Electronic Supplementary Information (ESI)

Experimental Section

Chemicals. Graphite and 4-aminothiophenol (4-ATP) were purchased from Alfa Aesar. Poly(N-vinyl-2-pyrrolidone) (PVP · K30, molecular weight = 30 000-40 000) was obtained from Shanghai Chemical Factory (Shanghai, China). Silver nitrate was purchased from Beijing Chemical Reagent Factory (Beijing, China). Other reagents were of analytical grade and were used as received without further purification. All aqueous solutions were prepared with Milli-Q water (>18.2MΩ.cm) from a Milli-Q Plus system (Millipore).

Apparatus. Atomic force microscopic (AFM) images were recorded by using a SPI3800N microscope (Seiko Instruments, Inc. Japan) operating in the contact mode with standard silicon nitride tips at room temperature under ambient conditions. The samples were drop-cast on freshly cleaved mica and dried at room temperature. UV-vis detection was carried out on a Cary 500 UV-vis-NIR spectrophotometer (Varian, U.S.A.). Raman spectra were acquired on a Renishaw (Renishaw, United Kingdom) 2000 model confocal microscopy Raman spectrometer with 514.5 nm wavelength incident laser light. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al Kα X-ray radiation as the X-ray source for excitation. The sample for XPS characterization was deposited onto a Si slide. X-ray diffraction (XRD) spectra was obtained on a D8 ADVANCE (Germany) using Cu Kα (1.5406 Å) radiation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with a TECNAI G_2 high-resolution transmission electron microscope (Holland) with an accelerating voltage of 200 kV and Hitachi H600 electron microscope (Japan) with an accelerating voltage of 100 kV. The sample for TEM characterization was prepared by placing a drop of prepared solution on carbon-coated copper grid and drying at room temperature. Thermogravimetric analysis (TGA) of sample was performed on a Pyris Diamond TG/DTA thermogravimetric analyzer (Perkin-Elmer Thermal Analysis). Sample was heated under an air atmosphere from room temperature to 850°C at 10 °C/min.

Preparation of GO. The graphite oxide was synthesized from natural graphite powder according to the literature.[1] Then, exfoliation of graphite oxide into graphene oxide (GO) was achieved by sonication of the dispersion for 60 min (80 W, 90% amplitude). The obtained brown dispersion was then subjected to centrifugation at 3,000 r.p.m for 30 min with a rotor radius of 8 cm in order to remove any unexfoliated graphite oxide. Finally, a homogeneous aqueous GO dispersion (about 0.5 mg/mL) was obtained.

Preparation of AGCN. In a typical synthesis, 1.88 g PVP was dissolved in 8 mL of different concentrations of GO aqueous solution, and heated to 60 ^{o}C in air under magnetic stirring. Meanwhile, 3 mL of an aqueous solution of $AgNO_3$ (188 mM) was rapidly added into the above solution and stirred for 5 min to ensure complete mixing, and then, the reaction was allowed to proceed without agitation for different reaction time from 10 h, through 24h, to 48 h at 60 ^{o}C. The weight ratio between the $AgNO_3$ and GO was varied from 384, 192, 96, 48, to 24. The product was centrifuged at 8000 r.p.m. for 20 min (with a rotor radius of 8 cm) and washed with Milli-Q water to remove excess PVP. The obtained AGCN was redispersed into 5 mL Milli-Q water by sonication for further use.

Preparation of Ag NPs. For comparison, the citric-capped Ag NPs were prepared as the typical method reported by Lee and Meisel.[2] In brief, 9 mg $AgNO_3$ was dissolved in 50 mL H_2O and brought to boiling, a solution of 1% sodium citrate (1 mL) was added rapidly. The solution was kept on boiling for approximately 1 h.

SERS experiments. 4-ATP was used as the probe molecule. Soaking was used to absorb the molecule on the surfaces of AGCN. 100 μL of 4-ATP aqueous solutions with concentration of 2×10^{-6} M was mixed with 100 μL of as-prepared AGCN composite nanosheets colloid. After shaking several times, the mixture was allowed to stay for 3 hours to reach the adsorption equilibrium for direct SERS detection in liquid environment.

References

1. V. C. Tung, L. M. Chen, M. J. Allen, J. K. Wassei, K. Nelson, R. B. Kaner and Y. Yang, *Nano Lett.*, 2009, **9**, 1949-1955.
2. P. C. Lee and D. Meisel, *J. Phys. Chem.*, 1982, **86**, 3391-3395.

