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Contributed Paper

# Self-Reduction of Gold on Activated Carbon Cloth

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## ABSTRACT

Activated carbon cloths (ACCs) were used as a support for preparation of Au nanoparticles. Pretreatment of ACCs was performed by using oxidizing agent $HNO_3$ in order to introduce surface oxygen complex. Au nanoparticles were prepared by impregnation of tetrachloroauric acid ($HAuCl_4$) without reducing agents in deionized water and ethanol. It was found that the preparation in ethanol solution achieved uniformly dispersed Au nanoparticles with diameter 10-100 nm on the support surfaces. X-ray diffraction (XRD) was employed to verify structural characteristics of Au metal adsorption on oxidized ACC surfaces. Morphology and composition were carried out by Scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDS), respectively.

**Keywords:** Au nanoparticles, activated carbon cloth.

## 1. INTRODUCTION

Activated carbon is generally known as the exceptional and adaptable adsorbents [1-3]. It is employed to remove the dissolved organic and inorganic substance from gas and liquid phase. The activated carbon has also been the traditional supports used in heterogeneous catalysis as its porous structure leading to large internal surface area per unit weight. High surface areas of the activated carbon can accommodate adsorbates. It is also excellent electrical conductivity, impurity free and resistance to corrosion.

Activated carbon cloths (ACCs) potentially present a number of significant advantages with respect to conventional activated carbon in powder or granule for instance high rate of mass transfer from liquid phase, no need of decantation or filtration and high flexibility to fit into any reactor size [4]. The porous networks with plentiful functional groups on the surface of carbon fiber are formed by a uniform distribution of micropore providing faster adsorption-desorption rate, faster equilibrium rate and high fluid permeability [5]. As ACCs are so reductive, it can reduce metal ions into metallic elements.

An acid-base character is associated with oxygen functionalities [6, 7]; the acidic character is associated with oxygen functionalities such as carboxyls, lactones and phenol whilst pyrones, chromenes, ethers and carbonyls imply the basic properties. The acidic and basic character of carbon surface depends on the conditions of preparation. $HNO_3$ is one of well known oxidizing agent for ACC pretreatment. Our work has used $HNO_3$ to treat ACCs before adsorption.

Metallic catalyst (e.g. Pt, Pd, Au) on various

supports (e.g. metal oxide and carbon) has been accomplished in many applications [3]. Au catalyst is one of attractive catalysts recently as it is active under mild conditions and could enhance the selectivity of the reaction, moreover it has a lot of applications for pollution such as air cleaning and light-off autocatalysts and purification of hydrogen stream in fuel cell [8]. As standard reduction of Au is lowest compared with Pt and Pd, in the beginning of research, Au is the first target to start with, before the further study of other metal catalysts on ACC support.

In this work, ACCs were treated and impregnated in solution of tetrachloroauric acid for the Au nanoparticle preparation without reducing agent.

## 2. MATERIALS AND METHODS

ACCs as a support used in the present work were obtained from AmeriAsia (made in China Jiansu), coded as ACC MY-QW-025 having a specific area of 1500 $m^2g^{-1}$ and $HAuCl_4$ precursor was from Merck.

Elimination of contaminations can be acomplished by over night stirring ACCs in 6

