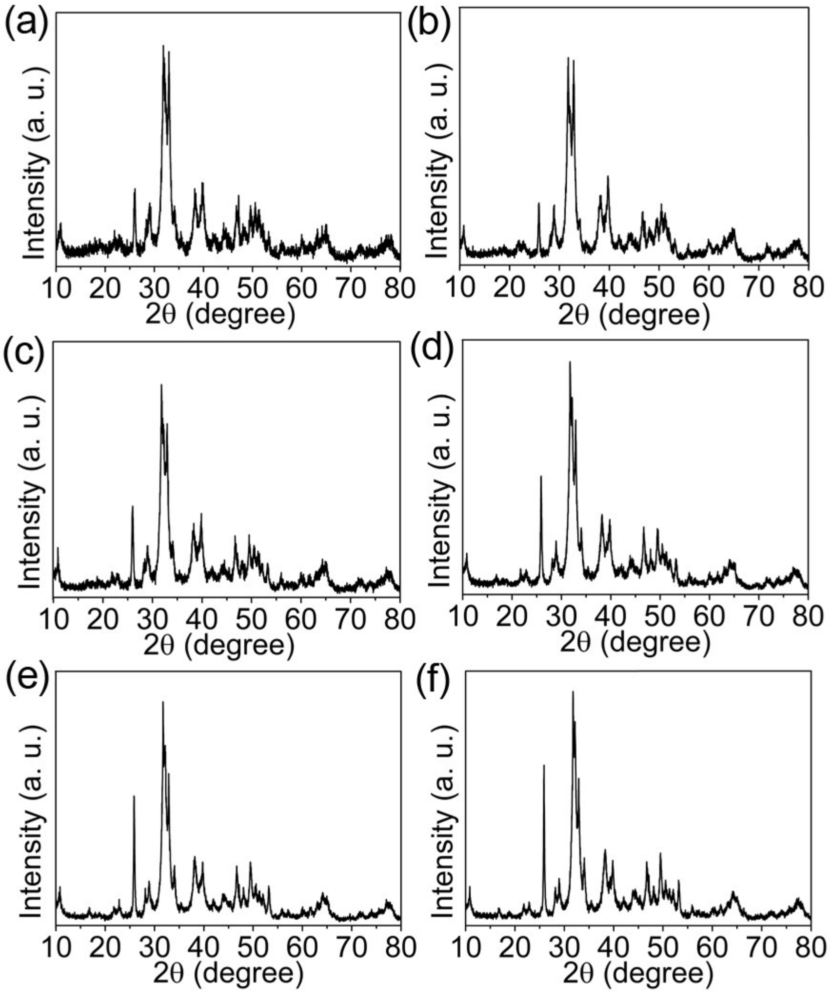

Fig. S25 XRD patterns of the HAPNW/AuNP layered catalytic paper sheets after heat treatment at different temperatures for 1 h: (a) 100 ^oC, (b) 150 ^oC, (c) 200 ^oC, (d) 250 ^oC, (e) 300 ^oC, and (f) 400 ^oC.

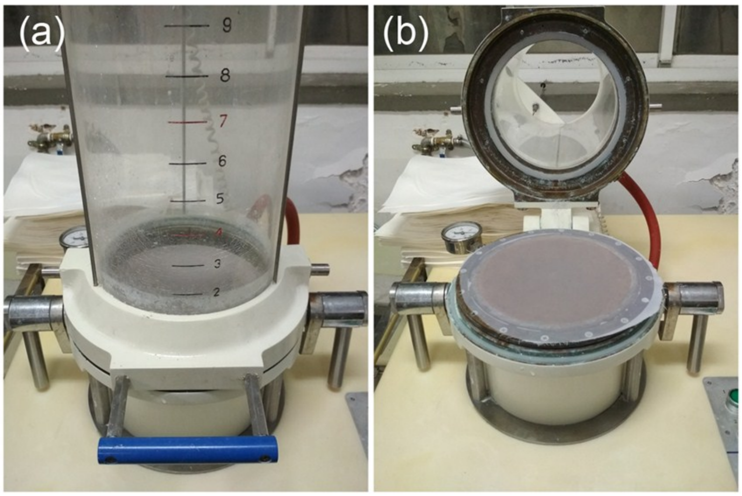

Fig. S26 A commercial paper sheet former used for the preparation of the large-sized HAPNW/AuNP layered catalytic paper with a diameter of 20 cm.