Legends

Scheme S1. Formulas of OH-terminated PVP and its structural changes involved in the oxidation by Ag^+.

Scheme S2. Illustration of the procedure for preparing AGCN.

Figure S1. TEM images and the corresponding histograms of Ag nanoparticles size distribution (inset) of AGCN prepared with different reaction time: 10 h (A, B), 24 h (C, D), and 48 h (E, F).

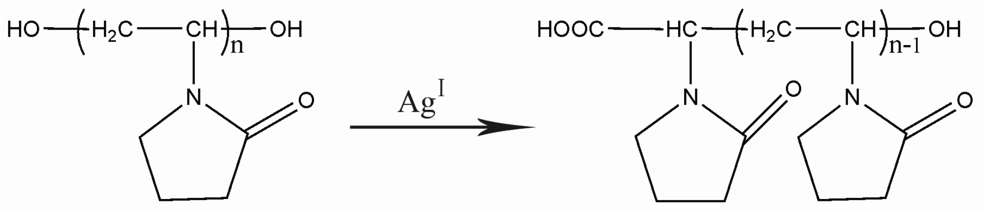
Figure S2. TEM images and the corresponding histograms of Ag nanoparticles size distribution (inset) of AGCN prepared with different weight ratio between the $AgNO_3$ and GO: 24 (A), 48 (B), 96 (C), and 192 (D).

Figure S3. TGA curves of AGCN prepared with different weight ratio between the $AgNO_3$ and GO: 24 (a), 48 (b), 96 (c), 192 (d), and 384 (e).

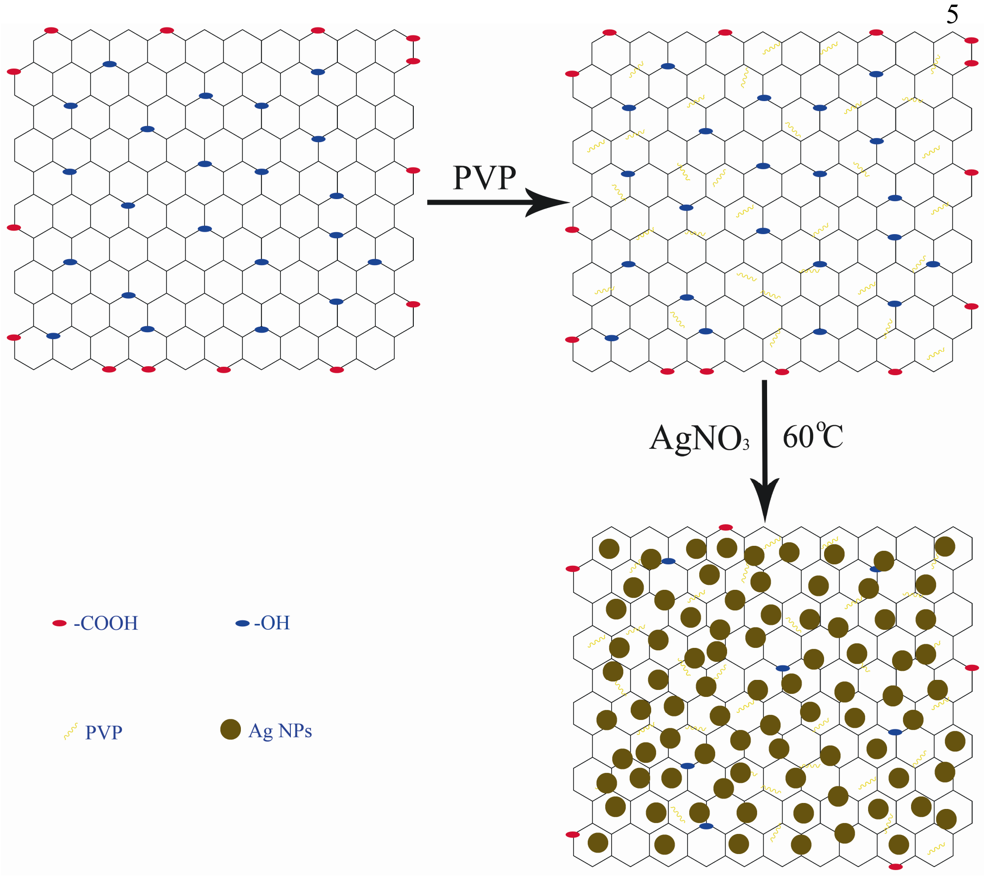
Figure S4. UV-vis absorption spectra of AGCN prepared with different reaction time: 10 h (a), 24 h (b), and 48 h (c).