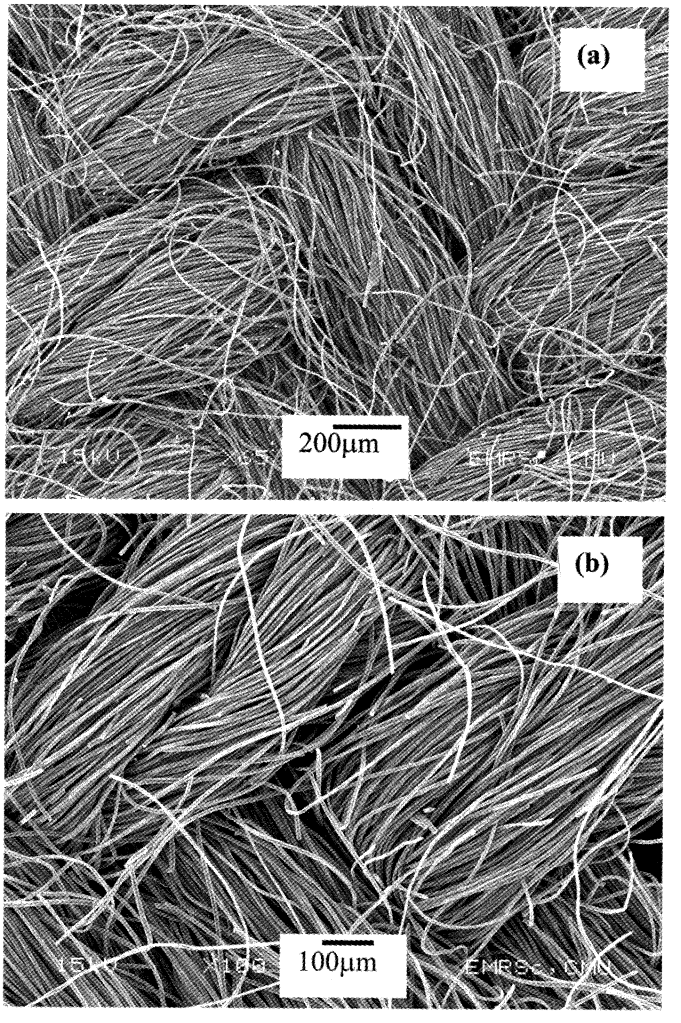


**Figure 1.** SEM of ACCs (a) before (magnification 65x) and (b) after (magnification 100x) oxidative treatment by 1M $HNO_3$ .

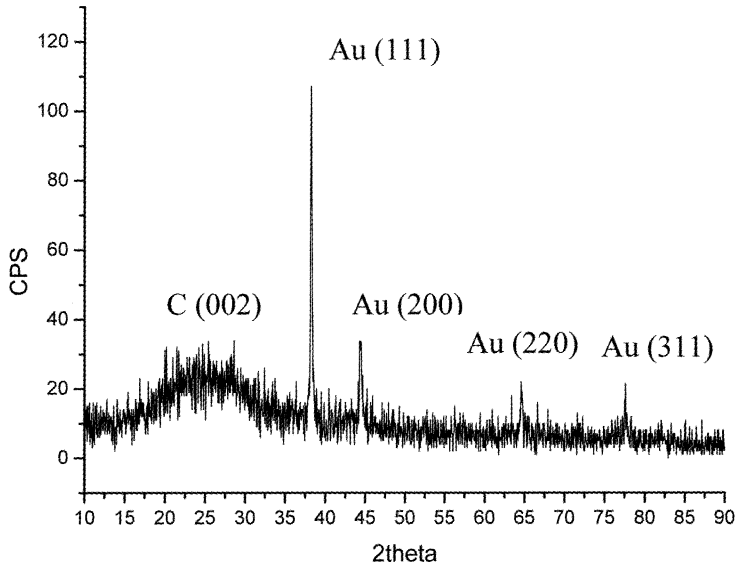


**Figure 2.** X-ray diffraction pattern of Au adsorption on Activated carbon cloths (ACCs).

M HCl (12-24 h), subsequently washed with deionized water until pH is constant and then dried in oven at 100 °C.

Modification of ACC surface can be made via oxidation. The pretreated ACC was stirred in 1.6 M $HNO_3$ solution for 6 h, then washed with deionized water for neutralization and the supports lastly were dried at temperature 100 °C overnight.

Au adsorbed cloths were prepared by incipient wetness impregnation method using 3 % wt Au/ACC solution. Deionized water and ethanol were chosen to be a solvent for the precursor solutions. The oxidized ACCs were vigorously stirred in brown-yellow solution for 30 min as the colored solution turned to be colourless indicating gold adsorbed on the surface of ACC support. After drying at 90°C in the oven overnight, SEM ( JEOL JSM-5910LV) and EDS (JEOL JSK-6335F) were used to characterized morphology and composition of nanoparticles, respectively.

