# Fabrication of Core-shell Structure Nanocomposites of Gold Nanoparticles@METAC

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Abstract: Novel core-shell structure nanocomposites are fabricated by grafting polymers of poly(［2-(Methacryloyloxy)ethyl］trimethylammonium chloride) onto gold nanoparticles through surface-initiated, atom-transfer radical polymerization (ATRP) in 2-propanol/water mixed solvents. The surface of citrate-stabilized gold nanoparticles was first modified by a disulfide initiator for ATRP. The Au@polymer nanocomposites display a well-defined core/shell nanostructure that were characterized by TEM, FTIR,XPS and UV-visible spectroscopy. Such core-shell nanocomposites can be considered as water-dispersible nanotanks for hydrophobic drugs in the development of multifunctional biodelivery systems

# 1 INTRODUCTION

Metal nanoparticles that are imbedded in polymer composites have been of intense recent interest [1] with regard to their fabrication and potential application in areas such as electronics, optics, magnetics, catalysts, and sensors [2-7]. As a well-known noble metal, gold is widely investigated due to its specific impact in the fields of biotechnology and bioscience [8-14]. A large number of polymer molecules have been selected to decorate the surface of gold nanoparticles in physical or chemical manners for different purposes [15-20].

In this paper, we report the fabrication of METAC modified gold nanoparticles as nanocomposite materials by SI-ATRP on a gold surface. The typical experimental procedure is illustrated in Scheme 1. First, the disulfide initiator was immobilized on the surface of gold nanoparticles (Au@initiator). Subsequently, ATRP o ［2-(Methacryloyloxy)ethyl］trimethylammonium chloride (METAC) occurred on gold nanoparticles catalyzed by N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA) and CuBr. Such environmentally responsive nanocomposites provide a smart supporter or carrier to transition metal ions and nanoparticles to construct novel bimetallic nanocomposites, especially in catalyst applications.

# 2 MATERIALS AND METHODS

## 2.1 Materials

The disulfide initiator ［$S-(CH_2)_2-OCOC(CH_3)_2Br$］$_2$, ［2-(Methacryloyloxy)ethyl］trimethylammoniumchloride(METAC),N,N,N’,N’,N’’-pentamethyl-diethylenetriamine (PMDETA) were purchased from Sigma Aldrich. CuBr, $HAuCl_4$, sodium citrate, and other chemicals were obtained from. METAC was purified to remove the inhibitor. The gold nanoparticles with an average diameter of 20 nm were prepared from $HAuCl_4$ and sodium citrate by conventional citrate-reduction methods [21].

## 2.2 Instrumentation

FTIR and UV-vis spectra, respectively, were recorded on a Excalibur HE 3100 instrument (Varian) and a U-4100 UV-vis spectrometer (HITACHI). TEM images were obtained by a Tecnai $G^2$ F30 transition electron microscope (FEI). X-ray photoelectron spectroscopy (XPS) was performed on an K-Alpha electron spectrometer (Thermofisher Scienticfic Company) using 300 W Al Kα radiation at about $1\times10^{-8}$ mbar,and the binding energies were referenced to the C1s line at 284.8eV from adventitious carbon.

### 2.3 Preparation of SI-ATRP Initiator

The initiator immobilized on gold nanoparticles (Au@initiator) was prepared from fresh gold nanoparticles through ligand exchange between disulfide initiator and citrates. Generally, a certain volume of fresh gold nanoparticles in water was slowly added to same volume of a N,N-dimethylformamide (DMF) solution that dissolved 3.0 mM initiator with stirring for 24 h. The Au@initiator was collected and washed with DMF and Millipore purified deionized water by centrifugation. Finally, Au@initiator was dispersed in DMF and stored at 20 °C under an argon atmosphere.

### 2.4 SI-ATRP Process of METAC

Polymerization of METAC on a gold surface was performed in a mixed solvent at ambient conditions according to the literature [22-25]. In detail, a round-bottom flask was added with CuBr (28.6 mg) and degassed by three freeze pump thaw cycles under $N_2$ atmosphere. A degassed mixture of Au@initiator (2 mg) dissolved in DMF (2 mL), PMDETA (0.208mL), 2-propanol (0.5 mL), and a certain amount of free initiator (0.5-20 mg) was injected into the flask through a syringe, followed by degassed METAC (1.05-2.10 g) with drastic stirring. The reaction was performed for 24 h and terminated by opening the system to air. The Au@METAC nanocomposites were purified by more than three cycles of centrifugation, 2-propanol/DMF washing.