Figure S5. UV-vis absorption spectra of AGCN prepared with different weight ratio between the $AgNO_3$ and GO: 24 (a), 48 (b), 96 (c), 192 (d), and 384 (e).

Figure S6. XPS general spectra of GO (a) and AGCN prepared with different reaction time: 10 h (b), 24 h (c), and 48 h (d).



Scheme S1



Scheme S2

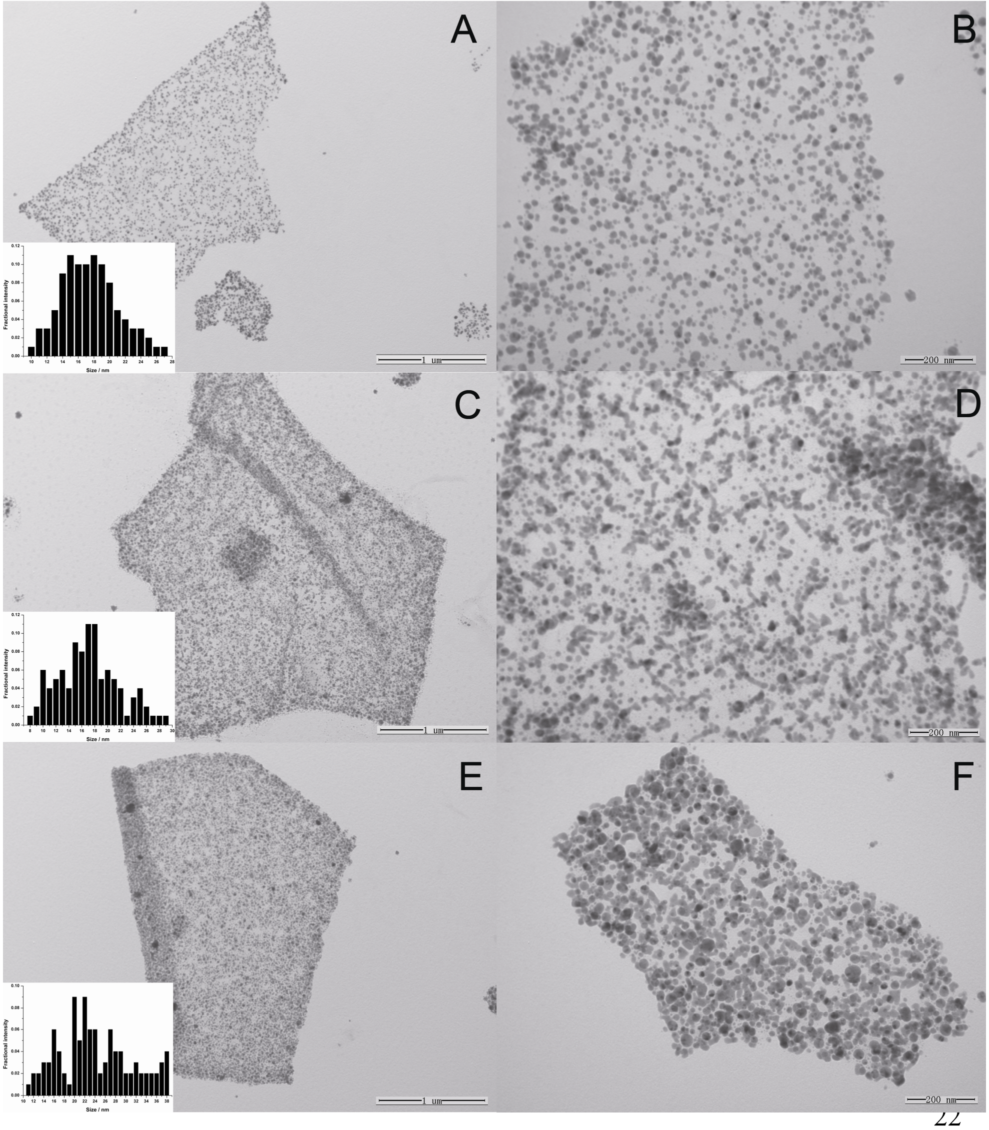

A
B
C
D
E
F
1 um
200 nm
1 um
200 nm
1 um
200 nm
Fractional intensity
0.00
0.02
0.04
0.06
0.08
0.10
0.12
Size / nm
10
12
14
16
18
20
22
24
26
28
Fractional intensity
0.00
0.02
0.04
0.06
0.08
0.10
0.12
Size / nm
8
10
12
14
16
18
20
22
24
26
28
30
Fractional intensity
0.00
0.02
0.04
0.06
0.08
0.10
Size / nm
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38