X-ray diffraction patterns of ACCs were taken on a Siemens D-500 using Cu ka radiation (l1.54, Ni filter, 2q=10-90°). The ACCs were cut into fine pieces for measurements.

## 3. RESULTS AND DISCUSSION

Pretreatment of ACC was performed by using 6 M HCl to get rid of some mineral impurities such as K, Mg, Ca, Al and Fe which are usually existed in an activated carbon cloth [9]. After that the surface of fabric was funtionalized by oxidative treatment.

The oxidative treatment of ACCs was performed by 1.6 M $HNO_3$ in order to produce oxide functional groups. Figure 1 shows ACCs before and after treatment by $HNO_3$ solution by SEM. Not only to get rid of an impurities covered on ACC surface, but carbon surface is also inert, functionalization of carbon surface or chemical modification is required to get favourably adsorbates adsorbed on the surface. Acid treatment introduces oxygen components formed (such as carboxylic, anhydride, phenolic and carbonyl groups) which generate the surface of ACC to be such reducing regions.

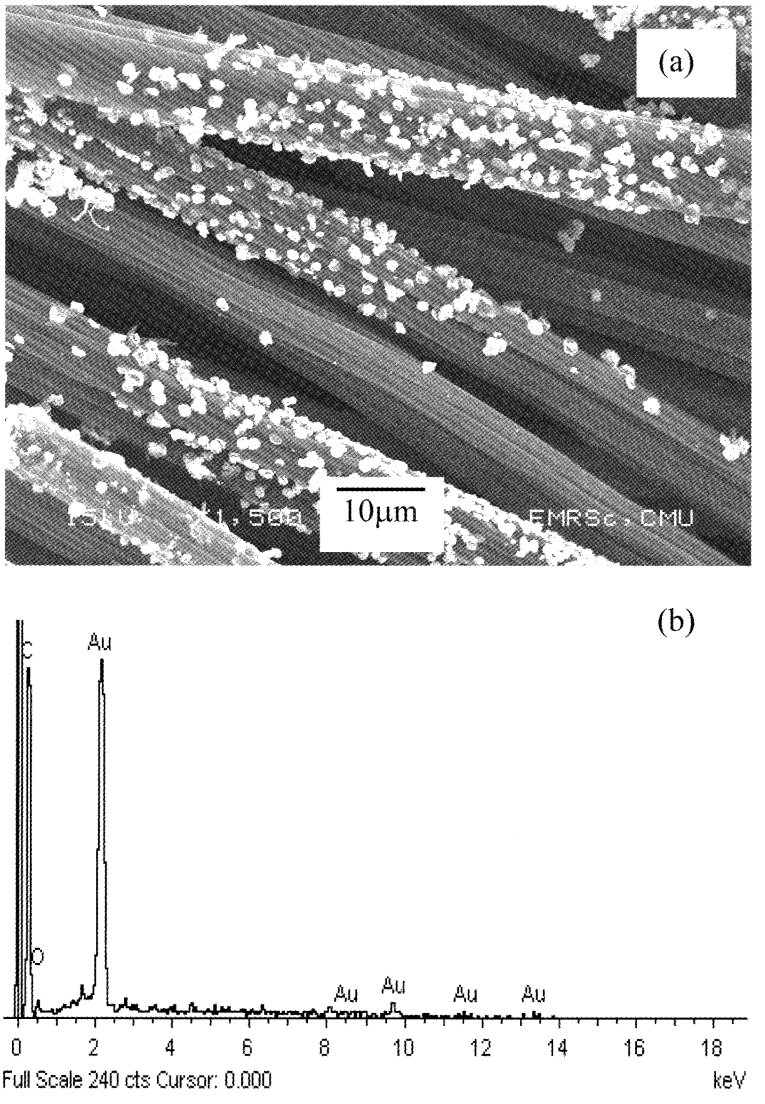


**Figure 3.** 3%wtAu/ACC by preparation in aqueous solution (a) SEM image (magnification 1500x) and (b) EDS of Au nanoparticles on ACC support.

