ABSTRACT: Highly dispersed Au nanoparticles (AuNPs) with different size were synthesized successfully on the surface of reduced graphene oxide (RGO), the binary AuNPs/RGO nanocomposites with smaller size (4 nm) show higher activity for photocatalytic hydrogen production and reaches a high H₂ production rate of 2.1 mmol h⁻¹g⁻¹. The detailed mechanism is discussed in the article.

1 INTRODUCTION

Since Fujishima and Honda reported TiO₂ photoanode for splitting water in 1972, the photocatalytic water splitting over semiconductor photocatalysts using solar energy has drawn increasing attention, which is considered to be a potential and environmentally friendly means to solve the increasingly serious energy shortages. Nanoparticles of noble metals such as Au has been widely employed in photocatalysis, because they exhibit unique optical properties in the visible region that arise from the localized surface plasmon resonance. Tatsuma et al. prepared Au-TiO₂ composites and the charge separation at the plasmon-excited Au nanoparticles incorporated in TiO₂ was verified. Subsequently, Furube et al. directly observed plasmon-induced electron transfer from Au nanodots to TiO₂ nanoparticles by using femtosecond transient absorption spectroscopy. The above results indicating Au nanoparticles may be utilized as a good electron source in photocatalysis if back electron transfer can be suppressed efficiently.

An effective way to suppress the back electron transfer is introduce support materials with excellent capability to accept and shuttle electrons. Graphene as a two-dimensional nanomaterial with unique chemical properties is an ideal candidate for support materials. In light of the above results, we intended to synthesize binary AuNPs/RGO nanocomposites, which combine the advantages of Au nanoparticles and RGO, and expected that the combination could result in a remarkable increase in the photocatalytic activity.
2 EXPERIMENTAL SECTION

2.1 Preparation of Au/RGO nanocomposites

First, GO was prepared from natural graphite powder through Hummers’ method. 2 ml of 0.2 M PDDA was added into 10 ml of 0.5 mg/mL GO aqueous solution, the above solution was heated in refluxing conditions at 90 °C for 5 h to complete the functionalization and reduction of GO. After that, 2 ml of 1 mg/mL PDDA functionalized RGO was added into 200 ml of 0.97 mmol HAuCl₄ solution, and then 5 mL of fresh 0.05 M NaBH₄ solution was added dropwise to reduce HAuCl₄ and the wine-colored solution was obtained. For comparison, the AuNPs with different size were prepared by citrate reduction method.

2.2 Photocatalytic H₂ evolution

The photocatalytic reaction was carried out in a closed gas circulation and evacuation system (LabSolar-IIJAG, Beijing) under a 300 W Xe lamp (PLS-SXE 300C, Beijing) equipped with a cut-off filter (λ > 420 nm). The photocatalyst (2.9 mg) was dispersed in aqueous solution (50 ml) containing 5 vol % TEA as electron donors by a magnetic stirrer. H₂ gas evolution was measured by on-line gas chromatography (GC–2014C, Shimadzu Co.).

3 RESULTS AND DISCUSSION

Figure 1A shows the UV-vis absorption spectra of GO, RGO and AuNPs/RGO nanocomposites (4 nm). GO exhibits a strong peak centered at ca. 226 nm and a shoulder peak at ca. 300 nm corresponding to n–n* transitions of aromatic C=C band and n–n* transitions of C=O band, respectively. After refluxing at 90 °C, the peak at 226 nm red-shifts to 250 nm, the shoulder peak at 300 nm disappears, and the absorbance in the whole spectral region increases, indicating the GO is reduced by PDDA. When HAuCl₄ and NaBH₄ were introduced into the system, the peak at 250 nm red-shifts to 264 nm, indicating the RGO is further reduced by NaBH₄. Moreover, an obvious plasmon absorption band characteristic of AuNPs is observed at 511 nm. It is worth mentioning that the RGO and AuNPs/RGO nanocomposites (4 nm) have a very good dispersion in aqueous solution (Figure 1, inset), which is beneficial to improve its photocatalytic activity. Figure 1B shows the corresponding Raman spectra. All the samples exhibit two characteristic bands: the D band at ~1356 cm⁻¹ and the G band at 1602 cm⁻¹. The obtained values of the ID/IG ratio are 0.82, 0.98 and 0.99 for GO, RGO, and Au/RGO nanocomposites (4 nm), respectively, which further confirm the reduction of GO.
Figure 1. (A) UV-vis absorption spectra and (B) Raman spectra of (a) GO, (b) RGO, and (c) AuNPs/RGO nanocomposites (4 nm). Inset is the corresponding digital photos of samples in aqueous solution (1 mg ml⁻¹) after aging for 24 h.

Figure 2 shows the TEM images of AuNPs and AuNPs/RGO nanocomposites with different size, indicating that AuNPs with size of 4 nm and 25 nm were successfully prepared. After introducing of RGO, a large amount of AuNPs are generated and well dispersed on the surface of RGO. The AuNPs present near spherical morphology and are well separated from each other, no aggregation is observed on the RGO surface.

Figure 2. TEM images of (a) AuNPs (4 nm), (b) AuNPs (25 nm), (c) AuNPs/RGO nanocomposites (4 nm) and AuNPs/RGO nanocomposites (25 nm).

Figure 3 shows the rate of H₂ evolution over photocatalysts. The rate of H₂ production is about 0, 0.88, 0.61, 2.1, 1.2 mmol h⁻¹g⁻¹ for RGO, AuNPs (4 nm), AuNPs (25 nm), AuNPs/RGO (4 nm) and AuNPs/RGO nanocomposites (25 nm), suggesting that the size of AuNPs has a very
important influence on its photocatalytic activity. The AuNPs/RGO nanocomposites (4 nm) show the highest H₂ production rate should be attributed to the smaller size and higher dispersion of AuNPs on the RGO with large specific surface area, and the excellent capability to transport electrons of RGO.

Figure 3. The rate of H₂ production over AuNPs (4 nm), AuNPs (25 nm), RGO, AuNPs/RGO (4 nm) and AuNPs/RGO (25 nm).

4 SUMMARY

The binary AuNPs/RGO nanocomposites with different size were successfully synthesized, and the AuNPs/RGO (4 nm) exhibit high photocatalytic activity with a maximum H₂ production rate of 2.1 mmol h⁻¹g⁻¹, which could be attributed to the intrinsic electron transfer characteristic of RGO sheet, the small size distribution and well dispersion of AuNPs on the RGO surface.

REFERENCES