Figure S1

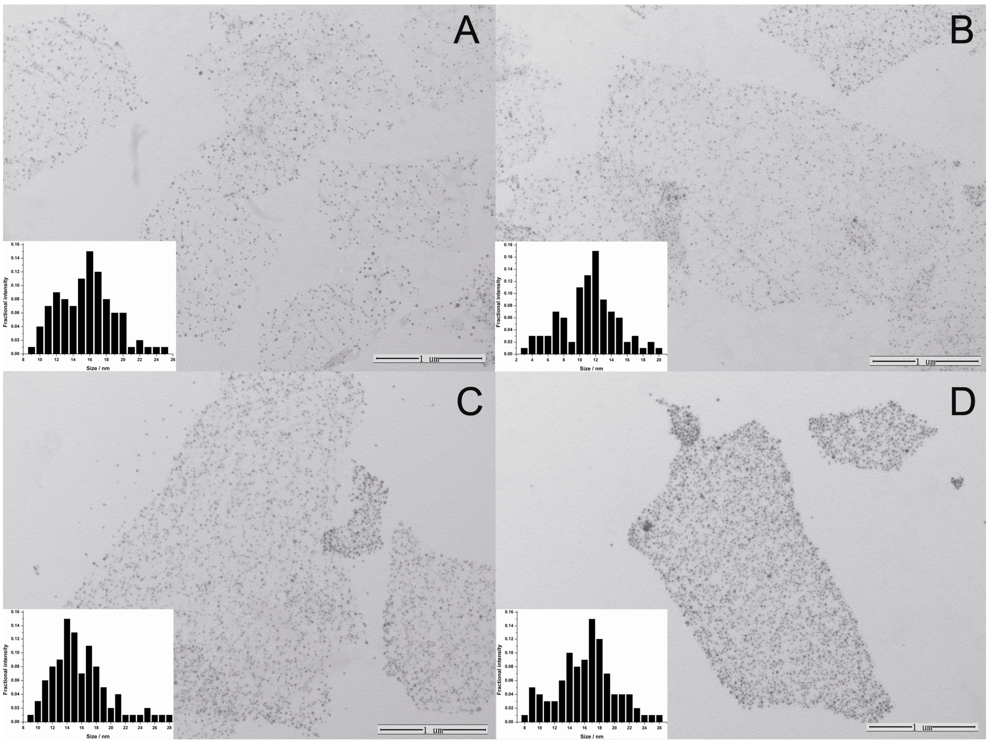


Figure S2

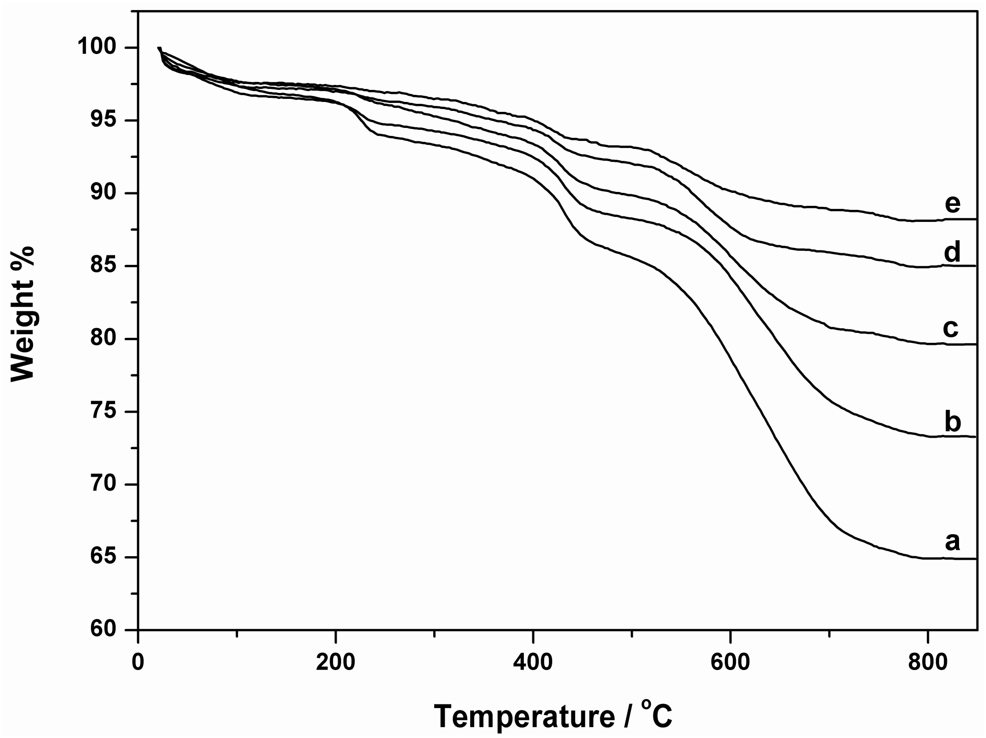

Weight %
100
95
90
85
80
75
70
65
60
0
200
400
600
800
Temperature / °C
e
d
c
b
a