Functionalities perform as holder for adsorbates and support their adsorption on carbon surface by numerous mechanisms included ion-exchange, coordination and adsorption reactions [6].

SEM images of ACC before and after treatment are shown in Figure 1 show that macro physical structures of ACC are maintained after acid treatment. Pretreatment of ACC resulted in flat surface of fiber as no hollow or bump of solid on the surface in the magnified image (image not shown). The smoothly ACCs can be attributed to be a favorable host for metal particles and fine dispersed particles to be adsorbed.

After impregnation, several techniques were used to characterize Au nanoparticles adsorbed activated carbon cloths. As it is well known that ACCs consist of randomly oriented graphitic microcrystalline unit, X-ray diffraction is suited for the structural characteristic of ACCs. X-ray diffraction

spectrum of Au-ACC composites is shown in Figure 2. The diffraction peak at 20-25° observed in all the diffraction patterns of carbon-supported metals is attributed to the (002) plane of the hexagonal structure of carbon [10]. The broadening of the peaks is an indication of structural disorder of the sample. Prepared Au nanoparticle samples show crystalline structure.

It is obviously shown main characteristic peaks of Au which match with JCPDS card no 4-784 at 2q : 38.2° (111), 44.4° (200), 64.6° (220) and 77.5° (311) indicating the successful reduction of Au ion to Au metal. XRD peaks at 25.9° are also observed resulting in hexagonal graphite structure (002). This signifies that oxidized ACCs have a high electrical conductivity and could be the support material for electrode application.

SEM image in Figure 3 shows 3% wt Au/ACC prepared in water. The mean particle size of metal was with wide range of size distribution ca. 80-200 nm. The results prove that nanoparticle size of Au can simply be prepared by our method. Hydrated halides are soluble $HAuCl_4$ (III) dissociate to $AuCl_4^-$, and $H^+$. Those anions can be adsorbed on porous activated carbon and then reduced to be metal ($Au^0$) resulting in the color change of solution from color to colorless. The