## 3 RESULTS AND DISCUSSION

### 3.1 Preparation and Component Analysis

Gold nanoparticles with diameters of 20 nm were synthesized by using the conventional citrate-reduction method and can be easily dispersed in warter without aggregation, as shown in Figure 1. The immobilization of disulfide initiator on the gold surface was achieved through ligand exchange between disulfide and citrate. The ATRP reaction of METAC from a free initiator or a macromolecular initiator was suggested to be carried out in a protic alcohol solvent [26-27]. Herein, the solvent is mixed protic 2-propanol with DMF according to the solubility of the Au@initiator and METAC chains. A large amount of PMDETA was used to maintain the activity of the catalytic system, and an appreciate amount of free initiator was added into the reaction mixture to control the polymerization [28]. Figure 3A shows the FT-IR spectra of Au@initiator and as-prepared Au@METAC nanocomposites. The profile of the Au@initiator (curve b) is similar to that of the pure disulfide initiator, whose characteristic absorbance at 2922, 2850 ($CH_2$ stretching), and 1729 $cm^{-1}$(ester carbonyl stretching) of Au@initiator (curve b) denotes the presence of the ATRP initiator on gold nanoparticles. For obtained Au@METAC (curve a), the characteristic peaks at 2968, 1730, and 1457 $cm^{-1}$ represent the $CH_3$ and $CH_2$ stretching vibrations, ester carbonyl stretching, $-CH_2-\ N^+(CH_3)_3$ bending vibrations according to the references [22,23]. 960$cm^{-1}$($N^+(CH_3)_3$),1166,1278$cm^{-1}$(C-O). It shows that the polymerization of METAC is performed successfully. So, the FT-IR results reveal that the Au@METAC nanocomposites are easily protonated by hydrochloride.

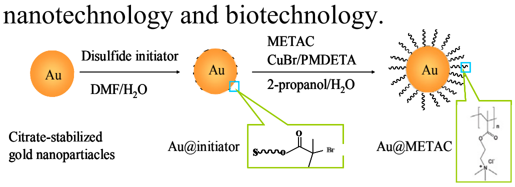
Moreover, the Au@METAC nanocomposite samples and pure METAC (sigma, as a comparison) were analyzed by X-ray photoelectronspectroscopy(XPS).The element components of Au@METAC nanocomposites are approximately contributed to C (41.2%), N (2.5%), O (11.6%), Au (43.4%), and Cl (1.3%). Figure 3B shows the binding-energy decrease of Au 4f within a range of 8.1 eV and 8 eV (95.4 to 87.3 eV for Au 4f5/2 and 91.6 to 83.6 eV for Au 4f7/2) after (a) and before (b) gold nanoparticle disulfide initiator modification by METAC. This proves the formation of Au-C bonds on the gold surface. All of these component analyses demonstrate that the designed Au@METAC nanocomposites were successfully obtained from a consecutive ATRP reaction.

### 3.2 Morphology and Structural Characterizations

Figure 2 show the transmission electron microscopy (TEM)images of Au@METAC nanocomposites under different magnifications. The well-dispersed nanostructures consist of a gold “core” with an average diameter of 20 nm and a polymer “shell” about 10 nm thick, which could be clearly observed after staining by phosphotungstic acid.

## 4 CONCLUSION

In summery, we have demonstrated that SI-ATRP of METAC can be performed on the surface of initiator modified gold nanoparticles to fabricate Au@polymer nanocomposites. The as-prepared Au@METAC nanocomposites have a distinct core shell nanostructure with gold cores and polymer shells. The polymer "shell" has a network scaffold. The biocompatible and amphiphilic core-shell nanostructures can be considered as water-dispersible nanotanks for hydrophobic drugs, which may have great potential in the multifunctional biodelivery of hydrophobic drugs. The fabrication strategy for core-shell nanostructures can be generalized to prepare novel structured materials in nanotechnology and biotechnology.



Scheme1. Au@METAC fabrication

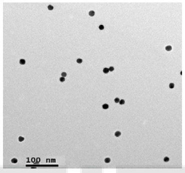


Figure 1.TEM image of GNP dispersed in THF. Scale bar:100 nm.

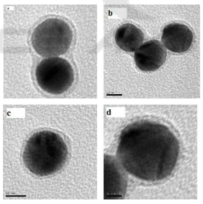
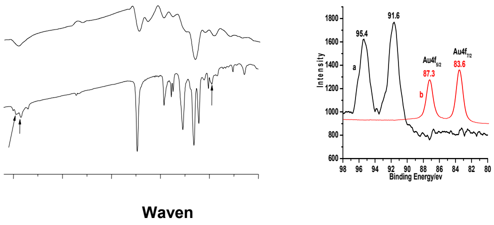


Figure 2. TEM images of Au@METAC nanocomposites dispersed in water.



(A) (B)

Figure 3. (A) FT-IR spectra of Au@initiator (a) and Au@METAC nanocomposites washed by 2-propanol,(B)Au 4f spectra from XPS analysis of Au@initiator (a) and Au@METAC nanocomposites (b).

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