Figure S3

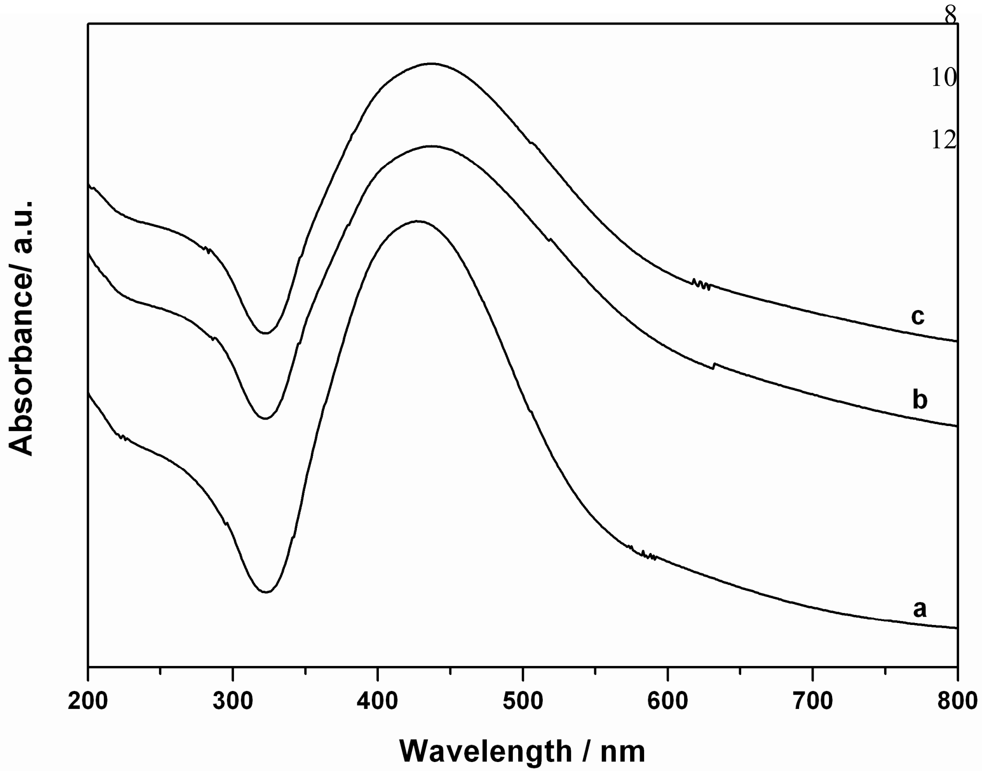


Figure S4

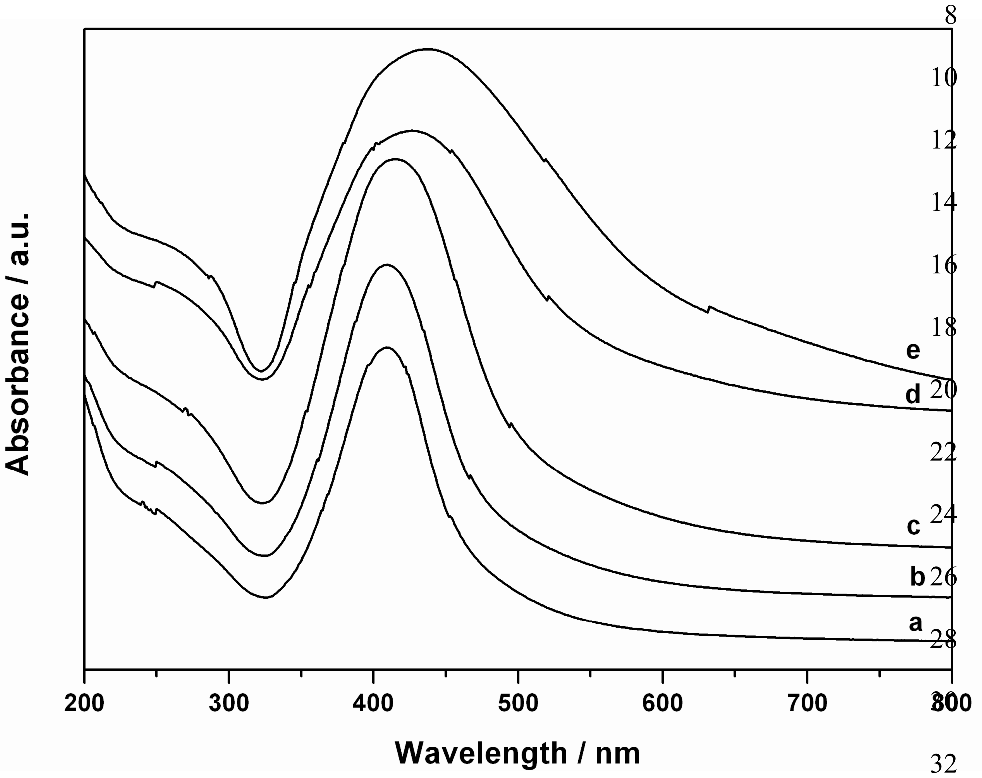

Absorbance / a.u.
e
d
c
b
a
200
300
400
500
600
700
800
Wavelength / nm