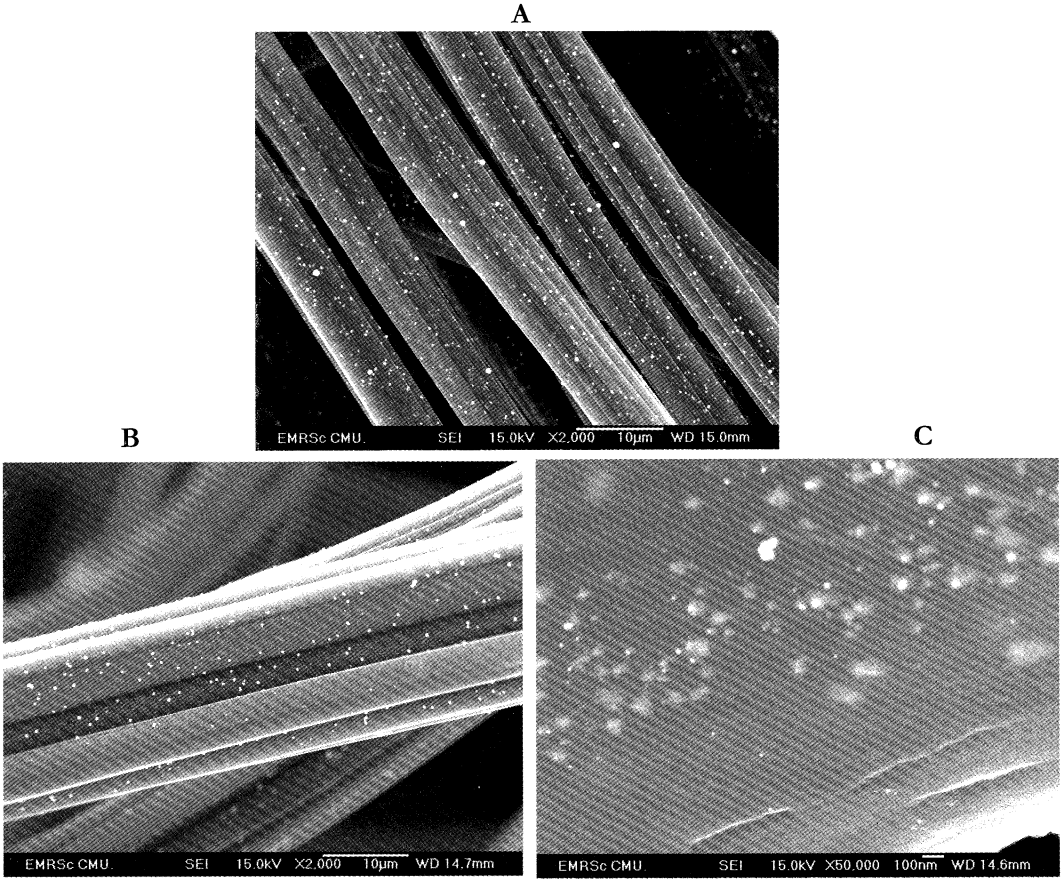


**Figure 4.** SEM images of Au nanoparticles on ACC from 3% wt Au/ACC in ethanol solution (a) various sizes of Au nanoparticles (magnification 2,000x), (b) another selected area image (magnification 2,000x) and (c) magnification image of Au nanoparticles adsorbed inside the fabric surface (magnification 50,000x).

adsorption rate of anion on activated carbon cloth is high as the color is clear in very short time.

It can also propose that metal firstly deposits into the micropores and further aggregates to the outer surface of carbon fibers as macroparticles observes on the surface. Figure 3(b) confirmed Au particles by EDS spectra.

It can be obviously seen the smaller Au nanoparticles adsorbed with size 5-80 nm after impregnation in ethanol (Figure 4 (a) and (b)). Higher magnification image shows other small structures on ACC surfaces and inside the surface (Figure 4(c)). White areas in lower level in Figure 4(c) could be Au clusters adsorbed inside the fiber surfaces. This makes prepared catalyst more interesting as there might be other kinds of catalytic mechanisms can occur on this area which will be the next target for further research.

From the result of particles' size on SEM, the polarity can be taken an acount for particle size distribution. $HAuCl_4$ is high polar due to it is ionic substance which is more soluble in water with high polarity (dielectric constant 80.1 at 20°C [11]). It could also discuss in an atomic level that weakening force on charges results from water molecules forming hydration shells around those $AuCl^-$ ions. Ionic bond is weakened in the presence of water solvent allowing ions to separate from the crystal and separate through solution. Ethanol is less polar than water (dielectric constant is 25.3 at 25°C[11]) indicating the reduction of charge screening. As the activated carbon cloths were oxidized, the functional groups introduced on ACCs support must be compatible with Au ion in ethanol. Therefore, the nanoparticle size prepared in ethanol is smaller than that in water. So, the polarity of solvent affects the size of metal adsorption on ACC. The ethanol performed such a good solvent for $Au^{3+}$ adsorption on oxidized ACC surface and metal ion can also be reduced to be Au and adsorbed the surfaces.

## 4. CONCLUSIONS

Activated carbon cloths were oxidized by 1.6 M $HNO_3$ and loaded with gold metal by impregnation in $HAuCl_4$ solution resulting in Au nanoparticles adsorbed with various diameters. It was found that the type of solvent affects the particle size and particle distribution. Ethanol is a promising solvent as given smaller nanoparticles and uniform dispersion of nanoparticles adsorbed on the oxidized ACC support. The further study of metal adsorption preparation on ACC support is to be continued.

## ACKNOWLEDGEMENTS

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