Figure S5

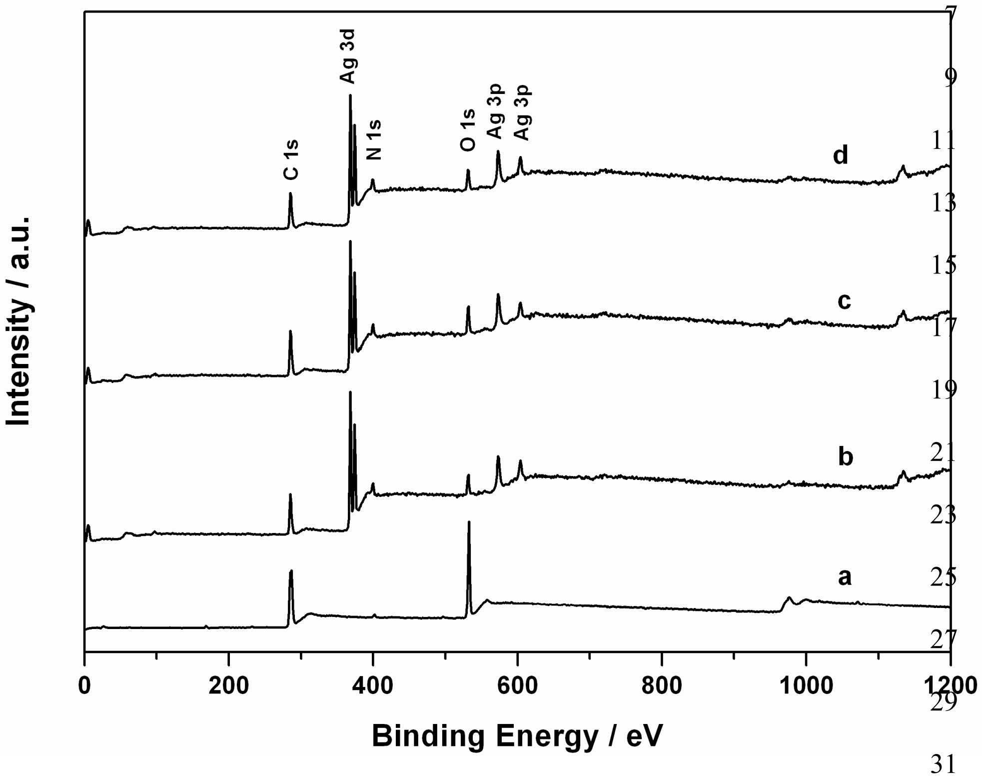

Intensity / a.u.
Binding Energy / eV
C 1s
Ag 3d
N 1s
O 1s
Ag 3p
Ag 3p
d
c
b
a
0
200
400
600
800
1000
1200

Figure S6